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CHELATING POLYAMIDO COMPLEXES OF RHENIUM, MOLYBDENUM, AND
HAFNIUM: ORGANOMETALLIC SYNTHESIS TO ZIEGLER-NATTA CATALYSIS

BY

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B.S. in Chemistry
University of California, Davis
June, 1993

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements
for the Degree of

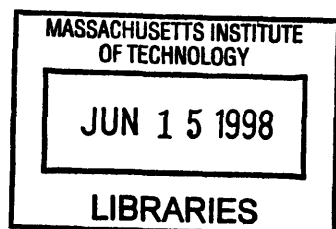
DOCTOR OF PHILOSOPHY
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
June, 1998

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Science

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To Lisa

*And shall an atom of this atom world
Mutter the theme of heaven?*

—Young

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ABSTRACT

Several triamidoamine complexes of Re(III) were prepared by the reduction of paramagnetic $[\text{N}_3\text{NF}] \text{ReBr}$ in the presence of a variety of two electron ligands to give complexes of the type $[\text{N}_3\text{NF}] \text{Re(L)}$, ($[\text{N}_3\text{NF}]^{3-} = (\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}^{3-}$; $\text{L} = \text{H}_2$, ethylene, propylene, CO, N_2 , phosphines, pyridine, tetrahydrothiophene, acetonitrile, or silanes). Protonation of phosphine complexes gave Re(V) hydrido phosphine species. The X-ray crystal structure of $\{[\text{N}_3\text{NF}] \text{Re}(\eta^2\text{-HPHPh}_2)\}^+$ showed that one proton is terminally bound to phosphorus, while a second is bridging between Re and phosphorus.

Several related Mo complexes of $[\text{N}_3\text{NF}_{18}]^{3-}$ were prepared to investigate their viability as intermediates in a dinitrogen reduction cycle ($[\text{N}_3\text{NF}_{18}]^{3-} = [(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_3\text{N}]^{3-}$). Reduction of $[\text{N}_3\text{NF}_{18}] \text{MoI}$ under dinitrogen gave first an isolable bimetallic bridging dinitrogen complex. Stepwise reduction of the dinitrogen ligand eventually furnished $[\text{N}_3\text{NF}_{18}] \text{Mo(R)NNMe}_2$ ($\text{R} = \text{Me}$ or Ph). Cleavage of the N-N bond in these dimethylhydrazido species at 100°C in C_6D_6 generated $[\text{N}_3\text{NF}_{18}] \text{MoN}$ in low yields and a mixture of organic products. These results are compared to the chemistries of other trigonally symmetric complexes of Mo known to react with dinitrogen.

Hafnium complexes of $[(^t\text{Bu-d}_6\text{N-}o\text{-C}_6\text{H}_4)_2\text{O}]^{2-}$ ($[\text{NON}]^{2-}$) were synthesized by aminolysis of $\text{Hf(NMe}_2)_4$ by $[\text{NON}]\text{H}_2$ to give $[\text{NON}]\text{Hf(NMe}_2)_2$ which reacted with excess trimethylsilylchloride in hot toluene to afford the synthetically versatile $[\text{NON}]\text{HfCl}_2$. Thermally stable dialkyl complexes $[\text{NON}]\text{HfR}_2$ ($\text{R} = \text{Me}$, Et , ^iBu , Bz) or $[\text{NON}]\text{HfRR}'$ ($\text{R} = \text{Me}$, $\text{R}' = \text{Np}$ or Np') were prepared from $[\text{NON}]\text{HfCl}_2$ and primarily Grignard reagents. Protonolysis of $[\text{NON}]\text{HfMe}_2$ with $[\text{PhNMe}_2(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ in chlorobenzene gave thermally robust $\{[\text{NON}]\text{HfMe}(\text{Me}_2\text{NPh})\}[\text{B}(\text{C}_6\text{F}_5)_4]$ which polymerized 1-hexene to afford, in virtually quantitative yields, poly(1-hexene) of narrow polydispersities (1.3 - 2) and varying molecular weights, depending upon the temperature of polymerization ($20 - 80^\circ\text{C}$). Various methodologies led to a bridging methyl bimetallic cation, isolable alkyl cations $\{[\text{NON}]\text{HfR}(\text{B})\}\text{BPh}_4$ ($\text{R} = \text{Me}$ or Et , $\text{B} = \text{THF}$ or 0.5 DME), or rare neopentyl cations $\{[\text{NON}]\text{HfNp}(\text{NCR})\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ ($\text{R} = \text{Me}$, Ph). Reactions of dialkyl complexes $[\text{NON}]\text{HfR}_2$ ($\text{R} = \text{Me}$, Et , ^iBu) with $[\text{PhNMe}_2(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 or bromobenzene- d_5 proceeded *via* protonation of the $[\text{NON}]^{2-}$ ligand to give observable cationic species which contain coordinated amines before protonolysis of hafnium-carbon bonds occurred.

Several titanium complexes of the new triamidoamine ligand $(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}^{3-}$ ($[\text{N}_3\text{N}']^{3-}$) were prepared. Solution NMR studies revealed a rigid $[\text{N}_3\text{N}']^{3-}$ ligand backbone for crystallographically characterized $[\text{N}_3\text{N}']\text{TiCl}$ while that in the methyl derivative $[\text{N}_3\text{N}']\text{TiMe}$ was more fluxional.

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LIST OF ABBREVIATIONS USED IN THE TEXT

2,4-lut	2,4-lutidine
2,5-lut	2,5-lutidine
2,6-lut	2,6-lutidine
Å	angstrom
Ar ^F	3,5-(CF ₃) ₂ -C ₆ H ₃
br	broad
Bz	benzyl
C _{aryl}	general carbon in an aryl group
C _{ipso}	ipso carbon in an aryl group
C _{meta}	meta carbons in an aryl group
C _{ortho}	ortho carbons in an aryl group
C _{para}	para carbon in an aryl group
<i>o</i> -C ₆ F ₅	ortho carbon in C ₆ F ₅ R
<i>m</i> -C ₆ F ₅	meta carbon in C ₆ F ₅ R
<i>p</i> -C ₆ F ₅	para carbon in C ₆ F ₅ R
<i>ipso</i> -C ₆ F ₅	ipso carbon in C ₆ F ₅ R
χ _M	molar magnetic susceptibility
Cp	cyclopentadienyl (C ₅ H ₅)
Cp'	methylcyclopentadienyl (MeC ₅ H ₄)
Cp''	1,3-(TMS) ₂ -C ₅ H ₃
Cp*	pentamethylcyclopentadienyl (Me ₅ C ₅)
C _β	beta carbon
Cy	cyclohexyl
δ	chemical shift downfield from tetramethylsilane
δ _C	carbon chemical shift
δ _H	proton chemical shift
δ _P	phosphorus chemical shift
d	doublet
Δδ(<i>m, p</i> -F)	difference in chemical shift between meta- and para-fluorines in C ₆ F ₅ R
DBAr ₄	[D(OEt ₂) ₂] ⁺ (B(3,5-(CF ₃) ₂ C ₆ H ₃) ₄) ⁻
dm	doublet of multiplets
deg	degrees
DME	1,2-dimethoxyethane
EBTHI	ethylene-1,2-bis(η ⁵ -4,5,6,7-tetrahydro-1-indenyl)

equiv.	equivalent(s)
Et	ethyl (C ₂ H ₅)
η^x	hapticity of a ligand bound to a metal through x atoms
<i>fac</i>	facial isomer
F _{meta}	meta fluorines in C ₆ F ₅ R
F _{ortho}	ortho fluorines in C ₆ F ₅ R
F _{para}	para fluorine in C ₆ F ₅ R
GPC	gel permeation chromatography
h	hour(s)
H _{α}	alpha hydrogen
H _{β}	hydrogen attached to C _{β}
H _{meta}	meta hydrogens in an aryl group
H _{ortho}	ortho hydrogens in an aryl group
H _{para}	para hydrogen in an aryl group
HBAr ₄	[H(OEt ₂) ₂] ⁺ (B(3,5-(CF ₃) ₂ C ₆ H ₃) ₄) ⁻
HOMO	highest occupied molecular orbital
Hz	hertz
ⁱ Bu	isobutyl (CH ₂ CH(CH ₃) ₂)
ⁱ Pr	isopropyl (CH(CH ₃) ₂)
IR	infrared
J _{AB}	coupling constant between atoms A and B
k _i	rate of initiation
k _p	rate of propagation
L	ligand
μ	magnetic moment
μ_B	Bohr magneton
μ_{eff}	effective magnetic moment
m	multiplet
μ -Et	bridging ethyl group
μ -Me	bridging methyl group
μ -N ₂	bridging dinitrogen
Me	methyl (CH ₃)
Me _{ortho}	ortho methyl group in a lutidine
Me _{meta}	meta methyl group in a lutidine
Me _{para}	para methyl group in a lutidine
<i>mer</i>	meridional isomer

MHz	megahertz
min	minute(s)
M _n	number average molecular weight
N _{ax}	axial nitrogen
ⁿ Bu	normal butyl (CH ₂ CH ₂ CH ₂ CH ₃)
N _{eq}	equatorial nitrogen
ⁿ Hex	normal hexyl (CH ₂ (CH ₂) ₄ CH ₃)
NMR	nuclear magnetic resonance
Np	neopentyl (CH ₂ C(CH ₃) ₃)
Np'	neophyl (CH ₂ C(CH ₃) ₂ Ph)
ⁿ Pr	normal propyl (CH ₂ CH ₂ CH ₃)
OTf	trifluoromethanesulfonate, triflate (O ₃ SCF ₃ ⁻)
P	polymer chain
PDI	polydispersity index
Ph	phenyl (C ₆ H ₅)
ppm	parts per million
θ	cone angle of a free phosphine
θ _P	pocket angle of a triamidoamine transition metal complex
q	quartet
s	singlet
SQUID	superconducting quantum interference device
T	temperature
t	triplet
^t Bu	tertiary butyl (C(CH ₃) ₃)
THF	tetrahydrofuran
THT	tetrahydrothiophene
TMS	trimethylsilyl (Me ₃ Si)
v br	very broad
VT	variable temperature
w _{1/2}	peak width at half height in Hertz
[N ₃ N'] ³⁻	[(Me ₃ SiNCH ₂ CH ₂ CH ₂) ₃]N ³⁻
[N ₃ NF ₁₈] ³⁻	[(3,5-(CF ₃) ₂ -C ₆ H ₃ NCH ₂ CH ₂) ₃]N ³⁻
[N ₃ NF] ³⁻	[(C ₆ F ₅ NCH ₂ CH ₂) ₃]N ³⁻
[NON] ²⁻	[(^t Bu- <i>d</i> ₆)N- <i>o</i> -C ₆ H ₄] ₂ O ²⁻

CHAPTER I

Synthesis of Re(III) and Re(V) Complexes That Contain the $[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]^{3-}$ Ligand

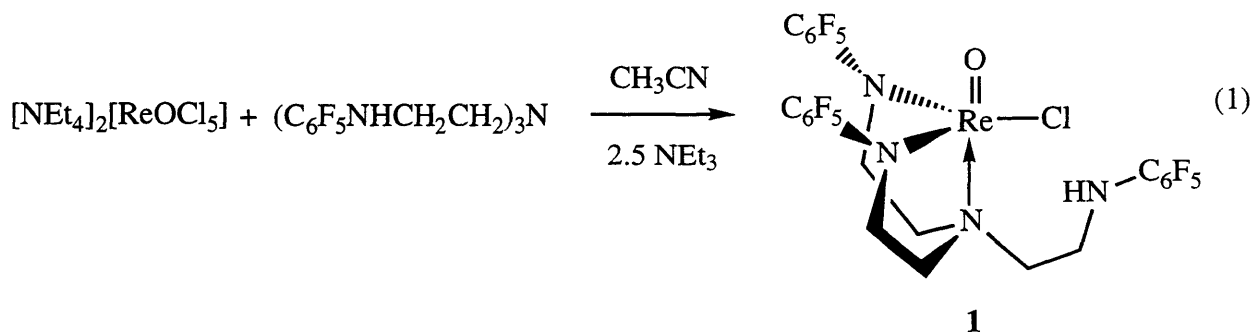
Most of the material in this chapter will appear in the literature:

Reid, S. M.; Neuner, B.; Davis, W. M.; Schrock, R. R. *Organometallics*; submitted for publication.

INTRODUCTION

A variety of complexes that contain a triamidoamine ligand $[(\text{RNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ and a metal in the 3+ or higher oxidation state have been prepared.¹⁻¹⁰ The two most readily accessible $[(\text{RNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ligands are those in which R is SiMe_3 (or another trisubstituted silyl group such as SiEt_3) or C_6F_5 . One attractive feature of the $[(\text{C}_6\text{F}_5)\text{NCH}_2\text{CH}_2]_3\text{N}^{3-}$ ($[\text{N}_3\text{NF}]^{3-}$) ligand (compared to silyl-substituted ligands) is the stability of the N- C_6F_5 bond toward hydrolysis. $[\text{N}_3\text{NF}]\text{ML}_x$ complexes have now been prepared that contain Mo or W,^{11,12} Ti,¹³ V,^{14,15} and Re.¹⁶ The Re complexes are relatively important, since $[(\text{R}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Re}$ analogs so far have not been prepared, and since the only other examples of Re complexes that contain a tripodal trianionic ligand appear to be $[(\text{SCH}_2\text{CH}_2)_3\text{N}]^{3-}$ complexes.¹⁷⁻¹⁹

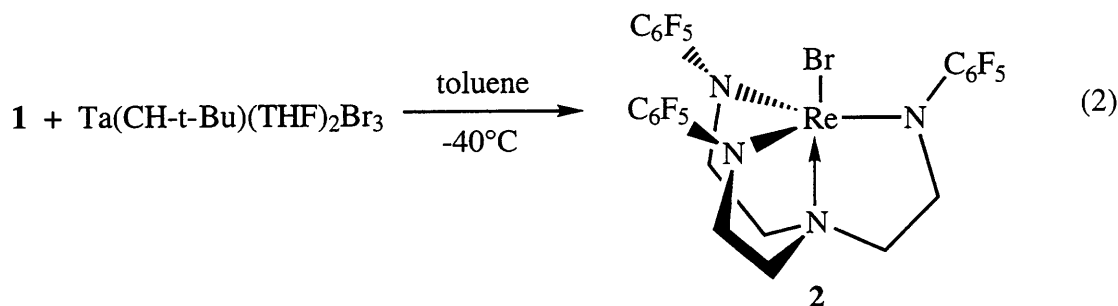
An important development in rhenium chemistry was advanced by Neuner and Schrock through the reaction between $[\text{Et}_4\text{N}]_2[\text{ReOCl}_5]$, $\text{H}_3[\text{N}_3\text{NF}]$, and NEt_3 in CH_3CN to give **1** (equation 1).¹⁶ Complex **1** contained one protonated "arm" of the $[\text{N}_3\text{NF}]^{3-}$ ligand that is not coordinated to Re and an attempted X-ray structure yielded data of sufficient quality to confirm that fact, although a disorder problem prevented a satisfactory solution of the structure.



This chapter begins by elaborating upon the entry into triamidoamine chemistry of rhenium. Then the syntheses of a variety of Re(III) complexes of the general form $[\text{N}_3\text{NF}]\text{Re}(\text{L})$ and related Re(V) complexes are described.

RESULTS

Starting Material. An attempt to exchange the oxo ligand in **1** with the neopentylidene ligand in $\text{Ta}(\text{CH}^t\text{Bu})(\text{THF})_2\text{Br}_3$ ²⁰ gave an olive-green paramagnetic species that is proposed to be $[\text{N}_3\text{N}_\text{F}]\text{ReBr}$ (**2**) in 91% yield (equation 2).¹⁶ This reaction consists of a formal exchange of the oxo ligand in **1** with Br_2 on Ta plus removal of HCl from Re. (The fate of the hypothetical tantalum product, " $\text{Ta}(\text{O})(\text{CH}_2^t\text{Bu})\text{Br}_2(\text{THF})_2$," was not determined.) It has not been possible to obtain any single completely satisfactory set of elemental analyses for **2**, although the average of six C, H, and N analyses and those of Cl and Br are consistent with the composition



$\text{C}_{24}\text{H}_{12}\text{N}_4\text{BrF}_{15}\text{Re} \cdot (\text{CH}_2\text{Cl}_2)_{0.5}$ (see Experimental section for details.) Several pieces of data suggest that the proposed formulation is correct. First, complex **2** should be paramagnetic in a low spin d^3 configuration with the electrons residing in the degenerate d_{xz}/d_{yz} orbitals pointing toward the bromide ligand. The presence of one unpaired electron was confirmed by a SQUID magnetic susceptibility measurement. A plot of the molar susceptibility, χ_M , as a function of temperature shows that **2** behaves as a Curie paramagnet with $\mu = 1.65(1) \mu_B$ between 5 and 300 K; the effective magnetic moment, μ_{eff} , remains constant in this temperature range (Figure 1.1). Second, an X-ray study revealed that a single ligand was present in the expected trigonal coordination pocket in an $[\text{N}_3\text{N}_\text{F}]\text{Re}$ species that refined most satisfactorily as a bromide ligand. A disordered molecule of dichloromethane could not be modeled and the quality of the structure therefore was not sufficiently high to confirm that the apical halide was exclusively bromide. It

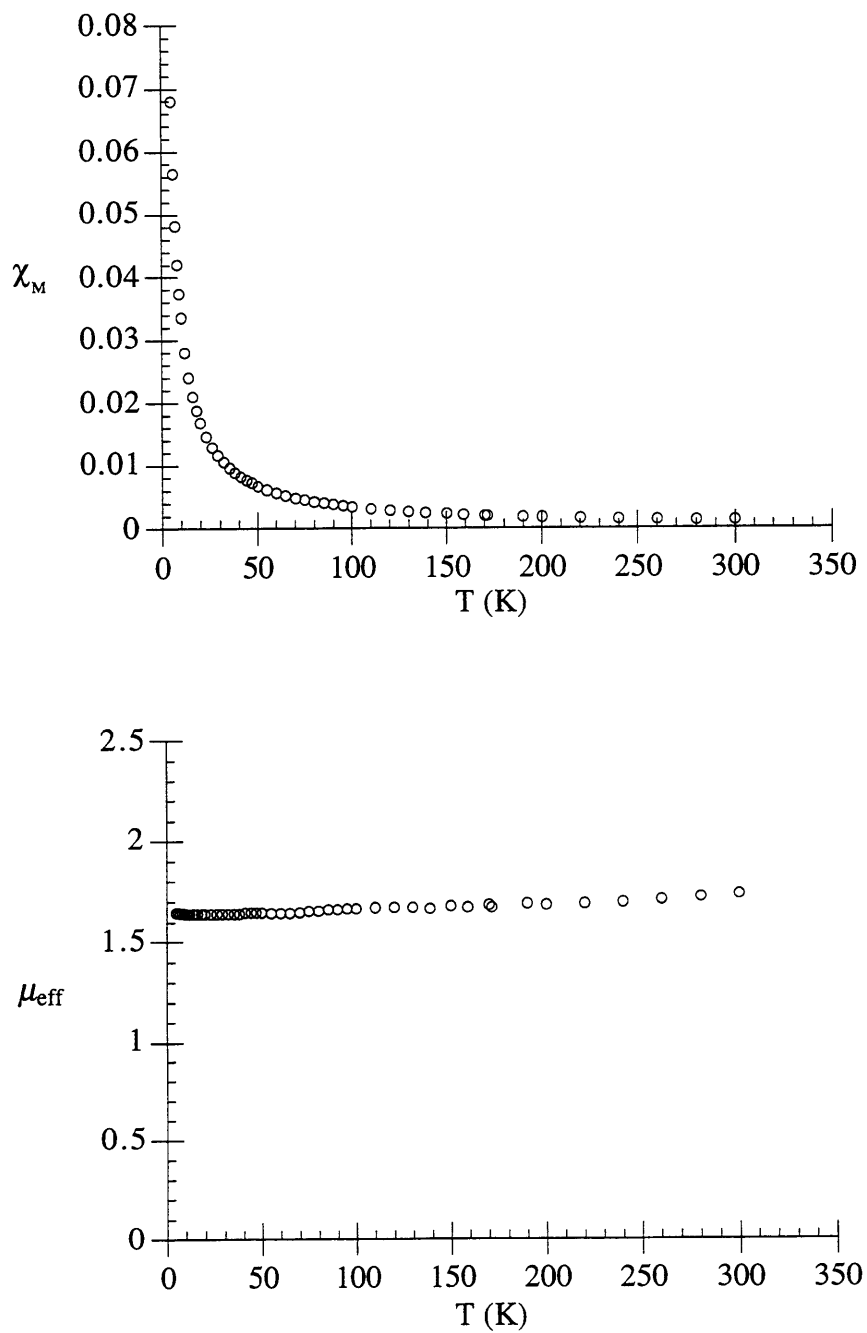


Figure 1.1 Plots of χ_M (top) and μ_{eff} (bottom) versus T for $[\text{N}_3\text{N}_\text{F}]\text{ReBr}$ (**2**).

was originally believed (for one C, H, and N analysis, and in the absence of Br and Cl analysis and SQUID data) that **2** was $\{[N_3N_F]ReBr\}Br$.¹⁶ Finally, **2** can be observed in mixtures from the reaction between $ReBr_4(tetrahydrothiophene)_2$, $H_3[N_3N_F]$, and NEt_3 , but cannot yet be synthesized in pure form and high yield in this manner. Therefore, in spite of the paucity of definitive proof of the proposed composition of **2** and its somewhat circuitous synthesis, **2** was employed as a starting material in this study.

Dihydrogen and Olefin Complexes. Early attempts to alkylate **2** with methyllithium revealed that it is instead readily reduced to $Re(III)$, and that in the presence of 2 electron donor ligands, complexes with the formula $[N_3N_F]Re(L)$ are produced.¹⁶ A smoother reduction of **2** may be effected by Mg powder and $MgBr_2$ is easily removed as insoluble $[MgBr_2(dioxane)]_x$. Reduction of **2** by Mg is also more straightforward and is less likely to be susceptible to side reactions. Therefore reduction of **2** by Mg was the method of choice for preparing lower oxidation state Re species although yields were not in any case necessarily greater.

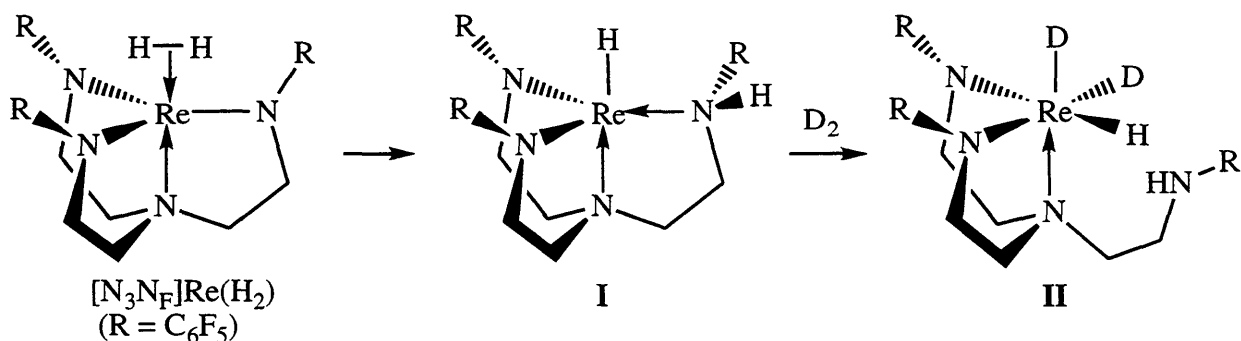
Neuner and Schrock reported that reduction of **2** under dihydrogen gave $[N_3N_F]Re(H_2)$.¹⁶ Pertinent findings from this study include a sharp resonance for the "hydride" ligands at -0.89 ppm in the ^1H NMR spectrum in CD_2Cl_2 , but no peak could be located in the IR spectrum. Furthermore, a T_1 measurement at 21°C yielded a value of 138 ms, a possibly nonminimal value that would favor $[N_3N_F]Re(H_2)$ being a classical dihydride complex.²¹⁻²³ On the other hand, the J_{HD} coupling constant in $[N_3N_F]Re(HD)$ (15 Hz) is more consistent with it being a dihydrogen complex (typically $J_{HD} = 30 \pm 4$ Hz).²¹⁻²³ Therefore neither description may be totally satisfactory.²⁴ Finally, it was concluded that $[N_3N_F]Re(H_2)$ may be viewed as an 18e dihydrogen complex of hypothetical $Re[N_3N_F]$, in which the two orthogonal filled d_{xz} and d_{yz} orbitals contain the four d electrons. Backbonding to the dihydrogen ligand does not "lock" the dihydrogen ligand in any given orientation,^{21,22,25,26} as the d_{xz} and d_{yz} orbitals are equivalent in C_{3v} symmetry.

Approximately 2 equiv of D_2 was added to an NMR tube charged with $[N_3N_F]Re(H_2)$ in toluene- d_8 . At room temperature, the ^1H NMR spectrum showed only $[N_3N_F]Re(H_2)$, but after

heating the sealed sample to 120°C overnight the H_2 resonance at -0.58 ppm was replaced by a triplet at -0.63 ppm ($J_{\text{HD}} = 17$ Hz) arising from $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{HD})$. The same experiment was repeated in toluene and monitored by ^2H NMR whereupon a doublet at -0.51 ppm ($J_{\text{HD}} = 17$ Hz) and a singlet at -0.60 ppm in approximately a 1:1 ratio were observed for $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{HD})$ and $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D}_2)$, respectively (by comparison to authentic samples of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{HD})$ and $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D}_2)$). The possibility that solvent was playing a role in H/D exchange was ruled out since no H/D exchange occurred when $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H}_2)$ was heated to 100°C in degassed toluene- d_8 . Similar behavior was observed in ^1H and ^2H NMR experiments in which $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D}_2)$ was treated with H_2 in toluene- d_8 and toluene, respectively.

Loss of H_2 to give " $\text{Re}[\text{N}_3\text{N}_\text{F}]$ " cannot alone explain the H/D exchange results above. However, since bound dihydrogen is known to behave as an acid, I propose that one of the amido nitrogens is protonated to give an alternative Re(III) monohydride complex (**I**, Scheme 1.1). Compound **I** would be an 18e complex if the two equatorial amido nitrogens form two π bonds to Re. Dissociation of the equatorial amine to yield an analogous 16e species followed by further reaction with D_2 would then yield **II**. Loss of HD from **II** would complete the H/D exchange

Scheme 1.1. Hydrogen/Deuterium Scrambling in a Dihydrogen Complex.



process. Oxidation of a Re(III) complex to give a Re(V) complex is a central theme in this chapter, and therefore a reasonable step to propose in the exchange process. An intermediate that contains "one arm off" is feasible in view of the structure of **1** and that of a related complex,

$\{[(C_6F_5NCH_2CH_2)_2NCH_2CH_2NHC_6F_5]V(O)\}_2$,¹⁴ which clearly reveals a coordination geometry in which the two amido ligands occupy equatorial positions in a pseudo-trigonal bipyramidal arrangement about the metal. Several examples of TBP complexes that contain a diamido/donor ligand have appeared in the literature in the last several years.²⁷⁻³² A structure in which the two amido ligands occupy equatorial positions and the donor an axial position is the one that is most often observed in the solid state. Finally, a structurally characterized d² molybdenum species related to **I** contains an amine donor, $\{[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NMe_2]Mo(N=NSiMe_3)\}^+$, and the X-ray structure of trigonal bipyramidal $[(Me_3SiNCH_2CH_2)_2NCH_2CH_2NMe_2]Mo(N=NSiMe_3)(Me)$ shows that the dimethylamino fragment is not bound to the metal.³³ Therefore, both **I** and **II** are plausible intermediates in the proposed mechanism of the H/D exchange reaction shown in Scheme 1.1.

A ¹H NMR spectrum of $[N_3N_F]Re(C_2H_4)$ (**3a**; prepared in this study by the reduction of **2** by Mg under an atmosphere of ethylene) in THF-*d*₈ revealed a resonance for coordinated ethylene at 2.61 ppm.¹⁶ The ¹H NMR spectrum of $[N_3N_F]Re(^{13}C_2H_4)$ showed the expected pattern for an AA'A"A'XX' system³⁴ with a ¹J_{H¹³C coupling of ~152 Hz. A non-first-order multiplet was observed in CD₂Cl₂ at δ 54.7 in the ¹³C NMR spectrum and a singlet was observed with no discernible coupling to fluorine upon decoupling ¹H. The only significant change in the ¹H NMR spectrum upon cooling an NMR sample of $[N_3N_F]Re(C_2H_4)$ to -90° was a resolution of four types of $[N_3N_F]^{3-}$ methylene resonances as a consequence of the $[N_3N_F]^{3-}$ ligand becoming locked in a conformation that has true C₃ symmetry. The d_{xz} and d_{yz} orbitals are still degenerate in the C₃ point group, so there is no "electronic" barrier that would prevent free rotation of the ethylene ligand. There is no evidence that ethylene rotation slows on the NMR time scale for steric reasons; that is, a complex with C_s or C₁ symmetry is not produced.}

The structure of $[N_3N_F]Re(C_2H_4)$ was elucidated in an X-ray study. Selected bond distances and angles are listed in Table 1.1 while crystallographic parameters are presented in Table 1.2. Two ORTEP views are depicted in Figure 1.2, which shows that the ethylene ligand

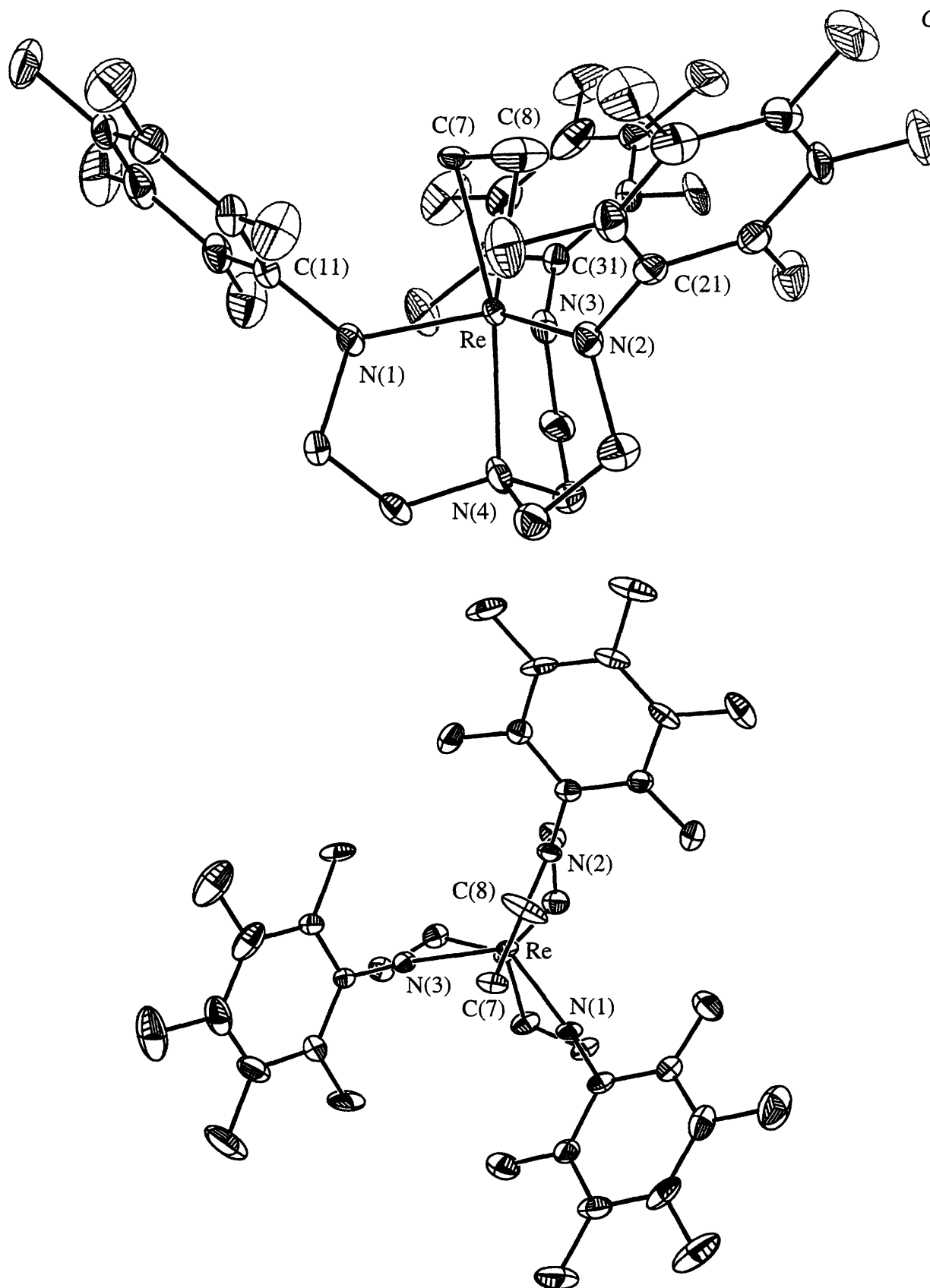


Figure 1.2. Side and Top ORTEP Views of the Structure of [N₃N_F]Re(C₂H₄) (3a).

Table 1.1 Selected Bond Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms in [N₃N_F]Re(C₂H₄) (**3a**).

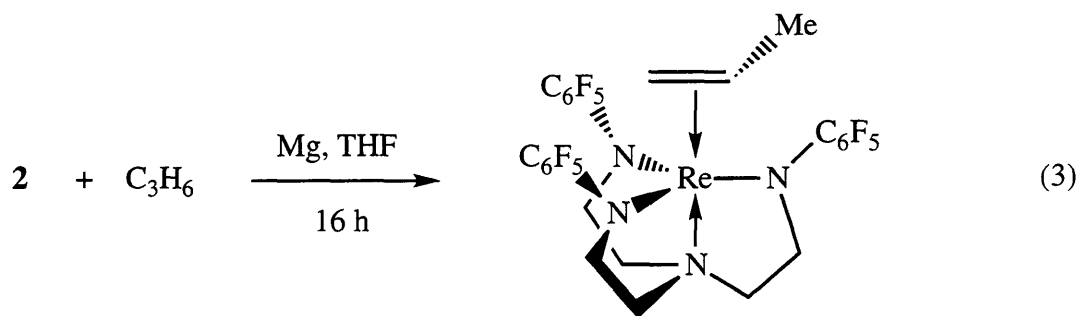
Bond Lengths			
Re - N(1)	1.930(7)	Re - C(7)	2.182(8)
Re - N(2)	1.965(7)	Re - C(8)	2.147(11)
Re - N(3)	1.940(7)	C(7) - C(8)	1.406(14)
Re - N(4)	2.178(8)		
Bond Angles			
N(1) - Re(1) - N(2)	116.9(3)	Re - C(8) - C(7)	72.4(6)
N(2) - Re(1) - N(3)	118.3(3)	Re - C(7) - C(8)	69.7(5)
N(1) - Re(1) - N(3)	117.1(3)	Re - N(2) - C(21)	130.8(6)
Re - N(1) - C(11)	129.7(6)	Re - N(3) - C(31)	130.4(6)

Table 1.2. Crystallographic data, collection parameters, and refinement parameters for $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{C}_2\text{H}_4)$ (**3a**).

Empirical Formula	$\text{C}_{26}\text{H}_{16}\text{N}_4\text{F}_{15}\text{Re}$
Formula Weight	855.63
Diffractometer	Siemens SMART/CCD
Crystal Dimensions (mm)	0.21 x 0.18 x 0.13
Crystal System	Triclinic
a (Å)	11.151 (2)
b (Å)	11.421 (2)
c (Å)	11.937 (2)
α (deg)	105.622 (2)
β (deg)	107.363 (2)
γ (deg)	93.121 (2)
V (Å ³)	1382.2 (5)
Space Group	$P\bar{1}$
Z	2
D _{calc} (Mg/m ³)	2.056
F ₀₀₀	820
λ , radiation	0.71073, MoK α
Scan Type	ω
Temperature (K)	293 (2)
θ Range for Data Collection (deg)	1.87 to 23.27
Independent Reflections	3860
Absorption Correction	None
Refinement Method	Full-matrix least squares
Data/Restraints/Parameters	3853/0/415
Final R Indices [$I > 2\sigma(I)$]	R1 = 0.0471, wR2 = 0.1180
R Indices (all data)	R1 = 0.0489, wR2 = 0.1281
GoF	1.079
Largest Diff. Peak and Hole (eÅ ⁻³)	2.459 and -2.675

lies approximately in the N(4)-Re-N(2) plane. The C(7)-C(8) bond length (1.406(14) Å) is typical of a bound ethylene, as are the Re-C(ethylene) bond lengths. The Re atom is displaced above the equatorial nitrogen plane by 0.314 Å. Re-N_{eq} distances vary from 1.930 Å to 1.965 Å, Re-N_{eq}-C_{ipso} angles are all approximately 130°, and the Re-N(4) distance is 2.18 Å; all are typical for [N₃N_F] complexes of a second or third row metal.¹¹ The N(4)-Re-N_{eq}-C_{ipso} angles are all between 170 and 172°, which is also typical for known [N₃N_F]³⁻ complexes with pseudo three-fold symmetry.¹ Similar ligand arrangements were observed by Freundlich and Schrock who reported that the acetylene ligand in [(Me₃SiNCH₂CH₂)₃N]Ta(HC≡CH) lies in one of the N_{ax}-Ta-N_{eq} planes, and therefore one end points directly toward one of the trimethylsilyl substituents on the triamidoamine ligand.³⁵ Additionally, the X-ray crystal structure of [(Me₃SiNCH₂CH₂)₃N]W(H)(C₅H₈) showed that the cyclopentylidene and the hydride ligands lie in a N_{ax}-W-N_{eq} plane.³⁶ Therefore the most energetically favorable bonding situation appears to be that in which σ bonds are found in the N_{ax}-M-N_{eq} plane. If [N₃N_F]Re(C₂H₄) is viewed as a d² metallacyclopropane complex, the electron pair prefers to be in an orbital perpendicular to the plane in which the ethylene ligand lies, perhaps in order to minimize repulsion between that electron pair and the electron density in the Re-N_{eq} σ bonds.

A propylene complex, [N₃N_F]Re(CH₂=CHMe) (**3b**), could be prepared in 65% yield as sparingly soluble dark green prisms (equation 3). The ¹H NMR spectrum at room temperature reveals that the complex is three-fold symmetric and that the four resonances for a rapidly rotating propylene ligand are sharp and well-resolved. However, upon lowering the temperature of the sample two sets of propylene resonances are obtained along with two sets of overlapping



resonances characteristic of a C_3 -symmetric ligand backbone (Figure 1.3). The two sets of resonances are assigned to two diastereomers of approximately equal energy formed as a

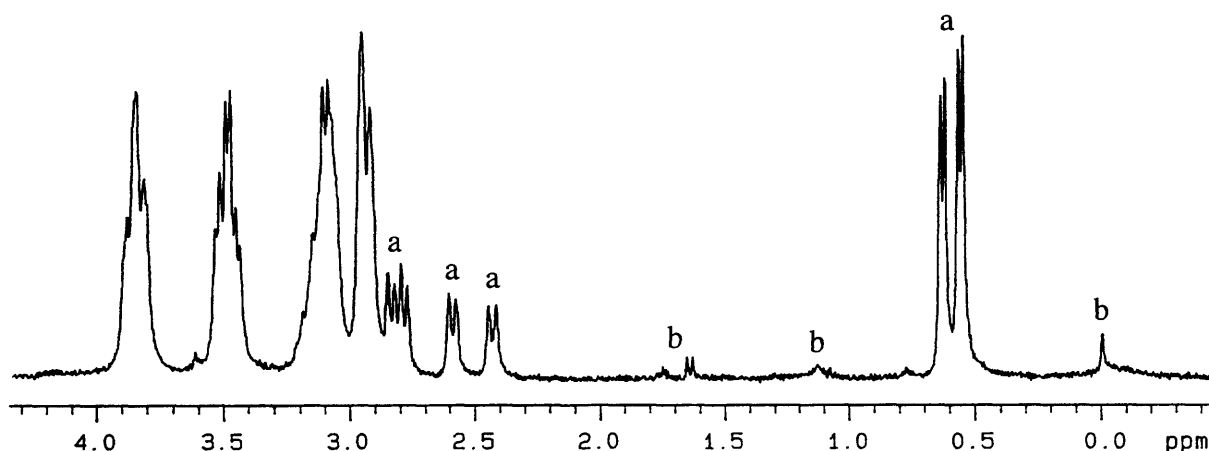
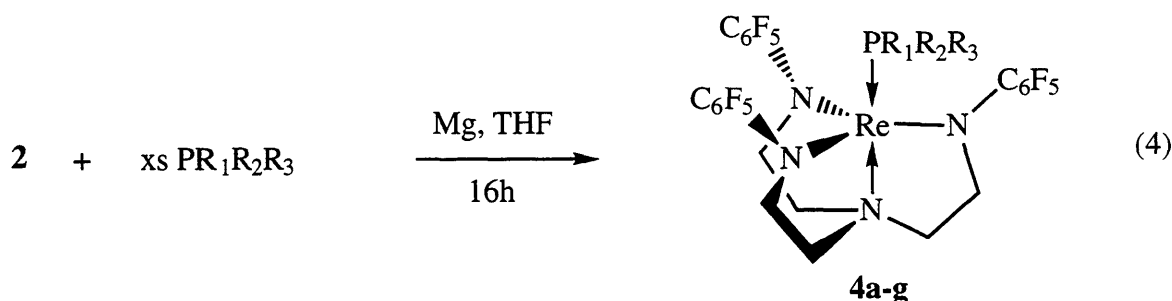


Figure 1.3. 300 MHz ^1H NMR Spectrum of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{CH}_2=\text{CHMe})$ in CD_2Cl_2 at -90°C .
^a Resonances of coordinated propylene; ^b Solvent impurities.

consequence of the faces of the propylene ligand being diastereotopic. In each diastereomer the propylene ligand rotates freely on the NMR time scale; the ligand backbone resonances and the three C_6F_5 rings, respectively, are therefore equivalent.

σ Donor Complexes. Several phosphine complexes of the general formula $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PR}_1\text{R}_2\text{R}_3)$ were synthesized by treating **2** with excess Mg and 2 - 4 equiv of phosphine in degassed THF (equation 4). It was found that mixtures of the desired complex and $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{N}_2)^{16}$ resulted if these reductions were performed in an atmosphere of dinitrogen. Addition of 1,4-dioxane and removal of $[\text{MgBr}_2(\text{dioxane})]_x$ allowed the isolation of the



diamagnetic phosphine complexes **4a-g** as moderately air-stable orange to red cubes. $^{31}\text{P}\{\text{H}\}$ chemical shifts for the complexes and cone angles for the free phosphines are summarized in Table 1.3. These species are soluble in dichloromethane, THF, and toluene and exhibit 3-fold symmetry in solution. A PPh_3 complex could not be prepared under these conditions, I assume

Table 1.3. Properties of Phosphine Complexes.

Complex	Color	δ_{P} (ppm)	θ (deg) ^a	δ_{H} (ppm)	J_{HP} (Hz)
$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PH}_3)$ (4a)	red	-138.18	87	-	-
$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PMe}_3)$ (4b)	red	-45.16	118	-	-
$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PEt}_3)$ (4c)	red	-24.92	132	-	-
$[\text{N}_3\text{N}_\text{F}]\text{Re}[\text{P}(\text{iPr})_3]$ (4d)	green	-11.56	160	-	-
$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PMe}_2\text{Ph})$ (4e)	red-orange	-30.91	122	-	-
$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PMePh}_2)$ (4f)	red	-15.19	136	-	-
$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PPh}_2)$ (4g)	orange	1.24	128	-	-
$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PMe}_3)(\text{H})\}^+$ (4bH ⁺)	green	-14.88	-	0.26	7
$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PEt}_3)(\text{H})\}^+$ (4cH ⁺)	amber	23.02	-	3.76	64
$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PMePh}_2)(\text{H})\}^+$ (4fH ⁺)	red-brown	23.74	-	4.72	62
$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PPh}_2)(\text{H})\}^+$ (4gH ⁺)	flamingo	38.11	-	3.36	54 ^b

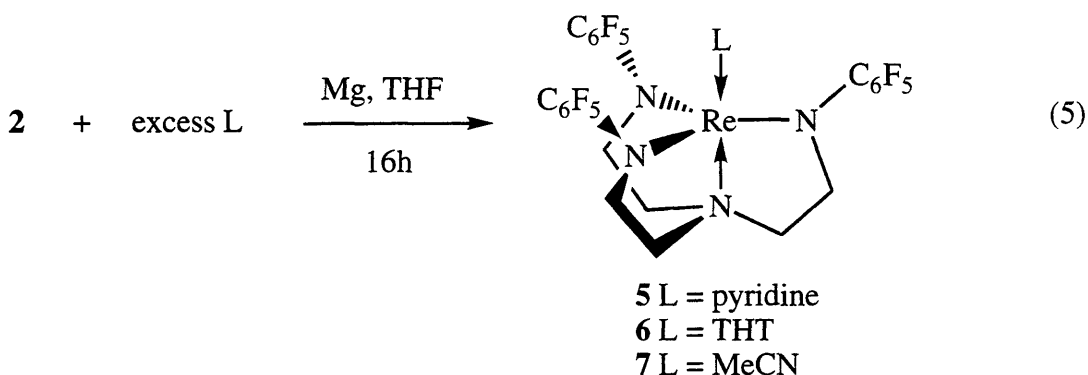
^a See reference 80.

^b $J_{\text{HH}} = 15$ Hz and $J_{\text{HP}} = 375$ Hz.

as a consequence of the relatively poor basicity of PPh_3 in combination with its large steric demands. The largest phosphine which can be accommodated is $\text{P}(\text{iPr})_3$ ($\theta = 160^\circ$) and is the only labile phosphine in this series. These are the only phosphine complexes known to date in the general category of triamidoamine complexes.

Several other complexes that contain σ donor ligands could be prepared readily (equation 5). A pyridine complex (**5**) was prepared in 48% yield and isolated as dark burgundy needles

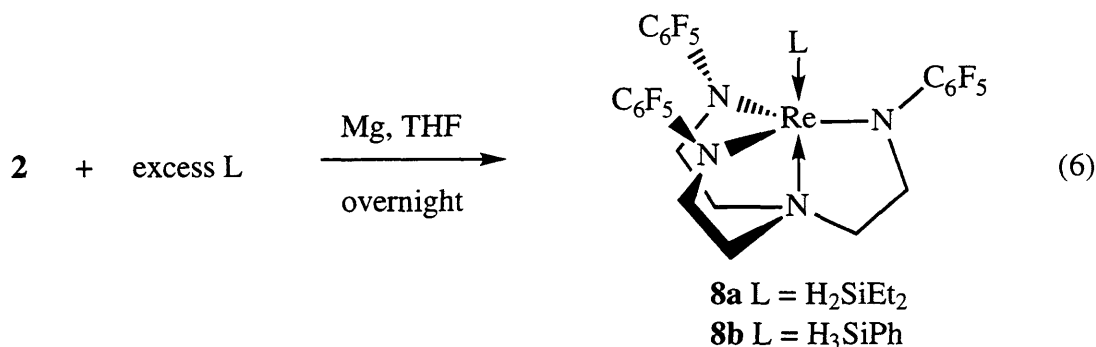
from cold dichloromethane/pentane. This complex is diamagnetic and 3-fold symmetric on the ^1H NMR time scale. Similarly, a tetrahydrothiophene complex (**6**) could be prepared in 68% yield as brown needles. The ^1H NMR spectrum of **6** in CD_2Cl_2 shows two triplets for the $[\text{N}_3\text{N}_\text{F}]^{3-}$ ligand and one broad singlet centered at 1.23 ppm which I ascribe to an accidental overlap of two closely spaced resonances for each set of THT protons. The $^{13}\text{C}\{\text{H}\}$ NMR spectrum shows clearly two sharp resonances for the THT ligand. Acetonitrile complex (**7**) was



prepared in 61% yield as large olive-green prisms. The IR spectrum in Nujol shows the CN stretch at 2152 cm^{-1} . Reduction of **2** in THF in the absence of any other potential ligand resulted only in decomposition; no $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{THF})$ complex could be observed. This is somewhat surprising in view of the fact that $[\text{N}_3\text{N}_\text{F}]\text{V}(\text{THF})$ and $[\text{N}_3\text{N}_\text{F}]\text{V}(\text{CH}_3\text{CN})$ are known and have been structurally characterized.¹⁵

Silane Complexes. The synthesis of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H}_2)$ led me to speculate that silane complexes of the general form $[\text{N}_3\text{N}_\text{F}]\text{Re}(\eta^2\text{-alkylsilane})$ might be stable. Two examples could be prepared by reduction of **2** in the presence of excess silane as depicted in equation 6. The diethylsilane complex (**8a**) was isolated in 49% yield from cold DME/pentane as orange-red crystals. Its ^1H NMR spectrum in $\text{THF}-d_8$ showed that it has three-fold symmetry on the NMR time scale. The resonance for what is presumed to be the proton in the $\eta^2\text{-Si-H}$ unit is a singlet at -5.85 ppm ; the value for J_{SiH} (44 Hz) is in the upper range for $\eta^2\text{-silane}$ complexes.^{37,38} In contrast, the terminal Si-H proton is found at 5.83 ppm with $J_{\text{SiH}} = 186\text{ Hz}$. The methylene

resonances on the Et_2SiH_2 ligand are comprised of two multiplets centered at -0.01 and -0.74 ppm indicating that these protons are diastereotopic, while the equivalent methyl groups give rise



to one triplet at 0.32 ppm. The ^1H NMR spectrum of phenylsilane complex (**8b**) in CD_3CN showed that it is similar to **8a** in that the Re-Si-H proton resonance is found at -3.86 ppm with $J_{\text{SiH}} = 38$ Hz, whereas the two terminal protons are at 5.00 ppm with $J_{\text{SiH}} = 183$ Hz. The terminal and bridging silane protons do not exchange readily on the NMR time scale.

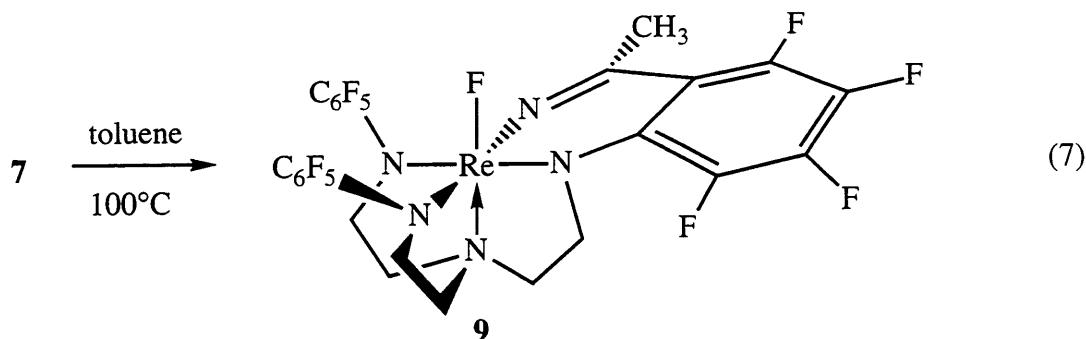
Transition metal complexes containing silane ligands bound in η^2 fashion are becoming more numerous.^{22,37-41} The most reliable indicator for distinguishing an η^2 silane ligand from a silyl hydride is J_{SiH} which for the former is about 15 to 60 Hz and less than 15 Hz (if observed at all) for the latter. Silane complexes **8a** and **8b** contain coordinated silane ligands for which $J_{\text{SiH}} = 44$ and 38 Hz, respectively, thus clearly establishing these as stretched σ complexes. The rhenium silane complexes of the type $(\text{R}_2\text{SiH}_2)\text{Re}_2(\text{CO})_8$ ($\text{R} = \text{Ph}$ or Me) by Hoyano and coworkers⁴² appear to have been the first reported examples, although others are now known in the literature.⁴³⁻⁵⁰

Ligand Substitution Reactions. Dichloromethane solutions of various phosphine complexes were treated with 3-5 equivalents of other phosphines, THT, or MeCN. These reactions were monitored by ^{19}F NMR and in no case was any phosphine found to exchange with another ligand (22°C, 3 days). However, $[\text{N}_3\text{N}_\text{F}]\text{ReH}_2$ (34.4 mM in CH_2Cl_2) reacted with PMe_3 (3 equiv.) to give **4b** after three days at room temperature while $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{propylene})$ was converted to **4b** in about 10% yield under the same conditions. Experiments in which solutions

of **4d** in degassed toluene (28.9 mM, 85-120°C, 16 h) were treated with other ligands (3 eq) showed that the P^iPr_3 ligand may be readily displaced by MeCN, N_2 , PMe_3 , and C_2H_4 . Under identical conditions, the silane ligands in **8a** and **8b** were not observed to exchange with H_3SiPh and H_2SiEt_2 , respectively.

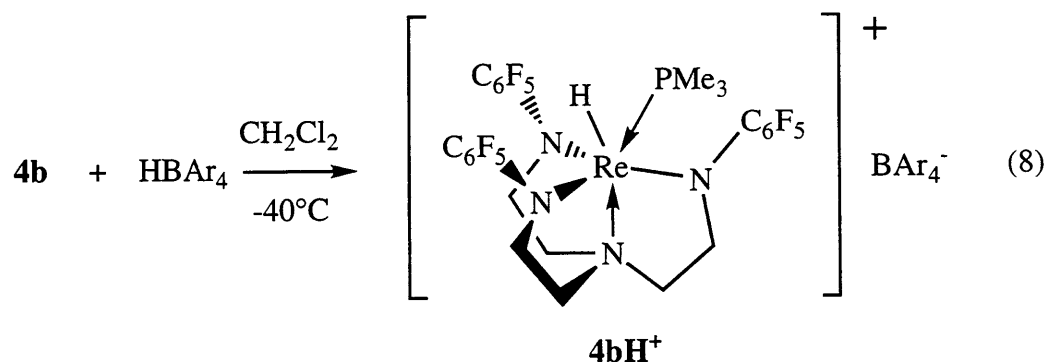
It is not surprising that soft ligands such as phosphines and THT in complexes with the general form $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{L})$ do not exchange with other ligands, even with heating. The only exception is P^iPr_3 which is displaced by weak donors such as C_2H_4 and N_2 at 100°C, presumably by a dissociative mechanism. Surprisingly, the N_2 ligand in $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{N}_2)$ was not found to be labile. For example, heating a THF solution of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{N}_2)$ (24 mM in THF, 50°C, 16 h) under 3 equivalents of CO in a sealed NMR tube did not result in the formation of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{CO})$.¹⁶ Heating a solution of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H}_2)$ (18 mM in toluene, 120°C, 16 h), under approximately 2 equivalents of N_2 led to quantitative formation of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{N}_2)$, but the reverse reaction to reform $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H}_2)$ was never observed. However, treating THF solutions of $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{N}_2)$ (6 mM) with 1 or 3 equivalents of $^n\text{BuNC}$ or $^t\text{BuNC}$, respectively, gave rapid decomposition to unidentifiable species.

Evidence for C-F Bond Activation. When acetonitrile complex (**7**) was heated in toluene at 100°C overnight, what appears to be the metallacycloimine (**9**) was formed via the activation of one C-F bond in a C_6F_5 ring (equation 7). The ^1H NMR spectrum of **9** in C_6D_6 reveals several complicated multiplets for the $[\text{N}_3\text{N}_\text{F}]^{3-}$ methylene protons as a consequence of the low symmetry of this molecule. The protons on the methyl group derived from the



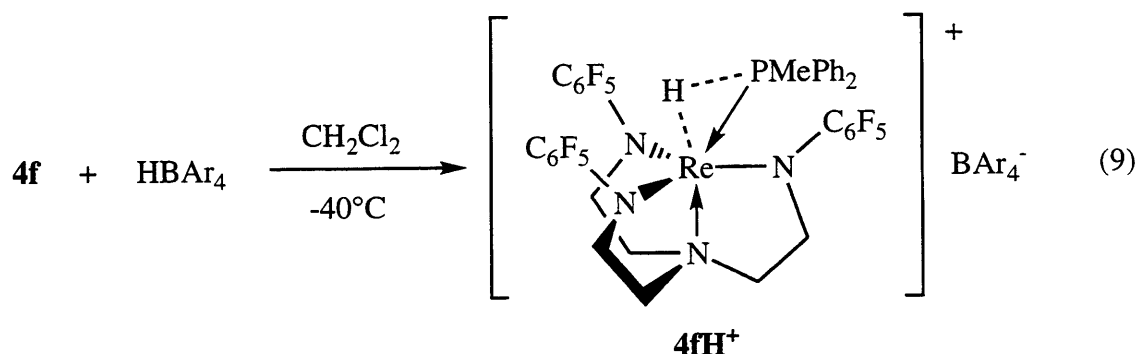
acetonitrile ligand in **9** give rise to a doublet at 5.08 ppm. They appear to be coupled to one *meta*-fluorine ($J_{\text{HF}} = 8$ Hz), similar to the interaction between *ortho*-fluorines and the methyl group in $[\text{N}_3\text{NF}]\text{Ti}(\text{CH}_3)$.¹³ The $^{13}\text{C}\{\text{H}\}$ NMR spectrum in THF/ C_6D_6 reveals that the methyl carbon at 8.23 ppm is also split into a doublet ($J_{\text{CF}} = 10$ Hz) but the imino carbon gives rise to a singlet at 145.15 ppm in the ^{13}C enriched compound. Additionally, six resonances between 70.70 and 54.55 ppm correspond to the inequivalent methylene groups. The ^{19}F NMR spectrum contains aryl fluoride resonances consistent with a low symmetry molecule, and also a singlet at -40.06 ppm. The CN stretch at 1648.6 cm^{-1} in the IR spectrum in Nujol confirms the presence of a reduced CN bond. Surprisingly, **7** decomposes to **9** even in the solid state at room temperature over several months. Despite persistent efforts, no crystals suitable for an X-ray crystallographic study could be grown. A completely satisfactory set of C, H, and N elemental analyses out of four attempts could not be obtained. Therefore, definitive proof of the identity of **9** is lacking at present.

Protonation Reactions. In d^4 complexes with the general formula $[\text{N}_3\text{NF}]\text{Re}(\text{L})$, at least one of the two filled π orbitals (d_{xz} and d_{yz}) should react with a proton to yield cationic hydrido complexes. Thus when red **4b** was treated with one equivalent of HBAr_4 in dichloromethane at -40°C , kelly green $\{[\text{N}_3\text{NF}]\text{Re}(\text{H})\text{PMe}_3\}\text{BAr}_4$ (**4bH**⁺) formed rapidly as shown as in equation 8 ($\text{HBAr}_4 = [\text{H}(\text{OEt}_2)_2]^+[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$).⁵¹ After adding pentane to the reaction mixture and cooling it to -40°C , **4bH**⁺ was isolated as thermally stable large green cubes in 76% yield. Complex **4bH**⁺ is diamagnetic and has 3-fold symmetry on the NMR time scale at 25°C in

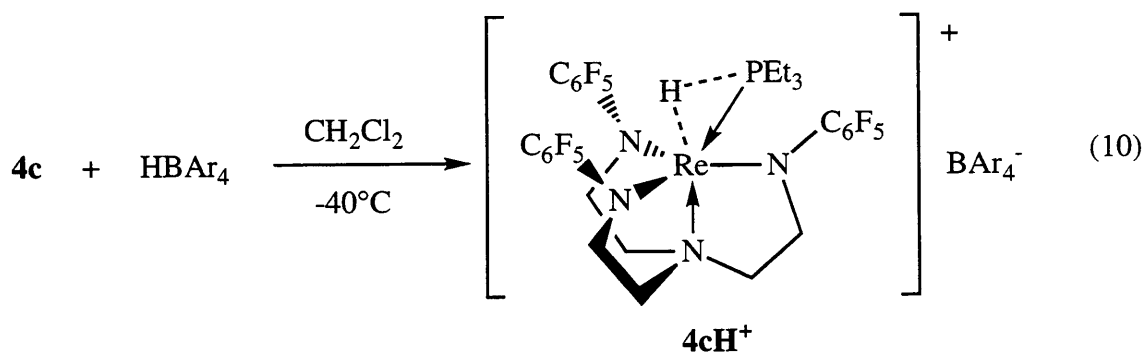


CD_2Cl_2 ; the hydride resonance is observed as a doublet at 0.26 ppm ($J_{\text{PH}} = 7$ Hz; Table 1.3). The $^{31}\text{P}\{\text{H}\}$ NMR spectrum indicates that the phosphorus resonance is shifted downfield from that in **4b** to -14.88 ppm, consistent with the cationic formulation of **4bH⁺**. The reaction shown in equation 8 is reversible; **4bH⁺** is deprotonated over a period of days by excess Et_3N to afford **4b** quantitatively (according to ^{19}F NMR).

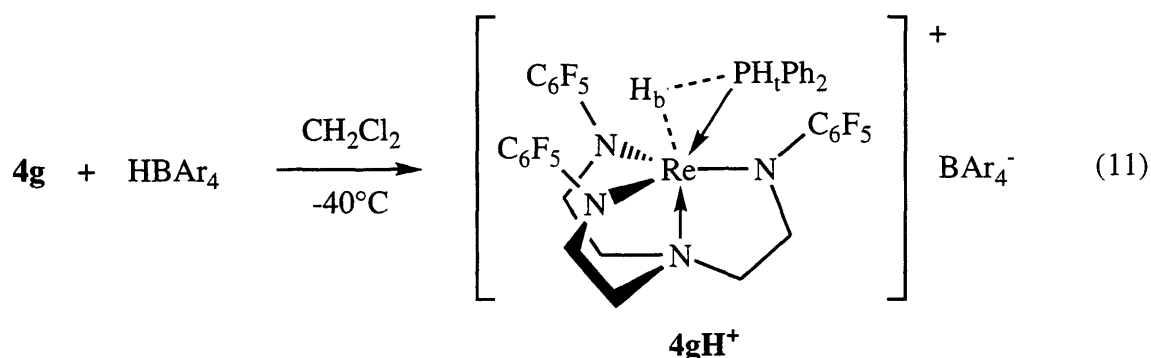
When **4f** was protonated in a similar reaction, little color change occurred and $\{[\text{N}_3\text{NF}]\text{Re}(\text{H})\text{PMePh}_2\}\text{BAr}_4$ (**4fH⁺**) was isolated as red-brown blocks from dichloromethane/pentane at -40°C in 66% yield (equation 9). The ^1H NMR spectrum reveals the "hydride" resonance as a doublet at 4.72 ppm with a relatively large value for J_{PH} (62 Hz). These data suggest that the "hydride" ligand is coupled more strongly to phosphorus than in



4bH⁺, but not as strongly as a proton bound to phosphorus, for which J_{PH} is typically 180 - 230 Hz (in uncomplexed phosphines⁵²). As shown in equation 10, protonation of **4c** with one



equivalent of HBAr_4 in cold dichloromethane gave amber crystals of $\mathbf{4cH}^+$ in 97% yield upon crystallization from dichloromethane/pentane. The ^1H NMR spectrum of $\mathbf{4cH}^+$ in CD_2Cl_2 shows that the "hydride" resonance is a doublet at 3.71 ppm ($J_{\text{PH}} = 64$ Hz), similar to what was found for $\mathbf{4bH}^+$. Protonation of the PPh_2 complex ($\mathbf{4g}$) with HBAr_4 in cold dichloromethane gave flamingo colored needles of $\mathbf{4gH}^+$ in 69% yield (equation 11). The ^1H NMR spectrum of $\mathbf{4gH}^+$ in CD_2Cl_2 reveals a doublet of doublets at 6.97 ppm with $J_{\text{PH}} = 373$ Hz and $J_{\text{HH}} = 15$ Hz, clearly consistent with a terminal phosphorus-bound proton, H_t . Another doublet of doublets at



3.36 ppm with $J_{\text{PH}} = 54$ Hz arises from the bridging Re "hydride", H_b , by comparison to similar chemical shifts and coupling constants in similar compounds.

Addition of one equivalent of DBAr_4 to $\mathbf{4g}$ gave $\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D})\text{PPh}_2\}\text{BAr}_4$ ($\mathbf{4gD}^+$) in 74% yield. The ^1H NMR spectrum of $\mathbf{4gD}^+$ in CD_2Cl_2 is identical to that of $\mathbf{4gH}^+$ except that the resonances from the terminal and "bridging" protons each integrate to ~0.5. The ^2H NMR spectrum in dichloromethane reveals a doublet at 6.86 ppm ($J_{\text{DP}} = 56$ Hz) and another doublet at 3.24 ppm ($J_{\text{DP}} = 7$ Hz) showing that deuterium has been incorporated into both the PH (6.97 ppm in $\mathbf{4gH}^+$) and the "hydride" sites (3.36 ppm in $\mathbf{4gH}^+$). These results are corroborated by the $^{31}\text{P}\{\text{H}\}$ NMR spectrum which consists of a triplet at 37.36 ppm ($J_{\text{DP}} = 56$ Hz) which arises from a terminal PD and a singlet at 38.11 ppm corresponding to $\mathbf{4gH}^+$. This singlet partially obscures another triplet with small J_{PD} which most likely arises from a species that contains D in the "hydride" site. Therefore the species observed by $^{31}\text{P}\{^1\text{H}\}$ NMR are

$\{[N_3N_F]Re(D)(PPh_2)\}BAr_4$, $\{[N_3N_F]Re(H)(PPh_2)\}BAr_4$, and $\{[N_3N_F]Re(H)(PPh_2)\}BAr_4$. If $\{[N_3N_F]Re(D)(PPh_2)\}BAr_4$ is present, as it most likely is, it would have virtually identical ^2H - and $^{31}P\{^1H\}$ NMR spectra as the other isotopomers. It is not known, though, how all isotopomers form. One reasonable proposal is that intramolecular exchange of ^1H and ^2H between bridging and terminal positions occurs at a rate that is competitive with incorporation of deuterium into these sites, and in a reversible manner. Therefore $HBAr_4$ and $[N_3N_F]Re(PPh_2)$ are available and all possible isotopomers can form competitively.

Further proof of the unusual ligand arrangement in $4gH^+$ was garnered from an X-ray crystallographic study. Two views of the cation are shown in Figure 1.4. Selected bond distances and angles are presented in Table 1.4 and crystallographic parameters are listed in Table 1.5. The terminal proton H(1) was located and successfully refined during the intermediate stages of refinement; the P-H(1) bond distance (1.408(5) Å) falls within the expected range. A second proton, H(2), was located between Re and P but became lost repeatedly in the electron density of Re during subsequent refinement. Therefore the Re-H(2) bond distance was arbitrarily constrained to 1.698(5) Å and the P-H(2) bond distance was constrained to 1.481(5) Å, both of which are consistent with values found in other phosphine complexes of Re hydrides.⁵³ The PPh_2 ligand is clearly tipped to one side ($N(4)-Re-P = 160.2(2)^\circ$) in order to allow H(2), which lies in the same plane as the Re-N(3) bond, to reside between Re and P. The Re- N_{eq} bond distances and the Re-N(4) bond distance are slightly longer than those in $[N_3N_F]Re(C_2H_4)$, consistent with more "steric pressure" in the coordination pocket where the phosphine resides. There is no feature of the triamido ligand in this complex that would be consistent with one of the amido nitrogens being protonated. Interestingly, both phenyl rings of the PPh_2 ligand are roughly parallel to two C_6F_5 rings on the $[N_3N_F]^{3-}$ ligand ~ 4 Å away, and clearly tipped to one side. This configuration appears to be a manifestation of the proposed interaction between C_6H_5 and C_6F_5 rings.⁵⁴⁻⁵⁶ The BAr_4^- anion suffered from some disorder in the CF_3 groups, several of which therefore were refined isotropically. An alternative description of a species that contains a proton "bridging" between Re and P is a

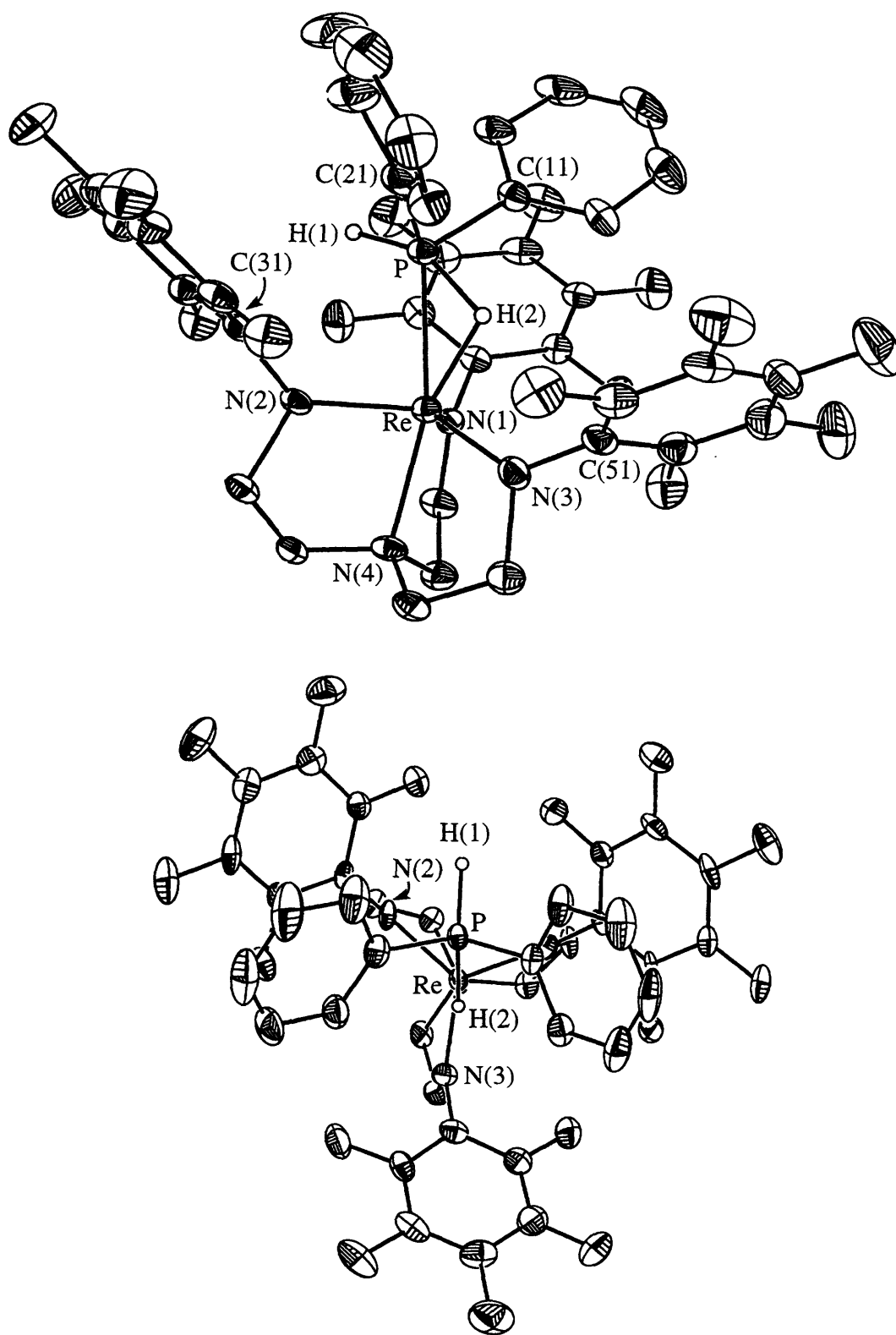


Figure 1.4. Side and Top ORTEP Views of the Structure of $\{[N_3NF]Re(PHPh_2)(H)\}^+ (4gH^+;$
 BAr_4^- anion not shown).

Table 1.4. Selected Bond Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of $\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H})(\text{PPh}_2)\}\text{BAr}_4$ (**4gH⁺**).

Bond Lengths			
Re - N(1)	1.949(7)	Re - N(4)	2.198 (6)
Re - N(2)	1.991(7)	P - H(1)	1.408(5)
Re - N(3)	1.998(7)	Re - P	2.410(2)
Bond Angles			
N(1) - Re - N(2)	114.5(3)	Re - N(3) - C(51)	129.0(5)
N(2) - Re - N(3)	121.0(3)	Re - P - H(1)	93.38(6)
N(1) - Re - N(3)	115.4(3)	C(11) - P - C(21)	103.3(4)
Re - N(1) - C(41)	129.5(5)	C(21) - P - H(1)	111.1(3)
Re - N(2) - C(31)	133.2(5)	C(11) - P - H(1)	111.1(3)
N(4) - Re - P	160.2(2)		

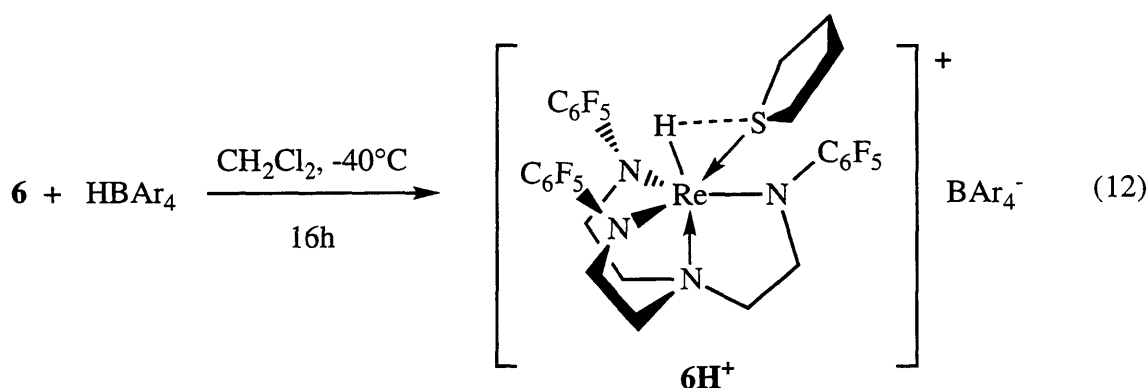
Table 1.5. Crystallographic data, collection parameters, and refinement parameters for $\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H})\text{PPh}_2\}\text{BAr}_4$ (**4gH⁺**).

Empirical Formula	$\text{C}_{68}\text{H}_{36}\text{N}_4\text{BF}_{39}\text{Re}$
Formula Weight	1877.99
Diffractometer	Siemens SMART/CCD
Crystal Dimensions (mm)	0.20 x 0.15 x 0.30
Crystal System	Monoclinic
a (Å)	21.0214 (1)
b (Å)	17.0496 (2)
c (Å)	22.7095 (3)
α (deg)	90
β (deg)	116.759 (1)
γ (deg)	90
V (Å ³)	7267.5 (1)
Space Group	P2 ₁ /c
Z	4
D _{calc} (Mg/m ³)	1.716
F ₀₀₀	3672
λ , radiation	0.71073, MoK α
Scan Type	ω
Temperature (K)	188 (2)
θ Range for Data Collection (deg)	1.56 to 22.96
Independent Reflections	9940
Absorption Correction	None
Refinement Method	Full-matrix least-squares on F ²
Data/Restraints/Parameters	9933/171/1042
Final R Indices [$I > 2\sigma(I)$]	R1 = 0.0632, wR2 = 0.1395
R Indices (all data)	R1 = 0.0779, wR2 = 0.1493
GoF	1.180
Extinction Coefficient	0.00029 (6)
Largest Diff. Peak and Hole (eÅ ⁻³)	1.527 and -1.475

phosphonium complex, $[\text{N}_3\text{N}_\text{F}]\text{Re}(\eta^2\text{-PR}_3\text{H}^+)$. Rotation of the " $[\eta^2\text{-PR}_3\text{H}]^+$ " ligand about the Re-ligand bond axis must be facile, since the complexes shows no evidence in solution of the approximate C_s symmetry found in the solid state.

$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D})\text{PMe}_3\}\text{BAr}_4$ (**4bD**⁺) was prepared in 66% yield by addition of DBAr_4 to **4b** in cold dichloromethane. The ^1H NMR spectrum of **4bD**⁺ in CD_2Cl_2 revealed a *hydride* ligand at 0.26 ppm ($J_{\text{PH}} = 7$ Hz), characteristic of $\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H})\text{PMe}_3\}^+$. The ^2H NMR spectrum in dichloromethane revealed a broad singlet at 1.82 ppm which is proposed to arise from the "deuteride" ligand in $\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D})\text{PMe}_3\}^+$; the explanation for the difference in this chemical shift from δ_{H} in **4bH**⁺ is obscure at present. Additionally, a doublet centered at 4.02 ppm ($J_{\text{HD}} = 12$ Hz) is ascribed to deuterium in a methylene unit in the $[\text{N}_3\text{N}_\text{F}]^{3-}$ backbone (see Discussion). The $^{31}\text{P}\{\text{H}\}$ NMR spectrum in CD_2Cl_2 reveals a triplet at -14.43 ppm ($J_{\text{DP}} = 4$ Hz) which arises from a P-Re-D moiety and a singlet at -14.78 ppm from P-Re-H.

Protonation of the $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{THT})$ complex (**6**) with one equivalent of HBAr_4 in cold dichloromethane yielded **6H**⁺ in 51% yield as green prisms upon crystallization from dichloromethane/pentane (equation 12). The ^1H NMR (CD_2Cl_2) spectrum of **6H**⁺ shows it to be C_3 symmetric on the NMR time scale with a "hydride" resonance at 3.50 ppm, similar to the chemical shifts observed in the large phosphine complexes. Four multiplets between 3.26 and

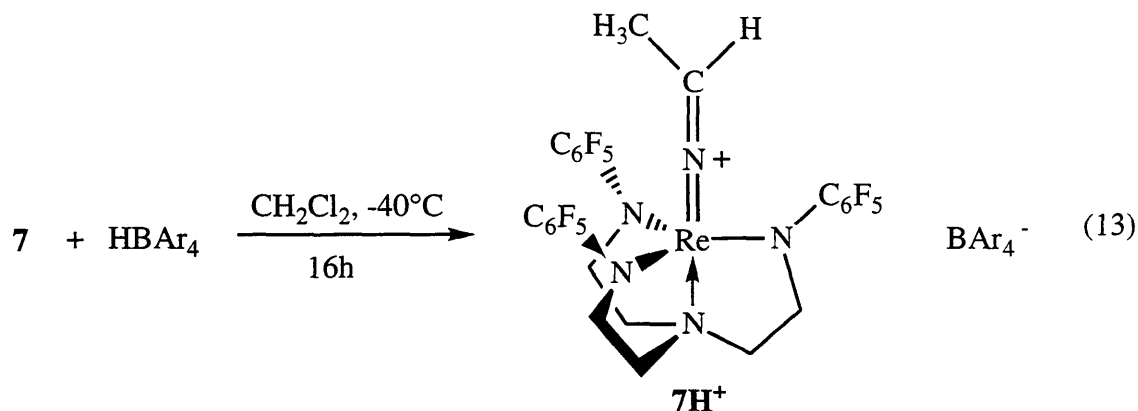


1.38 ppm were assigned to the eight THT protons, consistent with the tetrahydrothiophene ligand being constrained on the NMR time scale so that exo and endo protons are not equilibrated by

rotation about the Re-S bond. The $^{13}\text{C}\{\text{H}\}$ NMR CD_2Cl_2 spectrum in CD_2Cl_2 shows only two THT resonances at 45.69 and 29.97 ppm, indicating that a plane of symmetry passes through the THT ligand. I propose that the proton in 6H^+ is bridging between Re and S. Alternatively, 6H^+ could be regarded as an $\eta^2\text{-[THTH]}^+$ complex of $[\text{N}_3\text{NF}]\text{Re}$.

Interestingly, 4bH^+ , 4fH^+ , and 6H^+ all react with CO in CD_2Cl_2 to give $[\text{N}_3\text{NF}]\text{Re}(\text{CO})$ and the $(\text{HL})\text{BAr}_4$ salt (where L = a phosphine or THT). Depending on the degree of interaction of the "hydride" with the neutral donor ligand, this reaction might be construed as involving a reduction of the metal from Re(V) to Re(III), or, in the other extreme, simple displacement of the protonated phosphine or thiophene from what is already a Re(III) center.

Protonation of $[\text{N}_3\text{NF}]\text{Re}(\text{NCCH}_3)$ (**7**) led to formation of the cationic azavinylidene complex 7H^+ in 75% yield as green-black crystals from cold dichloromethane/pentane (equation 13). The ^1H NMR spectrum in CD_2Cl_2 indicates that the molecule has C_3 symmetry on the



NMR time scale, suggesting that the azavinylidene ligand is linear and rotates freely with respect to the $[\text{N}_3\text{NF}]^{3-}$ ligand. The methyl protons resonate at 3.57 ppm and are split into a doublet ($J_{\text{HH}} = 7$ Hz) by the azavinylidene proton, which in turn gives rise to a quartet at 1.54 ppm. The ^{13}C NMR spectrum reveals the β -carbon as a doublet at 118.25 ppm with $^1J_{\text{CH}} = 163$ Hz. Treatment of 7H^+ with DBN (DBN = 1,5-diazabicyclo[4.3.0]non-5-ene) produced **7** rapidly. Azavinylidene complexes in general are rare and there appears to be only one other example of

an azavinylidene complex of Re.⁵⁷ The methyl azavinylidene ligand in **7H⁺** is formulated as a linear species with the positive charge formally located on the nitrogen atom. In this manner the d_{xz} or d_{yz} orbitals are both utilized, one to contain two electrons and one to form the Re=N covalent double bond. Therefore the complex is three-fold symmetric in solution.

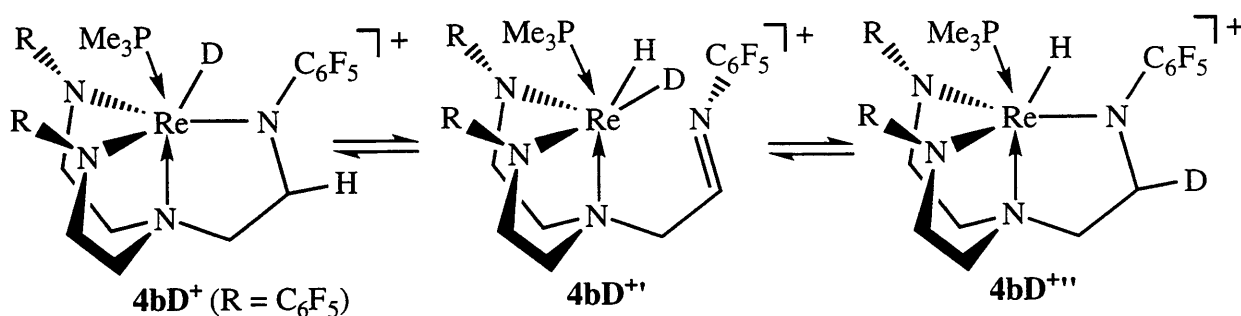
DISCUSSION

A theme that runs throughout this work is the prevalence of what are, or could be called, Re(III) species over Re(V) tautomers. It is tempting to propose that steric factors play a significant role in stabilizing Re(III) species over Re(V) tautomers, if not in $[N_3N_F]Re(H_2)$, then certainly in cationic complexes that are formed by protonating a $[N_3N_F]Re(L)$ species. The C_6F_5 rings are oriented in a manner that creates a bowl-like trigonal cavity (as in **3a**; see Figure 1.2). However, in the "bowl-like" configuration the $F_{ortho} \cdots F_{ortho}$ distances are on the order of 3.1 Å. (In **3a** they are 3.12, 3.08 and 3.11 Å.) Therefore the trigonal arrangement is maintained to a significant degree by steric interaction between C_6F_5 rings on the three equatorial amido nitrogen atoms. Opening one of the $N_{eq}-Re-N_{eq}$ angles to a significant degree beyond 120° would induce steric interactions that would cause the C_6F_5 rings to rotate, ultimately to the point where a C_6F_5 ring lies approximately in the Re- N_{eq} - C_{ipso} plane. The C_6F_5 rings in $[N_3N_F]^{3-}$ complexes have been observed to orient in a more "perpendicular" manner, but only when there is no ligand in the the apical cavity. For example, in monopyramidal $[N_3N_F]V$ the three C_6F_5 rings are turned such that three *ortho*-fluorines point toward V.¹⁴ The short $V \cdots F_{ortho}$ bond distance (2.652 Å) even suggests a weak interaction of the *ortho*-fluorines with the metal. Therefore one might expect a considerable degree of steric interaction between a C_6F_5 ring that lies approximately in the Re- N_{eq} - C_{ipso} plane and any ligand in the coordination cavity in the apical position. Therefore when a ligand is (or ligands are) present in the trigonal cavity the "bowl-like" shape maintains the trigonal configuration and at the same time exerts some steric pressure on the ligand or ligands in that cavity. This "steric factor" would seem to be an important means of stabilizing $[N_3N_F]Re(\eta^2-L)$ complexes, especially those in which η^2-L is a phosphonium or

THTH⁺ ligand. One example of a proton bridging between a metal and phosphorus in a phosphine complex is known,⁵⁸ but I could find no example of what could be called an η^2 -phosponium complex.

It is plausible that deuteration of **4b** could occur initially at Re, but the ¹H NMR spectrum of **4bD⁺** reveals the presence of a *hydride* ligand while the ²H NMR spectrum shows a deuteride ligand and deuterium in one of the [N₃NF]³⁻ backbone methylene units. To account for these observations, I propose that in **4bD⁺** one C-H_β bond is activated in one "arm" of the [N₃NF]³⁻ ligand followed by β-hydride elimination to give 18 electron **4bD⁺** which contains an HD ligand and an uncoordinated imine (Scheme 1.2). Similar but *irreversible* C-H_β activation was observed when [(Me₃SiCH₂CH₂)₃N]Ta(Me)₂, [(Et₃SiCH₂CH₂)₃N]Ta(Me)₂, or

Scheme 1.2. Deuterium Scrambling into the [N₃NF]³⁻ ligand.



[(Et₃SiCH₂CH₂)₃N]Ta(C₂H₄) was thermolyzed in toluene at 110°C.⁵⁹ H/D scrambling may then occur on Re; deuteride migration to the β-methylene unit and reformation of the equatorial amide then gives **4bD⁺**. The finding of one deuterium per molecule of **4bD⁺** (or, equally, a hydride ligand with intensity 0.5 in the ¹H NMR spectrum of **4bH⁺**) would favor an intramolecular mechanism.

Examples of inter- and intramolecular C-F bond activation, though still rare, are becoming more numerous.^{60,61} Yet the stability of the [N₃NF]³⁻ ligand was thought to be rather robust previous to this work, so it was surprising to find that the strong C_{aryl}-F bond in **7** was readily activated, even in the solid state. Although the mechanism is uncertain at this stage, it is

possible that a filled orbital on Re is able to access one *ortho*-fluorine, perhaps as a consequence of the minimal steric congestion imposed by the acetonitrile ligand. The formation of a strong Re-F bond and an unusual six-membered metallocycloimine could explain the stability of **7**.

CONCLUSIONS

Several $[\text{N}_3\text{N}_\text{F}]\text{Re}$ complexes, especially those of Re(III), have been readily prepared from the facile reduction of a low spin d_3 starting material. Rhenium complexes which contain amido ligands are scarce and those that bear more than one amido ligand are extremely rare,⁶²⁻⁷⁹ thereby establishing the molecules presented in this chapter as a unique host of stable polyamido rhenium complexes. The preference of Re(III) species over Re(V) tautomers seems to be most readily acceptable in complexes where a ligand in the apical cavity can bind in η^2 fashion, an apparently energetically favorable scenario where the d^4 metal is capable of backbonding. This may work in concert with the steric pressure maintained in this cavity by the amido nitrogen substituents. Both of these factors, explored again in Chapter II, appear to be emerging as persuasive elements in the development of related ancillary ligands.

EXPERIMENTAL

General Procedures. All air sensitive manipulations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or under argon when using Schlenk techniques. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under N_2 . Reagent grade diethyl ether, 1,2-dimethoxyethane, 1,4-dioxane, and tetrahydrofuran were distilled from sodium; dichloromethane was distilled from CaH_2 ; acetonitrile was distilled from P_2O_5 . Deuterated solvents were purified in a manner similar to that for protio solvents, degassed by three freeze-pump-thaw cycles, and vacuum transferred to solvent storage flasks until use. $[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NHC}_6\text{F}_5]\text{Re}(\text{O})\text{Cl}$ (**1**), $[\text{N}_3\text{N}_\text{F}]\text{ReBr}$ (**2**), $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{C}_2\text{H}_4)$ (**3a**), $[\text{N}_3\text{N}_\text{F}]\text{ReH}_2$, $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{HD})$, $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D}_2)$, $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{N}_2)$, $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{CO})$;¹⁶ 2,2',2''-

tris(pentafluoro-phenylamino)triethylamine ($\text{H}_3[\text{N}_3\text{NF}]$);¹¹ $\text{Ta}(\text{CH}^t\text{Bu})\text{Br}_3(\text{THF})_2$;²⁰ and $[\text{H}(\text{OEt}_2)_2]^+[(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4\text{B}]^-$ (HBAr_4)⁵¹ were prepared by published methods. Phosphines and silanes were purchased from commercial sources and used as received. THT and pyridine were distilled from CaH_2 (THT = tetrahydrothiophene).

NMR operating frequencies and reference standards for heteronuclei on the scale of ^1H (300 MHz, $\text{SiMe}_4 = 0$ ppm) are as follows: ^{13}C (75.4 Hz, $\text{SiMe}_4 = 0$ ppm), ^{31}P (121.4 MHz, 85% $\text{H}_3\text{PO}_4 = 0$ ppm), ^{19}F (282.2 Hz, $\text{CFCl}_3 = 0$ ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal reference. Fluorine and phosphorus spectra were referenced externally. Multiplicities in fluorine spectra are quantified as “J”, a pseudo coupling constant. Chemical shifts are reported in ppm and coupling constants are in hertz. All spectra were acquired at $\sim 22^\circ\text{C}$ unless otherwise noted.

IR spectra were recorded on a Perkin-Elmer FT-IR 16 spectrometer as Nujol mulls between KBr plates in an airtight cell. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratory or by Microlytics (South Deerfield, MA) or Schwarzkopf Micoranalytical Laboratory (Woodside, NY).

$[\text{N}_3\text{NF}]\text{ReBr}$ (2). A solution of $\text{Ta}(\text{CH}^t\text{Bu})\text{Br}_3(\text{THF})_2$ (9.041 g, 14.238 mmol) in 45 mL of toluene was slowly added to a stirred suspension of **1** (11.933 g, 13.560 mmol) in 150 mL of toluene at 22°C whereupon the mixture rapidly turned brown. After stirring the viscous solution overnight, the volume was reduced to 30 mL and the green-brown precipitate was filtered off and washed twice with toluene, Et_2O , and pentane. The precipitate was crystallized from CH_2Cl_2 /pentane at -40°C to yield 11.218 g of olive green crystals (91%): ^1H NMR (CD_3CN) δ -34 (very broad), -138 (very broad); ^{19}F NMR (CD_3CN) δ -132.1 (br s), -151.2 (br s), -156.9 (br s); MS 907 (M^+). Anal. Calcd for $\text{C}_{24}\text{H}_{12}\text{N}_4\text{BrF}_{15}\text{Re}(\text{CH}_2\text{Cl}_2)_{0.5}$ or $\text{C}_{49}\text{H}_{26}\text{N}_8\text{Br}_2\text{F}_{30}\text{Cl}_2\text{Re}_2$: C, 30.98; H, 1.38; N, 5.90; Br, 8.41; Cl, 3.73. Found: C, 31.20; H, 1.39; N, 6.01; Br, 8.00, 8.22; Cl, 3.81, 3.85. (The C, H, and N values are the average of six determinations ranging from 29.73 to 31.82 in C, 1.19 to 1.49 in H, and 5.43 to 6.19 in N.)

[N₃N_F]Re(C₂H₄) (3a). One side of a two-chamber vessel was charged with an olive-brown solution of **2** (400 mg, 0.608 mmol) in 40 mL THF. The other side was charged with Mg powder (295 mg, 12.150 mmol) and a stir bar. The solution was degassed by three freeze-pump-thaw cycles and ethylene (excess) was condensed into the vessel. The solution was combined with the Mg and stirred vigorously at room temperature overnight. All solvents were then removed *in vacuo* from the olive green mixture. The residue was extracted with 3x15 mL THF. The extract was filtered and excess 1,4-dioxane was added to the combined extracts. After 24 h [MgBr₂(1,4-dioxane)]_x was filtered off, THF was removed *in vacuo*, and the product was crystallized from CH₂Cl₂/pentane at -40°C. Small olive-green crystals were collected and dried *in vacuo* (346 mg, 65%): ¹H NMR (THF-*d*₈) δ 2.61 (s, 4), 3.27 (t, 6, ³J = 5.7), 3.87 (t, 6, ³J = 5.7); ¹H NMR (CD₂Cl₂, 22°C) δ 2.57 (br s, 4), 3.12 (t, 6, ³J = 5.7), 3.79 (t, 6, ³J = 5.7); ¹H NMR (CD₂Cl₂, -90°C) δ 3.87 (m, 3), 3.55 (m, 3), 3.15 (m, 3), 3.04 (m, 3), 2.30 (s, 4); ¹⁹F NMR (THF-*d*₈) δ -150.9 (m), -164.3 (t, ³J = 21), -166.6 (m); ¹⁹F NMR (CD₂Cl₂) δ -151.1 (m), -163.2 (t, ³J = 21), -165.7 (m). Calcd for C₂₆H₁₆N₄F₁₅Re: C, 36.50; H, 1.88; N, 6.55. Found: C, 36.70; H, 1.81; N, 6.88.

The analogous compound prepared from doubly ¹³C labelled ethylene showed a non-first-order multiplet in CD₂Cl₂ at δ 54.7 in the ¹³C NMR spectrum. In the ¹³C{¹H} NMR spectrum a singlet was observed with no discernible coupling to fluorine.

[N₃N_F]Re(C₃H₆) (3b). One side of a two-chamber vessel was charged with an olive-brown solution of **2** (600 mg, 0.608 mmol) in 40 mL THF. The other side was charged with Mg powder (295 mg, 12.150 mmol) and a stir bar. The solution was degassed by three freeze-pump-thaw cycles and propylene (excess) was condensed into the vessel. The solution was combined with the Mg and stirred vigorously at room temperature overnight. All solvents were then removed *in vacuo* from the olive green mixture. The residue was extracted with 3x15 mL THF. The extract was filtered and excess 1,4-dioxane was added to the combined extracts. After 24 h [MgBr₂(1,4-dioxane)]_x was filtered off, THF was removed *in vacuo*, and the product was crystallized from CH₂Cl₂/pentane at -40°C. Very dark green prisms were collected and dried *in vacuo* (346 mg, 65%): ¹H NMR (CD₂Cl₂) δ 3.76 (m, 6, NCH₂CH₂), 3.34 (m, 1, CH₃CHCH₂),

3.12 (d, 1, CH_3CHCHH , $J_{\text{HH}}(\text{vic, cis}) = 8.1$), 3.05 (t, 6, NCH_2CH_2), 2.73 (d, 1, CH_3CHCHH , $J_{\text{HH}}(\text{vic, trans}) = 9.3$), 0.75 (d, 3, CH_3CHCH_2 , $J_{\text{HH}} = 5.4$); $^{13}\text{C}\{\text{H}\}$ NMR (THF/ C_6D_6) δ 148-132 (m, NC_6F_5), 67.63, 61.56 (CH_3CHCH_2), 60.11 (CH_3CHCH_2), 56.46, 20.60 (CH_3CHCH_2); ^{19}F NMR (CD_2Cl_2) δ -150.20(m), -162.88 (m), -165.69 (m). Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{N}_4\text{F}_{15}\text{Re}$: C, 37.29; H, 2.09; N, 6.44. Found: C, 37.40; H, 1.90; N, 6.79.

$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PH}_3)$ (4a). One side of a two-chamber vessel was charged with a solution of **2** (485 mg, 0.491 mmol) in 50 mL of THF. The other side was charged with Mg powder (358 mg, 14.736 mmol) and a stir bar. The solution was degassed by three freeze-pump-thaw cycles and PH_3 (~10 equiv) was condensed into the vessel. The mixture was warmed to room temperature, combined with the Mg, and stirred vigorously at room temperature for six hours. Solvents were then removed from the red mixture *in vacuo*. Excess PH_3 was decomposed by venting the trap to a saturated aqueous solution of CuSO_4 . The red residue was extracted with 3x15 mL THF. The extract was filtered and excess 1,4-dioxane was added to the combined extracts. After 16h $[\text{MgBr}_2(1,4\text{-dioxane})]_x$ was filtered off, THF was removed *in vacuo*, and the product was crystallized from CH_2Cl_2 /pentane at -40°C . Light red crystals were collected in two crops; yield 171 mg (40%): ^1H NMR (CD_2Cl_2) δ 5.38 (d, 3, $J_{\text{PH}} = 305$) 3.79 (t, 6, NCH_2CH_2), 3.00 (t, 6, NCH_2CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 148-132 (m, NC_6F_5), 65.49, 57.09; ^{19}F NMR (CD_2Cl_2) δ -152.50(m), -165.34 (t, $J_{\text{FF}} = 21$), -166.16 (m); $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2) δ -138.18 (s). Anal. Calcd for $\text{C}_{24}\text{H}_{15}\text{N}_4\text{F}_{15}\text{PRe}$: C, 33.46; H, 1.75; N, 6.50. Found: C, 33.11; H, 1.55; N, 6.38.

$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{PMe}_3)$ (4b). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), PMe_3 (123 mg, 1.620 mmol) in 50 mL THF, Mg powder (295 mg, 12.150 mmol), and a stir bar; yield 274 mg, 75%): ^1H NMR (CD_2Cl_2) δ 3.63 (t, 6, NCH_2CH_2), 2.82 (t, 6, NCH_2CH_2), 0.14 (d, 9, $J_{\text{PH}} = 5.4$, PCH_3); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 148-132 (m, NC_6F_5), 67.21, 56.60, 23.27 (d, $J_{\text{PC}} = 26.6$, PCH_3); ^{19}F NMR (CD_2Cl_2) δ -150.74 (m), -164.85 (t, $J_{\text{FF}} = 21$), -165.90 (m); $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2) δ -45.16 (s). Anal. Calcd for $\text{C}_{27}\text{H}_{21}\text{N}_4\text{F}_{15}\text{PRe}$: C, 35.89; H, 2.34; N, 6.20. Found: C, 35.83; H, 2.37; N, 6.20.

[N₃N_F]Re(PEt₃) (4c). The procedure was analogous to that used to prepare **4a** employing **2** (500 mg, 0.506 mmol), PEt₃ (90 mg, 0.760 mmol) in 40 mL THF, Mg powder (369 mg, 15.180 mmol), and a stir bar; yield 313 mg (65%) of dark red crystals: ¹H NMR (CD₂Cl₂) δ 3.60 (t, 6, NCH₂CH₂), 2.77 (t, 6, NCH₂CH₂), 0.43 (m, 15, PEt₃); ¹³C{H} NMR (THF/C₆D₆) δ 148-132 (m, NC₆F₅), 68.58, 56.29, 24.70 (d, CH₂, J_{CP} = 24.8), 8.51; ¹⁹F NMR (CD₂Cl₂) δ -149.00 (b), -164.53 (t, J_{FF} = 21), -166.18 (m); ³¹P{H} NMR (CD₂Cl₂) δ -24.92 (s). Anal. Calcd for C₃₀H₂₇N₄F₁₅Pre: C, 38.10; H, 2.88; N, 5.92. Found: C, 38.35; H, 2.56; N, 5.94.

[N₃N_F]Re[P(*i*Pr)₃] (4d). The procedure was analogous to that used to prepare **4a** employing **2** (600 mg, 0.608 mmol), P(*i*-Pr)₃ (146 mg, 0.912 mmol) in 50 mL THF, Mg powder (443 mg, 18.230 mmol), and a stir bar; yield 408 mg (68%) of dark green crystals: ¹H NMR (CD₂Cl₂) δ 3.53 (t, 6, NCH₂CH₂), 2.67 (t, 6, NCH₂CH₂), 0.81 (dd, 18, J_{HH} = 7, J_{PH} = 12, PCHCH₃), 0.48 (m, 3, PCHCH₃); ¹³C{H} NMR (THF/C₆D₆) δ 145-135 (m, NC₆F₅), 71.41, 55.55, 33.19 (d, CHP, J_{PC} = 18.4), 19.69; ¹⁹F NMR (CD₂Cl₂) δ -146.52 (m), -163.69 (t, J_{FF} = 21), -165.97 (m); ³¹P{H} NMR (CD₂Cl₂) δ -11.56 (s). Anal. Calcd for C₃₃H₃₃N₄F₁₅Pre: C, 40.13; H, 3.37; N, 5.67. Found: C, 40.21; H, 3.33; N, 5.55.

[N₃N_F]Re(PMe₂Ph) (4e). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), PMe₂Ph (168 mg, 1.215 mmol) in 50 mL THF, Mg powder (295 mg, 12.150 mmol), and a stir bar; yield 165 mg (42%) of a red-orange microcrystalline solid: ¹H NMR (CD₂Cl₂) δ 7.08-6.77 (m, 5, Ph), 3.67 (t, 6, NCH₂CH₂), 2.87 (t, 6, NCH₂CH₂), 0.54 (d, 9, J_{PH} = 6.4, PCH₃); ¹³C{H} NMR (CD₂Cl₂) δ 148-135 (m, NC₆F₅), 129.71 (d, Ph, J_{PC} = 10.9), 128.49 (s, Ph), 127.53 (d, Ph, J_{PC} = 8.4), 67.40, 56.14, 23.28 (d, CH₃, J_{PC} = 27.8); ¹⁹F NMR (CD₂Cl₂) δ -149.25 (m), -164.70 (t, J_{FF} = 21), -165.83 (m); ³¹P{H} NMR (CD₂Cl₂) δ -30.91 (s). Anal. Calcd for C₃₂H₂₃N₄F₁₅Pre: C, 39.75; H, 2.40; N, 5.80. Found: C, 39.36; H, 2.16; N, 5.64.

[N₃N_F]Re(PMePh₂) (4f). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), PMePh₂ (263 mg, 1.215 mmol) in 50 mL THF, Mg powder (295 mg, 12.150 mmol), and a stir bar; yield 349 mg (84%) of red crystals: ¹H NMR (CD₂Cl₂) δ

6.48-7.10 (m, 10, Ph), 3.66 (t, 6, NCH_2CH_2), 2.87 (t, 6, NCH_2CH_2), 1.02 (d, 3, $J_{\text{PH}} = 6.0$, PCH_3); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 148-132 (m, NC_6F_5), 130.87 (d, $J_{\text{PC}} = 9.5$), 128.46, 127.81 (d, $J_{\text{PC}} = 7.8$), 68.32, 56.18, 22.10 (d, $J_{\text{PC}} = 28.3$, PCH_3); ^{19}F NMR (CD_2Cl_2) δ -148.76 (bs), -164.62 (t, $J_{\text{FF}} = 21$), -165.48 (m); $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2) δ -15.19 (s). Anal. Calcd for $\text{C}_{37}\text{H}_{25}\text{N}_4\text{F}_{15}\text{PRe}$: C, 42.84; H, 2.20; N, 5.19. Found: C, 43.19; H, 2.45; N, 5.45.

$[\text{N}_3\text{NF}]\text{Re}(\text{PPh}_2)$ (4g). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol), PPh_2 (226 mg, 1.215 mmol) in 50 mL THF, Mg powder (295 mg, 12.150 mmol), and a stir bar; yield 376 mg (91%) of orange cubes: ^1H NMR (CD_2Cl_2) δ 9.40 (d, 1, $J_{\text{PH}} = 319$, PH), 6.45-7.12 (m, 10, Ph), 3.73 (t, 6, NCH_2CH_2), 2.96 (t, 6, NCH_2CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 142-135 (m, NC_6F_5), 136.67, 131.92, 128.81, 128.33, 67.39, 56.63; ^{19}F NMR (CD_2Cl_2) δ -150.38 (m), -165.00 (t, $J_{\text{FF}} = 21$), -165.53 (m); $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2) δ 1.24 (s). Anal. Calcd for $\text{C}_{36}\text{H}_{23}\text{N}_4\text{F}_{15}\text{PRe}$: C, 42.65; H, 2.29; N, 5.53. Found: C, 42.71; H, 2.48; N, 5.36.

$[\text{N}_3\text{NF}]\text{Re}(\text{pyridine})$ (5). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol) and pyridine (160 mg, 2.025 mmol) in 50 mL THF, and a solution of MeLi (1.4 M in Et_2O , 0.61 mL, 0.851 mmol) in 20 mL of diethylether. The residue was extracted three times with 15 mL of CH_2Cl_2 instead of THF; yield 179 mg (48%): ^1H NMR (CD_2Cl_2) δ 6.54 (d, 2, Ph), 6.15 (m, 2, Ph), 5.92 (m, 1, Ph), 3.64 (t, 6, NCH_2CH_2), 2.73 (t, 6, NCH_2CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 158.03, 142-135 (m, NC_6F_5), 130.59, 122.39, 70.09, 61.27; ^{19}F NMR (CD_2Cl_2) δ -150.57 (m), -165.47 (t, $J_{\text{FF}} = 21$), -166.59 (m). Anal. Calcd for $\text{C}_{29}\text{H}_{17}\text{N}_5\text{F}_{15}\text{Re}$: C, 38.42; H, 1.89; N, 7.72. Found: C, 38.28; H, 2.02; N, 7.84.

$[\text{N}_3\text{NF}]\text{Re}(\text{THT})$ (6). The procedure was analogous to that used to prepare **4a** employing **2** (400 mg, 0.405 mmol) and THT (179 mg, 2.025 mmol) in 50 mL THF, and on the other side Mg powder (295 mg, 12.150 mmol) and a stir bar; yield 252 mg (68%): ^1H NMR (CD_2Cl_2) δ 3.62 (t, 6, NCH_2CH_2), 2.80 (t, 6, NCH_2CH_2), 1.23 (br s, 8, THT); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 148-132 (m, NC_6F_5), 68.14, 59.82, 45.69, 29.97; ^{19}F NMR (CD_2Cl_2) δ -150.68 (m), -165.10 (t,

$J_{\text{FF}} = 21$), -165.91 (m). Anal. Calcd for $\text{C}_{28}\text{H}_{20}\text{N}_4\text{F}_{15}\text{ReS}$: C, 36.73; H, 2.20; N, 6.12. Found: C, 36.59; H, 2.29; N, 6.17.

$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{NCMe})$ (7). The procedure was analogous to that used to prepare **4a** employing **2** (2.000 g, 2.026 mmol) and MeCN (249 mg, 6.077 mmol) in 40 mL THF and Mg powder (1.477 g, 60.780 mmol); yield 1.079 g (61%) of olive green prisms: ^1H NMR (CD_2Cl_2) δ 3.80 (t, 6, NCH_2CH_2), 3.51 (s, 3, NCCCH_3), 2.84 (t, 6, NCH_2CH_2); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 148-132 (m, NC_6F_5), 130.18, 65.97, 60.20, 0.93; ^{19}F NMR (CD_2Cl_2) δ -152.62 (m, 6F), -167.75 (m, 9F). IR (Nujol) 2151.8 cm^{-1} ($\text{C}\equiv\text{N}$). Anal. Calcd for $\text{C}_{26}\text{H}_{15}\text{N}_5\text{F}_{15}\text{Re}$: C, 35.95; H, 1.74; N, 8.06. Found: C, 35.81; H, 1.67; N, 8.26.

$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H}_2\text{SiEt}_2)$ (8a). The procedure was analogous to that used to prepare **4a** employing **2** (2.000 g, 2.026 mmol) and Et_2SiH_2 (536 mg, 6.077 mmol) in 50 mL THF and Mg powder (1.477 g, 60.78 mmol). The product was crystallized from DME/pentane at -40°C ; yield 911 mg (49%) or orange-red microcrystals: ^1H NMR (THF-d_8) δ 5.83 (s, 1, SiH, $J_{\text{SiH}} = 186$), 3.80 (t, 6, NCH_2CH_2), 3.11 (t, 6, NCH_2CH_2), 0.32 (t, 9, SiMe_3), -0.01 (m, 2, SiCH_2), -5.85 (s, 1, Si-H, $J_{\text{SiH}} = 44$); $^{13}\text{C}\{\text{H}\}$ NMR ($\text{THF/C}_6\text{D}_6$) δ 148-132 (m, NC_6F_5), 66.53, 55.93, 10.16 (s, SiCH_2CH_3), 7.38 (s, SiCH_2CH_3); ^{19}F NMR (CD_2Cl_2) δ -149.58 (b), -164.97 (t, $J_{\text{FF}} = 21$), -166.85 (m). Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{N}_4\text{F}_{15}\text{ReSi}$: C, 36.72; H, 2.64; N, 6.12. Found: C, 36.53; H, 2.47; N, 6.11.

$[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H}_3\text{SiPh})$ (8b). The procedure was analogous to that used to prepare **4a** employing **2** (500 mg, 0.506 mmol) and PhSiH_3 (110 mg, 1.013 mmol) in 30 mL THF and Mg powder (369 mg, 15.18 mmol). Orange-red needles were obtained from DME/pentane at -40°C ; yield 431 mg (89%): ^1H NMR (CD_3CN) δ 7.07 (m, 1, Ph), 6.94 (m, 2, Ph), 6.60 (m, 2, Ph), 5.00 (s, 2, SiH, $J_{\text{SiH}} = 183$), 3.81 (t, 6, NCH_2CH_2), 3.15 (t, 6, NCH_2CH_2), -3.86 (s, 1, Si-H-Re, $J_{\text{SiH}} = 38$); $^{13}\text{C}\{\text{H}\}$ NMR ($\text{THF/C}_6\text{D}_6$) 145-138 (m, NC_6F_5), 134.61, 128.47, 127.53, 65.94, 55.94; ^{19}F NMR (CD_3CN) δ -150.37 (m), -163.92 (t, $J_{\text{FF}} = 21$), -166.36 (m). Anal. Calcd for $\text{C}_{30}\text{H}_{20}\text{N}_4\text{F}_{15}\text{ReSi}$: C, 38.51; H, 2.15; N, 5.99. Found: C, 38.57; H, 2.14; N, 6.06.

Decomposition of 7, (9). A 50 mL pressure vessel was charged with a stir bar and a green-brown solution of **7** (500 mg, 0.576 mmol) in 20 mL toluene. The vessel was sealed under an atmosphere of N₂ and the solution was stirred at 100°C overnight. The resulting golden brown solution was concentrated and, upon addition of pentane and cooling to -40°C, black-green crystals were isolated and dried *in vacuo* (323 mg, 65%): ¹H NMR (C₆D₆) δ 5.08 (d, 3, NC=CH₃, J_{HF} = 8), 4.02 (m, 2H), 3.75 - 3.47 (m, 6H), 2.38 (m, 2H), 2.16 (m, 2H); ¹³C{¹H} NMR (THF/C₆D₆) δ 150-136 (C_{aryl}), 145.15 (s, NC=CH₃), 70.70, 66.99 62.75, 62.61, 57.99, 54.55, 8.23 (d, NC=CH₃, J_{CF} = 10, J_{C¹³C} = 47); ¹⁹F NMR (C₆D₆) d -40.06 (s, 1F), -139.37 (m, 1F), -147.81 (m, 5F), -157.91 (t, 1F), -163.96 (t, 2F), -165.85 (t, 4F), -168.90 (t, 1F). C, H, and N elemental analyses were variable in four attempts for C₂₆H₁₅N₅F₁₅Re.

[D(OEt₂)₂]⁺BAR₄⁻. A 250 mL round bottom Schlenk flask was charged with a stir bar and a solution of NaBAR₄ (5.000g, 5.642 mmol) in 125 mL Et₂O. The flask was transferred to a high vacuum line and cooled to -196°C whereupon a slight excess of DCl was condensed into the flask. Upon stirring and warming to room temperature NaCl precipitated. The mixture was allowed to stir for 5 minutes after which the flask was pumped into the drybox. The reaction mixture was chilled to -40°C and the reaction solution was filtered through a bed of Celite. The pale yellow filtrate was concentrated and the product was isolated as white crystals upon addition of pentane and cooling to -40°C overnight; yield 4.097 g (72%): ¹H NMR (CD₂Cl₂) δ 7.73 (b, 8, o-H), 7.58 (br, 4, p-H), 3.85 (q, 8, OCH₂CH₃), 1.31 (t, 12, OCH₂CH₃). ²H NMR (CH₂Cl₂) δ 12.84 (br).

{[N₃N_F]Re(H)(PMe₃)}⁺BAR₄⁻ (4bH**⁺).** A solution of **4b** (200 mg, 0.221 mmol) in 15 mL CH₂Cl₂ at -40°C was stirred as a solution of [(3,5-(CF₃)₂C₆H₃)₄B]⁻[H(OEt₂)₂]⁺ (224 mg, 0.221 mmol) in 2 mL CH₂Cl₂ at -40°C was added dropwise over a period of 1 minute. The reaction mixture turned dark red-green immediately and gradually faded to green after being stirred overnight. The solution was concentrated and the product was crystallized from CH₂Cl₂/pentane at -40°C as emerald green blocks; yield 281 mg (76%): ¹H NMR (CD₂Cl₂) δ 7.78 (s, 8, o-H), 7.59 (s, 4, p-H), 4.00 (t, 6, NCH₂CH₂), 3.43 (t, 6, NCH₂CH₂), 1.01 (d, 9, J_{PH} =

9, PMe), 0.26 (d, 1, $J_{\text{PH}} = 7$, Re-H); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 162.44 (q, C_{ipso} , $J_{\text{BC}} = 50$), 146-136 (m, NC_6F_5), 135.48 (s, C_{ortho}), 129.27 (q, C_{meta} , $J_{\text{CF}} = 32$), 125.25 (q, CF_3 , $J_{\text{CF}} = 272$), 118.11 (s, C_{para}), 66.98, 55.23, 21.57 (d, PCH_3 , $J_{\text{PC}} = 41$); ^{19}F NMR (CD_2Cl_2) δ -63.32 (m), -148.83 (m), -154.94 (t, $J_{\text{FF}} = 21$), -160.55 (m); $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2) δ -14.88. Anal. Calcd for $\text{C}_{59}\text{H}_{34}\text{N}_4\text{BF}_{39}\text{PRe}$: C, 40.08; H, 1.94; N, 3.17. Found: C, 40.21; H, 1.85; N, 3.11.

$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{D})(\text{PMe}_3)\}^+\text{BAr}_4^-$ (4bD**⁺).** This complex was prepared in identical fashion to **4bH**⁺ from **4b** (180 mg, 0.200 mmol) and $[\text{D}(\text{OEt}_2)_2]^+\text{BAr}_4^-$ (202 mg, 0.200 mmol) and isolated as large green blocks; yield 22 mg (66%). The spectroscopic properties are identical in every respect to those of **4bH**⁺. ^2H NMR (CH_2Cl_2) δ 4.02 (d, NCH_2CHD , $J_{\text{HD}} = 12$), 1.82 (bs, Re-D); $^{31}\text{P}\{\text{H}\}$ NMR (CH_2Cl_2) δ -14.43 (t, P-Re-D, $J_{\text{DP}} = 4$), -14.78 (s, P-Re-H).

$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H})(\text{PEt}_3)\}^+\text{BAr}_4^-$ (4cH**⁺).** This complex was prepared in a manner analogous to that employed to prepare **4bH**⁺ from **4c** (195 mg, 0.206 mmol) in 10 mL CH_2Cl_2 at -40°C and $[\text{H}(\text{OEt}_2)_2]\text{BAr}_4$ (209 mg, 0.206 mmol) in 2 mL CH_2Cl_2 at -40°C ; yield 323 mg amber crystals (97%): ^1H NMR (CD_2Cl_2) δ 7.72 (s, 8, o-H), 7.57 (s, 4, p-H), 3.98 (t, 6, NCH_2CH_2), 3.71 (d, 1, Re-H-P, $J_{\text{PH}} = 64$), 3.40 (t, 6, NCH_2CH_2), 1.19 (m, 6, $J_{\text{PH}} = 9$, PCH_2CH_3), 0.66 (m, 9, PCH_2CH_3); $^{13}\text{C}\{\text{H}\}$ NMR ($\text{THF}/\text{C}_6\text{D}_6$) δ 162.83 (q, C_{ipso} , $J_{\text{BC}} = 50$), 146-136 (m, NC_6F_5), 135.60 (s, C_{ortho}), 130.00 (q, C_{meta} , $J_{\text{CF}} = 32$), 125.50 (q, CF_3 , $J_{\text{CF}} = 272$), 118.15 (s, C_{para}), 67.45, 54.76, 21.61 (d, PCH_2CH_3 , $J_{\text{PC}} = 35$), 8.35 (d, PCH_2CH_3 , $J_{\text{PC}} = 6$); ^{19}F NMR (CD_2Cl_2) δ -63.30 (m), -147.55 (m), -154.84 (t, $J_{\text{FF}} = 21$), -160.77 (m); $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2) δ 23.02. Anal. Calcd for $\text{C}_{62}\text{H}_{40}\text{N}_4\text{BF}_{39}\text{PRe}$: C, 41.14; H, 2.23; N, 3.10. Found: C, 40.81; H, 2.12; N, 3.05.

$\{[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{H})(\text{PMePh}_2)\}^+\text{BAr}_4^-$ (4fH**⁺).** This complex was prepared in a manner analogous to that employed to prepare **4bH**⁺ from **4f** (200 mg, 0.195 mmol) in 15 mL CH_2Cl_2 at -40°C and $[\text{H}(\text{OEt}_2)_2]\text{BAr}_4$ (197 mg, 0.195 mmol) in 2 mL of CH_2Cl_2 at -40°C ; yield 243 mg (66%) of red-brown blocks: ^1H NMR (CD_2Cl_2) δ 7.73 (bs, 8, o-H), 7.56 (s, 4, p-H), 6.73-7.40 (m, 10, Ph), 4.72 (d, 1, $J_{\text{PH}} = 62$, Re-H), 4.04 (t, 6, NCH_2CH_2), 3.48 (t, 6, NCH_2CH_2), 2.01 (d, 3, $J_{\text{PH}} = 9.6$, PCH_3); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 148-132 (m, NC_6F_5), 162.50 (q, C_{ipso} , $J_{\text{BC}} = 50$),

145-136 (m, NC₆F₅), 136.01 (s, C_{ortho}), 133.40 (d, C_{ipso}, J_{PC} = 2), 131.27 (s, C_{ortho}), 130.40 (m, C_{meta}), 129.62 (q, C_{meta}, J_{CF} = 29), 125.22 (q, CF₃, J_{CF} = 272), 118.22 (s, C_{para}), 118.08 (s, C_{para}), 67.45, 53.51, 23.69 (d, PCH₃, J_{PC} = 48); ¹⁹F NMR (CD₂Cl₂) δ -63.24 (m), -146.03 (bs), -155.71 (t, J_{FF} = 21), -161.26 (m); ³¹P{H} NMR (CD₂Cl₂) δ 23.74. Anal. Calcd for C₆₉H₃₈N₄BF₃₉Pre: C, 43.80; H, 2.02; N, 2.96. Found: C, 43.88; H, 1.70; N, 2.82.

[[N₃N_F]Re(H)(PHPh₂)]⁺BAr₄⁻ (4gH⁺). This complex was prepared in a manner analogous to that employed to prepare **4bH⁺** from **4g** (200 mg, 0.195 mmol) in 15 mL CH₂Cl₂ at -40°C and [H(OEt₂)₂]BAr₄ (197 mg, 0.195 mmol) in 2 mL CH₂Cl₂ at -40°C; yield 257 mg pink needles (69 %): ¹H NMR (CD₂Cl₂) δ 7.73 (bs, 8, o-H), 7.56 (s, 4, p-H), 6.85-7.40 (m, 10, Ph), 6.97 (dd, 1, J_{HH} = 15, J_{PH} = 375, Re-H), 4.05 (t, 6, NCH₂CH₂), 3.57 (t, 6, NCH₂CH₂), 3.36 (dd, 1, J_{HH} = 15, J_{PH} = 54, Re-H); ¹³C{H} NMR (CD₂Cl₂) δ 162.42 (q, C_{ipso}, J_{BC} = 50), 145-136 (m, NC₆F₅), 135.44 (s, C_{ortho}), 133.00 (d, C_{ipso}, J_{PC} = 2), 131.22 (s, C_{ortho}), 130.40 (m, C_{meta}), 129.49 (q, C_{meta}, J_{CF} = 29), 125.24 (q, CF₃, J_{CF} = 272), 118.04 (s, C_{para}), 118.00 (s, C_{para}), 66.90, 55.51; ¹⁹F NMR (CD₂Cl₂) δ -63.28 (m), -149.04 (s), -155.41 (t, J_{FF} = 21), -161.18 (m); ³¹P{H} NMR (CD₂Cl₂) δ 38.11. Anal. Calcd for C₆₈H₃₆N₄BF₃₉Pre: C, 43.49; H, 1.93; N, 2.98. Found: C, 43.70; H, 1.84; N, 2.60.

[[N₃N_F]Re(D)(PHPh₂)]⁺BAr₄⁻ (4gD⁺). This complex was prepared in identical fashion to **4gH⁺** from **4g** (503 mg, 0.496 mmol) and [H(OEt₂)₂]BAr₄ (503 mg, 0.496 mmol); yield 691 mg (74%): ²H NMR (CH₂Cl₂) δ 6.86 (d, Re-D-P, J_{DP} = 56), 3.24 (d, P-D, J_{DP} = 7); ³¹P{H} NMR δ 38.11 (s), 38.10 (t, obscured by singlet at 38.11), 37.36 (t, J_{DP} = 56).

[[N₃N_F]Re(H)(THT)]⁺BAr₄⁻ (6H⁺). This complex was prepared in a manner analogous to that employed to prepare **4bH⁺** from **6** (200 mg, 0.218 mmol) in 15 mL CH₂Cl₂ at -40°C and [H(OEt₂)₂]BAr₄ (221 mg, 0.218 mmol) in 2 mL CH₂Cl₂ at -40°C; yield 193 mg green prisms (51%): ¹H NMR (CD₂Cl₂) δ 7.75 (s, 8, o-H), 7.57 (s, 4, p-H), 3.81 (t, 6, NCH₂CH₂), 3.50 (s, 1, Re-H), 3.26 (t, 6, NCH₂CH₂), 2.92 (m, 2, THT), 2.48 (m, 2, THT), 2.08 (m, 2, THT), 1.38 (m, 2, THT); ¹³C{H} NMR (CD₂Cl₂) δ 162.49 (q, C_{ipso}, J_{BC} = 50), 146-136 (m, NC₆F₅), 135.52 (s, C_{ortho}), 129.57 (q, C_{meta}, J_{CF} = 32), 125.32 (q, CF₃, J_{CF} = 272), 118.15 (s, C_{para}), 65.19 (THT),

61.80, 56.15, 29.28 (THT); ^{19}F NMR (CD_2Cl_2) δ -63.27 (m), -148.78 (m), -155.30 (t, $J_{\text{FF}} = 21$), -159.92 (m); $^{31}\text{P}\{\text{H}\}$ NMR (CD_2Cl_2) δ -14.88. Anal. Calcd for $\text{C}_{60}\text{H}_{33}\text{N}_4\text{BF}_{39}\text{ReS}$: C, 40.49; H, 1.87; N, 3.15. Found: C, 40.49; H, 1.57; N, 3.21.

$\{[\text{N}_3\text{N}_\text{F}]\text{Re}[\text{NC}(\text{H})\text{Me}]\}^+\text{BAr}_4^-$ (7H^+). This complex was prepared in a manner analogous to that employed to prepare 4bH^+ from **7** (200 mg, 0.230 mmol) in 15 mL CH_2Cl_2 at -40°C and $[\text{H}(\text{OEt}_2)_2]\text{BAr}_4$ (233 mg, 0.230 mmol) in 2 mL CH_2Cl_2 at -40°C . The solution was allowed to stir for 2 hours; yield 299 mg green-black crystals (75%): ^1H NMR (CD_2Cl_2) δ 7.77 (s, 8, o-H), 7.58 (s, 4, p-H), 4.18 (t, 6, NCH_2CH_2), 3.77 (t, 6, NCH_2CH_2), 3.57 (d, 3, $J_{\text{HH}} = 6.6$, $\text{NCCH}_3(\text{H})$), 1.54 (q, 1, $J_{\text{HH}} = 6$, $\text{NCCH}_3(\text{H})$); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 162.62 (q, C_{ipso} , $J_{\text{BC}} = 50$), 146-136 (m, NC_6F_5), 135.66 (s, C_{ortho}), 129.73 (q, C_{meta} , $J_{\text{CF}} = 32$), 125.25 (q, CF_3 , $J_{\text{CF}} = 272$), 118.25 (s, $\text{NCCH}_3(\text{H})$, $^1J_{\text{CH}} = 163$), 66.34, 57.78, -0.61 (s, $\text{NCCH}_3(\text{H})$); ^{19}F NMR (CD_2Cl_2) δ -63.22 (m), -149.14 (m), -154.67 (t, $J_{\text{FF}} = 21$), -160.98 (m). Anal. Calcd for $\text{C}_{58}\text{H}_{27}\text{N}_5\text{BF}_{39}\text{Re}$: C, 40.2; H, 1.63; N, 4.04. Found: C, 40.51; H, 1.54 N, 4.11.

Ligand Substitution Experiments. *Room temperature:* in a typical experiment, 20 mg complex was dissolved in CH_2Cl_2 (0.7 mL) with ca. 3 equiv of donor ligand in an NMR tube and allowed to stand at ca. 22°C for 1-3 days. Reactions were followed by ^{19}F NMR. *High temperature:* in a typical experiment, 20 mg complex was dissolved in toluene (0.7 mL) with ca. 3 equiv of donor ligand in an NMR tube which was flame sealed and then kept at $85\text{--}120^\circ\text{C}$ for hours to days. Reactions were monitored by ^{19}F NMR.

Reaction of 4bH^+ with CO. A 120 mL pressure vessel was charged with a green solution of 4bH^+ (500 mg, 0.299 mmol) in 25 mL CH_2Cl_2 . The solution was frozen to 77 K, the head space evacuated, and ~ 1 equivalent CO was introduced to the vessel which was then sealed. Upon warming to room temperature, the green slurry rapidly turned to a golden-brown solution and was stirred for two days after which it was concentrated *in vacuo*. Upon addition of pentane and cooling to -40°C , a green solid precipitated which contained $(\text{HPMe}_3)\text{BAr}_4$ as the only identifiable species (a similar NMR tube experiment also contained a detectable quantity of

[N₃N_F]Re(CO)): ¹H NMR (CD₂Cl₂) δ 7.91, 7.66, 6.22 (m, HP(CH₃)₃), 1.95 (dd, HP(CH₃)₃);
¹⁹F NMR (CD₂Cl₂) d -62.86 (s).

Reactions of 4fH⁺ and 6H⁺ with CO on an NMR scale. In a typical experiment, an NMR tube containing 20 mg complex dissolved in 0.7 mL CD₂Cl₂ was charged with ~1 equivalent CO and then flame-sealed. Reactions were followed by ¹H-, ¹⁹F-, and ³¹P{H} NMR. After one day, reaction mixtures contained only [N₃N_F]Re(CO) and the (HL)BAr₄ salt.

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CHAPTER II

Dinitrogen Fixation and Reduction by Triamidoamine Complexes of Mo

INTRODUCTION

Dinitrogen is one of the most plentiful and readily available molecules and is therefore an attractive source of nitrogen for organonitrogen compounds. The robust N-N triple bond, however, has precluded the facile utilization of relatively inert dinitrogen. The first and most dramatic man-made advance in dinitrogen fixation was made over eighty years ago when the heterogeneous iron-catalyzed Haber-Bosch process was implemented to catalytically reduce dinitrogen to ammonia with elevated temperatures and pressures. In the decades to follow, nitrogenases were discovered which reduce dinitrogen to ammonia, and protons to dihydrogen at ambient temperatures and pressures in a process which consists of an overall transfer of eight protons and eight electrons.^{1,2} The desire to achieve a similar mild reduction of dinitrogen to ammonia using transition metal catalysts was fueled by the discovery of the first transition metal complex which contains dinitrogen as a ligand in 1965.³ Such a reduction would require a formal delivery of six electrons and six protons per dinitrogen molecule and would probably involve a variety of intermediates.

More insight into dinitrogen fixation was garnered from the recently reported X-ray crystal structures of the Mo/Fe cores of nitrogenases from *Azotobacter vinelandii*⁴ and *Clostridium pasteurianum*.^{5,6} However, the structures provide scant evidence of the actual mechanism by which dinitrogen is reduced in these systems. Thus several challenges still remain for the inventive chemist who wishes to achieve dinitrogen reduction by using transition metal complexes. For example: What metals (other than Fe and Mo) may be employed for dinitrogen fixation? What oxidation state, ligand, and geometry requirements must be satisfied to achieve this? And finally, what is the mechanism of dinitrogen reduction (e.g. what are the key intermediates)?

First, transition metals in groups IV through X (except Pd and Pt) are known to form dinitrogen complexes and it has long been recognized that Mo and Fe play roles in the biological reduction of dinitrogen.⁷ Considerable attention, however, has recently been given to V as a consequence of its presence in V-containing nitrogenases⁸ and in V complexes capable of binding dinitrogen⁹⁻¹⁵ or N_xH_y ligands relevant to dinitrogen fixation.¹⁶ Scott recently reported a uranium

complex that contains coordinated dinitrogen, the first example of an actinide element playing this role.¹⁷ Second, a substantial number and variety of ancillary ligands have been shown to stabilize transition metal complexes of dinitrogen including ammonia (in $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$),³ phosphines (as in *trans*- $\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4$),⁷ cyclopentadienyl ligands (in $[\text{Cp}^*_2\text{Zr}(\text{N}_2)]_2(\mu\text{-N}_2)$),¹⁸ sulfur ligands (in *trans*- $\text{Mo}(\text{N}_2)_2(\text{Me}_8[16]\text{aneS}_4)$),¹⁹ mixed P/N macrocyclic ligands (in $\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu\text{-}\eta^2\text{-N}_2)$),²⁰ and terpyridine ligands (in $[(\text{tpy})\text{Cl}_2\text{Os}(\text{N}_2)\text{OsCl}_2(\text{tpy})]^+$).²¹ Finally, considerable knowledge of dinitrogen reduction has already been gained in the chemistry of low oxidation state dinitrogen chemistry. Recent studies in high oxidation state dinitrogen chemistry show that the metal (such as Mo or W) is found in its highest possible oxidation state at some stage during a hypothetical dinitrogen reduction cycle.²²

Some advances in high oxidation state dinitrogen chemistry suggested some minimal requirements for a transition metal complex to bind and reduce dinitrogen. First, while it appears that a d^2 electronic configuration of a group V metal is sufficient to form an initial monometallic dinitrogen complex, it is less clear for a group VI metal for which a d^3 configuration may be sufficient.²³ Nonetheless, nearly all examples of dinitrogen complexes containing metals in the d^2 electronic configuration exist as $\text{M}_2(\mu\text{-N}_2)$ species.¹⁰ Second, the findings that $\text{Cp}^*\text{Me}_3\text{W}=\text{NNH}_2$ and $[\text{Cp}^*\text{Me}_3\text{Mo}(\eta^2\text{-N}_2\text{H}_4)]^+$ both react with mild acid to furnish nearly two equivalents of NH_3 indicated that a single metal site is sufficient to split the N-N bond.²⁴ The frontier orbital set of the MCp^*Me_3 core is comprised of two nondegenerate and orthogonal orbitals of π symmetry (d_{xy} and d_{z^2} taking the Cp^* centroid - W vector as the z-axis) and one orbital of σ symmetry ($d_{x^2-y^2}$) which are available for binding a molecule of N_2 . As described in Chapter 1, triamidoamine ligands which impart C_3 symmetry about a metal also enforce a 2π , 1σ set of frontier orbitals (in this case the two orbitals of π symmetry are strictly degenerate) which also is an ideal arrangement for binding dinitrogen.²²

These findings have spurred studies of trigonally symmetric Mo complexes containing amide ligands which have been shown to react with dinitrogen to varying degrees. For example, Kol *et al.* showed that $[\text{N}_3\text{N}_\text{F}]\text{MoOTf}$ could undergo a two electron reduction with sodium in the

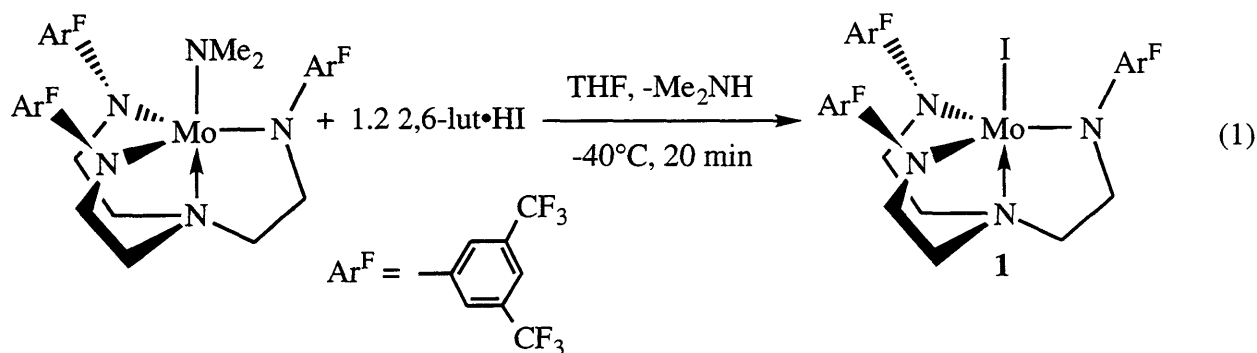
presence of dinitrogen to afford a sodium diazenido complex, $([N_3NF]Mo-N=N)^-(NaL_x)^+$, and a one electron reduction to give a bimetallic diazenido complex, $[N_3NF]Mo-N=N-Mo[N_3NF]$ (L = diethyl ether or THF, $[N_3NF]^{3-} = [(C_6F_5)NCH_2CH_2]_3N^{3-}$).²⁵ A related complex, $\{[(Me_2(tBu)SiNCH_2CH_2)_3N]Mo\}_2(N_2)$, was furnished in low yield from the reaction between $MoCl_3(THF)_3$ and $Li_3[(tBuMe_2SiNCH_2CH_2)_3N]$ and was crystallographically characterized.²⁶ The trigonal planar complex $Mo(anilide)_3$ reacts with dinitrogen to give the dimolybdenum diazenido complex, $[(anilide)_3Mo]_2(N_2)$, and then in an unprecedented symmetrical cleavage reaction, two equivalents of the nitrido complex $(anilide)_3Mo\equiv N$ ($anilide = [N(tBu)(3,5-C_6H_3Me_2)]^-$).^{27,28}

Other trigonally symmetric Mo complexes might be derived from triamidoamine ligands which bear a variety of substituents on the amido nitrogens. One ligand which has not been extensively employed is $[(3,5-(CF_3)_2C_6H_3)NHCH_2CH_2]_3N$ ($[N_3NF_{18}]H_3$) also reported by Kol as a white and crystalline solid.²⁵ Similarities of $[N_3NF_{18}]H_3$ to $[N_3NF]H_3$ include robust N-C_{aryl} bonds and strongly electron-withdrawing aryl groups. Complexes of $[N_3NF_{18}]^{3-}$ were anticipated to be more soluble than their $[N_3NF]^{3-}$ counterparts and display enlarged "steric pockets" in which coordinated ligands would be afforded more steric protection. Furthermore, $[N_3NF_{18}]^{3-}$ complexes contain no aromatic *ortho*-fluorines which were proposed to be a key feature in the decomposition of $[N_3NF]Re(NCMe)$ as described in Chapter I. This chapter will therefore describe the preparation of $[N_3NF_{18}]^{3-}$ complexes of Mo and their reactivity toward dinitrogen.

RESULTS

Starting Material. An attempt to prepare a Mo(IV) chloride from the reaction between $Li_3[N_3NF_{18}]$ (generated *in situ* from 3 BuLi and $[N_3NF_{18}]H_3$) and $MoCl_4(THF)_2$ ²⁹ gave $[N_3NF_{18}]MoCl$ in very poor yields (typically less than 10%) after crystallization from cold dichloromethane. Also, attempts to prepare $[N_3NF_{18}]MoCl$ from $[N_3NF_{18}]H_3$, $MoCl_4(THF)_2$, and Et_3N gave several products and the separation of $[N_3NF_{18}]MoCl$ from the partially soluble

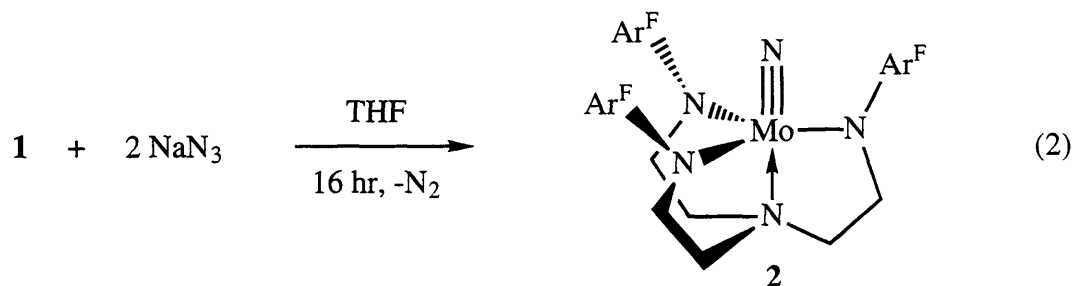
ammonium salts was problematic. Therefore a less direct but higher yielding route to $[\text{N}_3\text{NF}_{18}]\text{MoX}$ where X might be a halide or triflate was realized by utilizing the dimethylamide complex, $[\text{N}_3\text{NF}_{18}]\text{MoNMe}_2$.²⁵ The dimethylamide ligand was removed most cleanly in the reaction between $[\text{N}_3\text{NF}_{18}]\text{MoNMe}_2$ and a slight excess of 2,6-lutidinium iodide in THF at -40°C to furnish paramagnetic $[\text{N}_3\text{NF}_{18}]\text{MoI}$ (**1**) as orange needles in 87% yield when crystallized from cold dichloromethane (equation 1). The ^1H NMR spectrum of **1** in CD_2Cl_2 shows broadened resonances for the H_{ortho} and H_{para} resonances at 17.46 and 3.34 ppm, respectively. Resonances for the methylene protons of the $[\text{N}_3\text{NF}]^{3-}$ backbone are at -25.02 and -78.82 ppm, respectively,



which is consistent with spectroscopic data from other Mo complexes of this type.²² I felt that the readily prepared iodide complex **1** would be more easily reduced than the corresponding and less soluble OTf complex (prepared from **1** and TMSOTf).

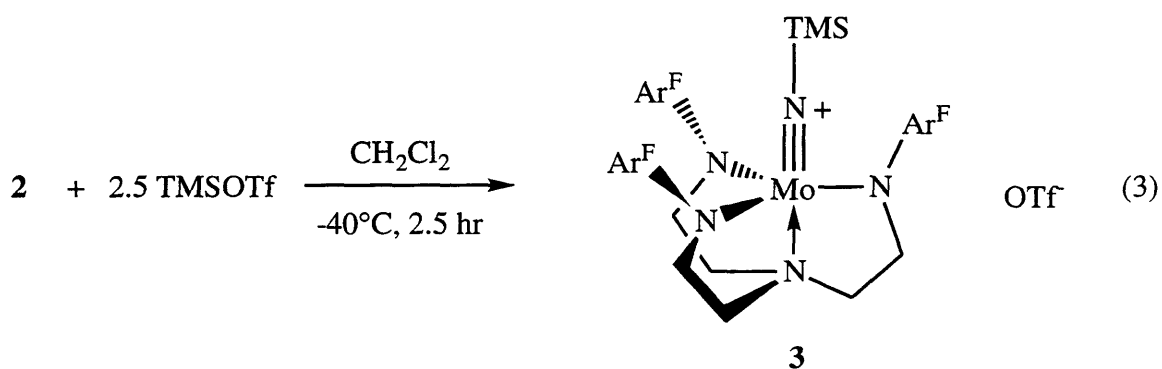
Preparation and Reactivity of a Terminal Nitrido Complex. In a hypothetical cycle in which a Mo complex containing a dinitrogen ligand is reduced in a stepwise manner, a possible intermediate is a terminal nitrido complex.^{7,30-32} If this cycle was in fact a catalytic system, then a controlled and well-defined route by which to remove the nitrido ligand would be necessary. Therefore, nitrido complex $[\text{N}_3\text{NF}_{18}]\text{MoN}$ (**2**) was prepared in the reaction between **1** and a two-fold excess of NaN_3 in THF as canary yellow needles in 83% yield when crystallized from cold dichloromethane (equation 2). It is presumed that the formation of **2** proceeds through an azide intermediate from which dinitrogen is lost, a type of reaction for which there is

considerable precedent.³³ The ^1H NMR spectrum in CD_2Cl_2 shows that diamagnetic **2** has 3-fold symmetry on the NMR time scale and is stable at room temperature for days. Many nitrido complexes are known, including those related to **2** such as $[\text{N}_3\text{NF}]\text{MoN}^{25}$ and $[\text{N}_3\text{N}]\text{MoN}$,³⁴



whereas monomeric complexes containing a triple bond between the metal and the higher pnictogens have only been reported recently ($[\text{N}_3\text{N}]^{3-} = (\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}^{3-}$).^{34,35}

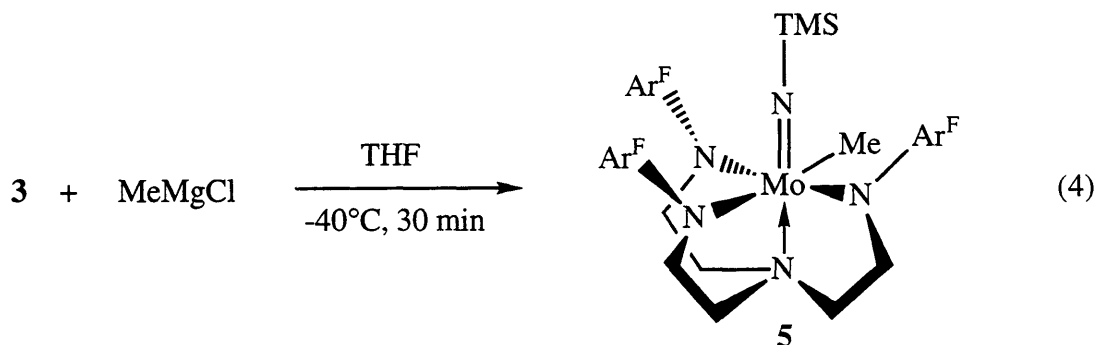
Terminal nitrido species can be readily attacked by electrophiles to give cationic imido complexes.³³ Thus addition of excess TMSOTf to **2** in dichloromethane led to the gradual precipitation of analytically pure, bright yellow, and diamagnetic $\{[\text{N}_3\text{NF}_{18}]\text{MoNTMS}\}\text{OTf}$ (**3**) in 91% yield (equation 3). The ^1H NMR of **3** in CD_3CN shows that it is 3-fold symmetric in solution which indicates that the imido ligand most likely is not bent and thus forms a pseudo triple



bond with Mo. No resonance for the triflate anion could be found in the $^{13}\text{C}\{\text{H}\}$ NMR spectrum and the ^{19}F spectrum contained a slightly broadened resonance at -78.87 ppm, suggesting that in

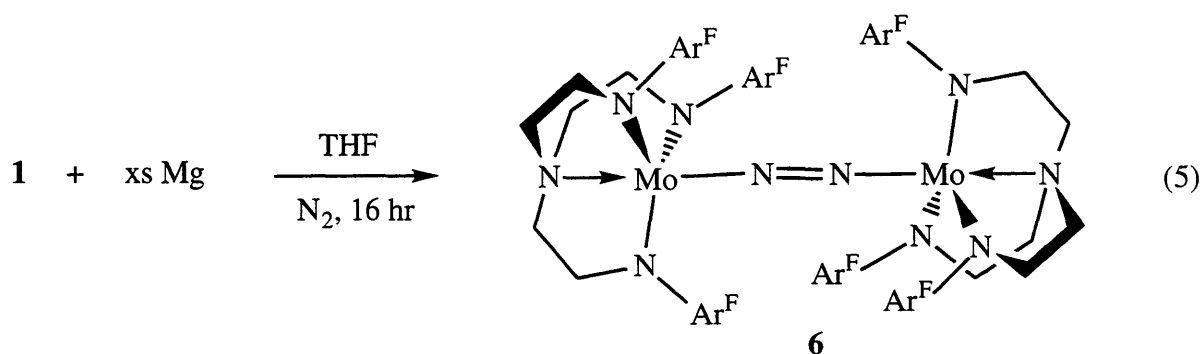
CD₃CN triflate may be only weakly bound. The iodo derivative of **3** could be prepared from **1** and excess TMSN₃ in THF at -40°C to afford purple microcrystals of [N₃NF₁₈]MoI(NTMS) (**4**) in 43% yield. Complex **4** may also be rapidly generated in the reaction between **2** or **3** and TMSI (see Experimental section for details). The ¹H NMR spectrum of **4** in C₆D₆ shows that it is 3-fold symmetric and most likely is a neutral complex, but broadened resonances for the methylene protons on the [N₃NF₁₈]³⁻ backbone suggest that the large iodide and imido ligands impede rapid rotation of the "I(NTMS)" unit with respect to the [N₃NF₁₈]³⁻ ligand on the NMR time scale. In toluene-*d*₈, the broad resonances observed at 22°C for the [N₃NF₁₈]³⁻ methylene protons gave rise to 5 featureless peaks in a ratio 1:1:1:1:2 when the sample was cooled to -85°C. This is most likely a consequence of the [N₃NF₁₈]³⁻ ligand becoming "locked" into two possible conformations, similar to what was observed in the low temperature ¹H NMR spectra of [N₃NF]Re(ethylene) and [N₃NF]Re(propylene) as described in Chapter I.

Further chemistry of **3** was not explored in much more detail. However, a plausible next step in the removal of the nitrido ligand from **3** would be reduction by one electron to give a Mo(V) imido complex.³⁴ No reaction was observed between **3** and Mg and only decomposition occurred when **3** was treated with Na or Li₂C₈H₈. Complex **3** was treated with MeMgCl in the hope of producing known [N₃NF₁₈]MoNMe₂, but instead dark purple and extremely soluble diamagnetic [N₃NF₁₈]Mo(Me)NTMS (**5**) was formed in nearly quantitative yield. The NMR spectra of **5** in C₆D₆ suggest that it has mirror symmetry and thus it seems reasonable that the methyl group attacked the metal to give a Mo(VI) species as shown in equation 4. Alkylation of a



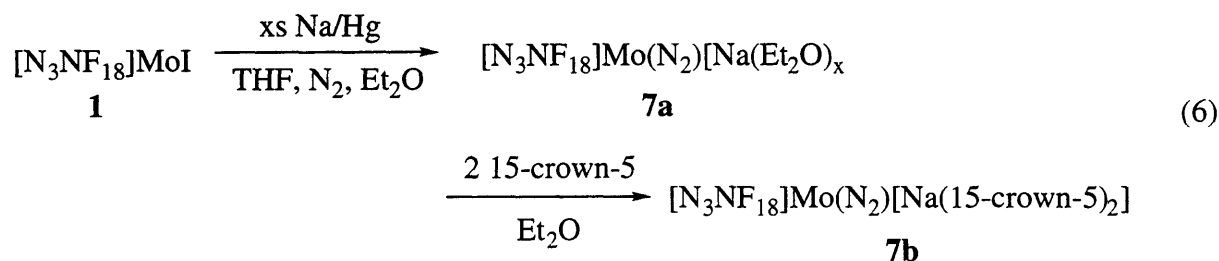
hydrazido cation also occurs at the metal center (*vide infra*). The relatively small chemical shift of the added methyl group in the ^1H NMR spectrum ($\delta = 0.63$ ppm) and data from an X-ray crystallographic study on the related complex $[\text{N}_3\text{N}]\text{Mo}(\text{Me})\text{NTMS}$ are consistent with this proposal.³⁴

Complexes Which Contain Dinitrogen. When a dark orange solution of **1** was stirred with excess Mg under an atmosphere of dinitrogen in THF, a dark purple mixture developed from which purple blocks were isolated when crystallized from dichloromethane/pentane at -40°C (equation 5). The product is a paramagnetic species which gives correct elemental analysis (C, H, and N) for $[\text{N}_3\text{NF}_{18}]\text{Mo}-\text{N}=\text{N}-\text{Mo}[\text{N}_3\text{NF}_{18}]$ (**6**). An attempted X-ray crystal structure on **6** yielded data of sufficient quality to confirm the diazenido linkage between two Mo centers and staggered Ar^{F} groups on the opposing $[\text{N}_3\text{NF}]^{3-}$ ligands, but the



structure could not be refined to an acceptable level. The ^{19}F NMR spectrum in CD_2Cl_2 showed two broad CF_3 resonances of equal intensity at -41.85 and -61.96 ppm which suggests that the $\mu\text{-N}_2$ ligand may force the two $[\text{N}_3\text{NF}_{18}]^{3-}$ ligands to adopt a "locked" conformation in which an equal number of CF_3 groups on twisted $3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3$ rings are oriented either toward or away from the steric pocket. Electrophiles such as MeOTf and TMSOTf do not react with **6** to give imido species such as **5** which is most likely a consequence of the severe steric congestion about the diazenido ligand.

Further reduction of **6** by one electron per Mo, however, could be effected by Na/Hg in THF to give port-red $\{[\text{N}_3\text{NF}_{18}]\text{Mo}(\text{N}_2)\}[\text{Na}(\text{L})_x]$ (**7a**) where L is THF or diethyl ether. Complex **7a** could also be prepared more directly by reduction of **1** with excess Na/Hg in THF (equation 6). The frontier orbitals in **7a** contain 4 electrons; therefore this complex is diamagnetic in a C_3 environment. It was characterized by sequestering the Na cation with two molecules of 15-

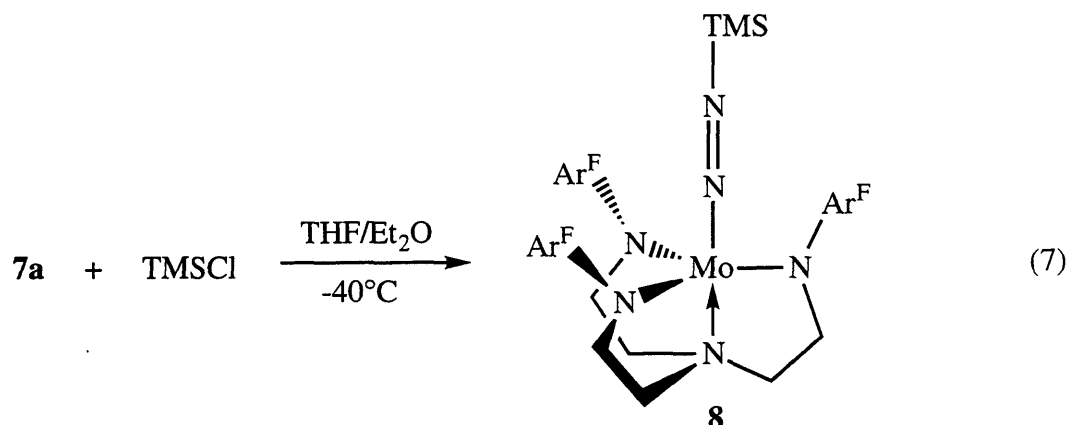


crown-5 to give **7b** in 48% yield. The IR spectrum of **7b** (in DME solution) reveals the NN stretch at 1850 cm^{-1} , a value which is consistent with the ionic description reported by Kol for the related anionic diazenido complex $\{[\text{N}_3\text{NF}]\text{Mo}(\text{N}_2)\}[\text{Na}(\text{15-crown-5})]$.²⁵

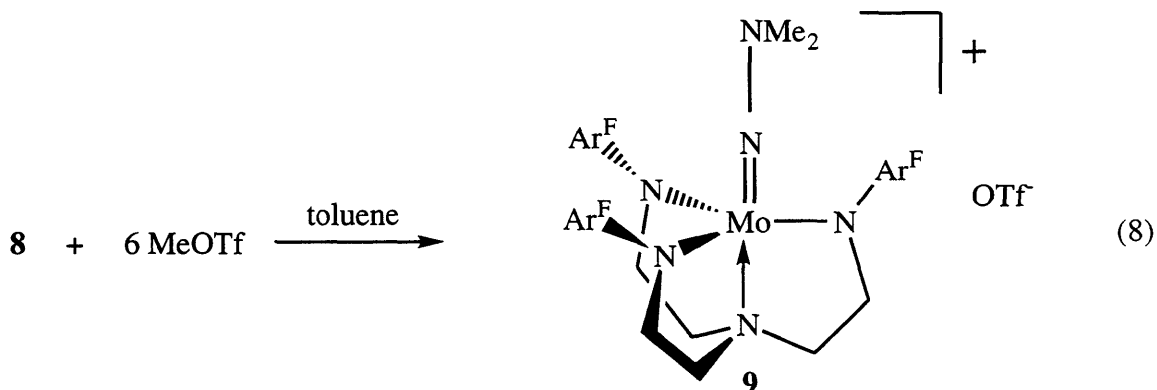
In the reduction of **1** by excess Na/Hg in the *absence* of N_2 (*in vacuo* or under Ar), a nondescript brown solid was isolated but not characterized. However, exposure of a THF solution of this product to N_2 gave rapidly deep purple **6** (according to ^1H and ^{19}F NMR). Since this reaction sequence could not be satisfactorily reproduced in three attempts, no further study was devoted to the identity of the brown intermediate.

A neutral diazenido complex may be prepared by addition of excess TMSCl to a cold THF solution of **7a** to give diamagnetic $[\text{N}_3\text{NF}_{18}]\text{MoNNTMS}$ (**8**) as deep yellow shards in 90% yield when crystallized from dichloromethane at -40°C (equation 7). The IR spectrum of **8** contains a $\text{N}=\text{N}$ absorption at 1698 cm^{-1} , indicating that this complex is a true diazenido complex. Interestingly, **7a** was oxidized by either $\text{MoCl}_3(\text{THF})_3$ ³⁶ or FeCl_2 to produce **6** and no detectable quantities of bimetallic diazenido species as was observed in the reaction between related $\{[\text{N}_3\text{N}]\text{MoNN}\}_2\text{Mg}(\text{THF})_2$ and FeCl_2 .³⁷ This was unexpected since $[\text{N}_3\text{N}]\text{MoNNTMS}$, an analog of **8**, was easily prepared in a similar manner from $\{[\text{N}_3\text{N}]\text{MoNN}\}_2\text{Mg}(\text{THF})_2$ and

TMSCl. Complex **8** did not react with Mg and decomposed when treated with Na/Hg. In light of the failures to reduce **8**, a different strategy was employed to further functionalize the dinitrogen ligand.



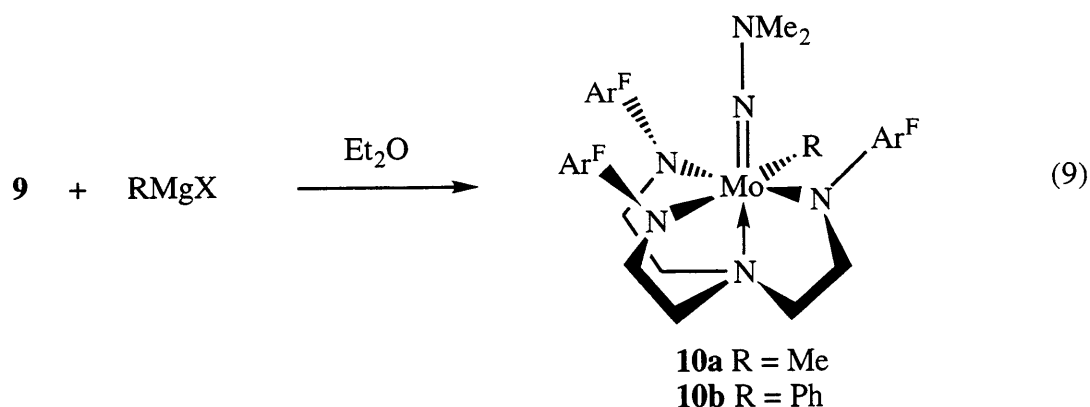
Since the β -nitrogen in **7a** and **7b** and related complexes has been shown to react with electrophiles to furnish neutral derivatives, it seemed reasonable to continue electrophilic attack on this atom. In reactions between **8** and TMSX, only starting material was recovered ($X = \text{Cl}, \text{OTf}$). As shown in equation 8, treating **8** with six equivalents of MeOTf in toluene gave the cationic



dimethyl hydrazido complex $\{[\text{N}_3\text{NF}_{18}]\text{Mo}=\text{N}-\text{NMe}_2\}\text{OTf}$ (**9**) in 72% yield as dark red crystals when crystallized from cold dichloromethane/pentane. The first step in this reaction probably involves electrophilic attack of MeOTf on **8** to furnish TMSOTf and unobserved neutral

"[N₃NF₁₈]MoNNMe" which reacts rapidly with another equivalent of MeOTf. The ¹H NMR spectrum of diamagnetic **9** reveals that the complex is trigonally symmetric and shows one sharp methyl resonance for the hydrazido ligand at 2.77 ppm, indicating that rotation about the N-N bond is rapid on the NMR time scale. A resonance for the OTf anion in the ¹³C{H} NMR spectrum could not be located in CD₂Cl₂ solution and the ¹⁹F NMR spectrum showed a broad signal at -78.88 ppm, most likely as a consequence of the anion being weakly coordinated to Mo. Interestingly, **9** is somewhat soluble in even less polar hydrocarbon solvents such as diethylether and toluene, a finding which would seem to favor a neutral formulation of **9** containing bound triflate (e.g. [N₃NF₁₈]MoNNMe(OTf)). The good yield of **9** in the reaction shown in equation 8 reflects the integrity of the [N₃NF₁₈]³⁻ ligand, which contrasts the ease of N-Si bond cleavage in the [N₃N]³⁻ ligand as observed in an analogous reaction between {[N₃N]MoNNTMS}OTf and MeOTf.³⁷

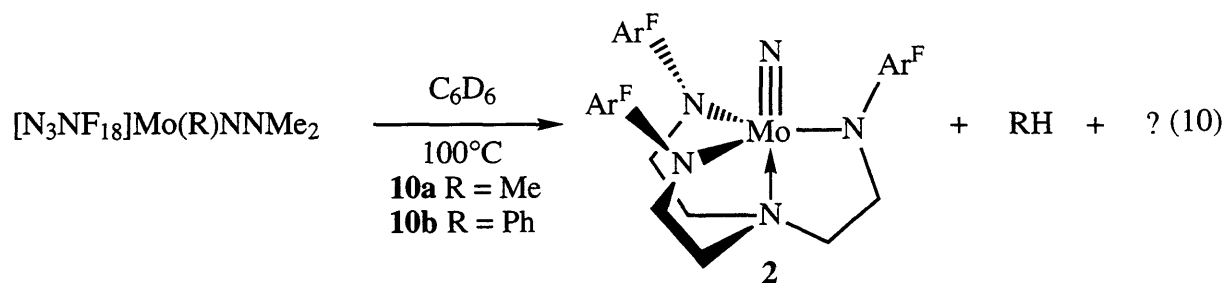
Addition of a good nucleophile to the α-nitrogen in **9** would constitute an important step in view of the fact that functionalization of this atom followed at some point by N-N cleavage would avoid the formation of the relatively unreactive nitrido complex (**2**). However, addition of MeMgI or PhMgBr to **9** in cold diethyl ether gave rapidly very dark purple [N₃NF₁₈]Mo(R)NNMe₂ (**10a**; R = Me) or (**10b**; R = Ph) in virtually quantitative yield (equation 9). Isolated yields after



crystallization from diethyl ether/pentane at -40°C are quite low due to their very high solubilities. NMR spectra of **10a** and **10b** in C₆D₆ suggest that these complexes have mirror symmetry as a

consequence of the alkyl group attacking the metal. The MoCH₃ resonance in the ¹H NMR spectrum in C₆D₆ appears at 0.36 ppm in **10a**, consistent with the added methyl group being bound to the metal, similar to what was observed for **5** and related Mo complexes containing the [N₃N]³⁻ ligand.³⁴

Evidence for N-N Bond Cleavage. Complexes **10a** and **10b** are thermally robust in the solid state, in C₆D₆ solution at 50°C for several days, and even at 90°C for several hours. However, heating separate solutions of **10a** and **10b** in C₆D₆ (typically 18 - 20 mM) for three days at 100°C in a sealed NMR tube gave [N₃NF₁₈]MoN as the major organometallic product and an unquantified amount of methane (δ_H = 0.16 ppm for **10a**) or benzene (δ_H = 7.15 ppm for **10b**) as shown in equation 10. Interestingly, thermolysis of **10b** even under these conditions did not result in complete consumption of **10b** (only ca. 40 % was observed). The fate of the second nitrogen atom and identity of other organic products observed in the ¹H NMR spectrum has yet to



be determined. It appears that N-N bond scission occurred, but it is uncertain why such harsh conditions (especially for **10b**) are required for this reaction, particularly in light of the relative ease with which related [(TMSNCH₂CH₂)₂(MeCH₂CH₂)N]Mo(Me)NNMe₂³⁷ and [N₃NF]Mo(Me)NNMe₂³⁸ decompose to nitrido complexes.

DISCUSSION

An important question concerns what electronic requirements at a metal must be satisfied in order for it to coordinate dinitrogen. One possibility is that dinitrogen may bind to a d³ "[N₃NF₁₈]Mo" species.²⁵ This hypothetical monopyramidal species, a relative of other [N₃N]³⁻

monopyramidal complexes of first row metals,³⁹ may be possibly formed in the reduction of **1** by one electron in the absence of N₂, but evidently cannot be synthesized reproducibly. The resulting terminal dinitrogen complex, [N₃NF₁₈]Mo(N₂), is never observed. A related "[N₃N]Mo" species also cannot be observed, but it readily binds dinitrogen to give [N₃N]Mo(N₂).³⁷ Furthermore, low spin d³ "[N₃NF]W", a third row relative of [N₃NF₁₈]Mo, has not been observed, but when generated from [N₃NF]W(OTf) and Na/Hg in the presence of various neutral ligands L, readily formed terminal [N₃NF]W(L) complexes (L = ^tBuNC, CO, and ethylene but not N₂).⁴⁰ If two electrons in "[N₃NF₁₈]Mo(N₂)" are transferred from Mo to the dinitrogen ligand, then a cationic Mo(V) center and a negative charge on N_β would be a reasonable description. Attack by N_β on **1** followed by a one electron reduction would then yield **6**.

Another possibility is that dinitrogen is bound first by a d⁴ Mo species such as "[N₃NF₁₈]Mo⁻", the product of a one electron reduction of hypothetical [N₃NF₁₈]Mo, to give directly [N₃NF₁₈]Mo-N=N⁻. This proposal is supported by the observation that the majority of *isolated* dinitrogen complexes contain metals in a low oxidation state,^{7,31,41,42} but what metal electronic configuration is responsible for initial formation of a M-N bond is still unclear. As was shown in Chapter I, the d⁴ [N₃NF]Re fragment readily binds a variety of two electron neutral ligands (including N₂), but no d³ complexes of the type [N₃NF]ReBr(L) were observed.

In a Mo-N=N-Mo fragment such as that found in **6**, the HOMO is comprised of two degenerate molecular orbitals containing one electron each, thus rendering this molecule paramagnetic.²⁵ Reduction of **6** by two electrons would fill the HOMO (primarily Mo-N antibonding character) and thus favor Mo-N cleavage to give **7a**. In contrast, silyl N_{eq} substituents in [(Me₂(^tBu)SiNCH₂CH₂)₃NMo]₂(μ-N₂)²⁶ and ([N₃N]Mo)₂(μ-N₂)³⁷ evidently render these complexes stable toward Mo-N bond cleavage by reductive routes, although the latter molecule was proposed to form via loss of N₂ from [N₃N]Mo(N₂) as the first step.

Since there exists precedent for homolytic N-N bond cleavage in M₂(μ-N₂) complexes, it seemed peculiar at first glance why **6** did not also exhibit the same. For example, homolytic cleavage of dinitrogen to Nb nitrides has been achieved with Nb calixerene complexes.⁴³

Complexes of the type (anilide)₃Mo form fleeting M₂(μ-N₂) species before decomposing to (anilide)₃MoN.^{27,28} In contrast to low spin "[N₃NF₁₈]Mo", the latter complexes are high spin d³ systems proposed to arise from small differences in energy between the d_{xz}, d_{yz}, and d_{z²} orbitals. Additionally, the apical amine donor in [N₃NF₁₈]³⁻ and related triamidoamine ligands may render homolytic N-N cleavage difficult. Theoretical calculations suggest that this process would be endothermic, a possible result of the so-called trans effect.⁴⁴

The thermolysis of complexes **10** to give **2** is a poorly understood reaction at present as the reaction mixtures are quite complex and appear to contain at least several organometallic species in addition to **2**. However, the observation that CH₄ (for **10a**; R = Me) and benzene (for **10b**; R = Ph) are formed in the reaction suggests that elimination of R as RNMe₂, although a possible pathway, may not occur at all. The presence of HNMe₂ also suggests that more obscure decomposition mechanisms, possibly involving solvent or the [N₃NF₁₈]³⁻ ligand itself, are playing roles as was suggested in the analogous [N₃N]³⁻ system.³⁷

CONCLUSION

The chemistry presented in this chapter may provide some hints about what directions to pursue in the future of triamidoamine dinitrogen chemistry. The [N₃NF₁₈]³⁻ ligand proved to be a robust ligand which imparted greater solubility to its complexes than those of [N₃NF]³⁻. A conspicuous absence of any aromatic *ortho*-fluorines on ligands of this type may be important in complexes which have the potential of forming monopyramidal species, no matter how fleeting they may be, to avoid possible C-F bond activation (see Chapter I). However, the *ortho*-fluorines in [N₃NF]³⁻ complexes of Re were proposed to stabilize the unusual (η²-PHR₃)⁺ moieties in complexes like {[N₃NF]Re(H)PPh₂}BAR₄ by creating steric pressure in the coordination pocket. For the same reason, the steric pressure created by *ortho*-substituents in general may be an important means to *destabilize* the hydrazido linkages as in **10a** and **10b** in order to facilitate more facile cleavage of N-N bonds. Preliminary results from Mo complexes of [N₃NF]³⁻ suggest that

this is the case and should provide motivation to develop similar ligands with larger but less reactive *ortho*- substituents.³⁸

EXPERIMENTAL

General Procedures. All air sensitive manipulations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or under argon when using Schlenk techniques. Pentane, diethyl ether, and tetrahydrofuran were purified by sparging with nitrogen and passing through scrubbing columns;⁴⁵ toluene, DME, and 1,4-dioxane were distilled from sodium; dichloromethane was distilled from CaH₂; and acetonitrile was distilled from P₂O₅. Deuterated solvents were passed through activated alumina and vacuum transferred to solvent storage flasks until use. [N₃NF₁₈]MoNMe₂ was prepared by a published method.²⁵

NMR operating frequencies and reference standards are as follows: ¹H (500 or 300 MHz, SiMe₄ = 0 ppm), ¹³C (125.80 or 75.4 MHz, SiMe₄ = 0 ppm), ¹⁹F (282.2 MHz, CFCl₃ = 0 ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal reference. Fluorine spectra were referenced externally. Chemical shifts are reported in ppm and coupling constants are in hertz. All spectra were acquired at ~22°C unless otherwise noted.

IR spectra were recorded on a Perkin-Elmer FT-IR 16 spectrometer as Nujol mulls between KBr plates in an airtight cell. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratory or by Microlytics (South Deerfield, MA).

2,6-lutidinium iodide. To a stirred solution of 2,6-lutidine (8.671 g, 0.089 mol) and n-propanol (5.106 g, 0.085 mol) in 250 mL Et₂O at -40°C was added dropwise neat TMSI (16.671 g, 0.083 mol) whereupon a white flocculent precipitate formed. After the mixture stirred for two hours, the white product was collected on a frit, washed with several portions of Et₂O, and dried *in vacuo*; yield 18.680 g (98%).

[N₃NF₁₈]MoI (1). To a stirred dark green solution of [N₃NF₁₈]MoNMe₂ (12.000 g, 0.013 mol) in 400 mL THF at -40°C was added solid 2,6-lutidinium iodide (3.667 g, 0.016 mol)

in one portion. The mixture was allowed to warm to room temperature over 20 minutes during which it turned dark orange. The volume was reduced by one half and the mixture was filtered through Celite. THF was removed *in vacuo* from the filtrate to leave a dark orange residue which was taken up in CH₂Cl₂ and stored at -40°C. Fluffy orange needles were filtered collected on a frit, washed with several portions of pentane, and dried *in vacuo*; yield 4.028 g (87%): ¹H NMR (CD₂Cl₂) δ 17.46 (br, 6, w_{1/2} = 53, H_{ortho}), 3.34 (br, 3, w_{1/2} = 9, H_{para}), -25.02 (br, 6, w_{1/2} = 136), -78.82 (br, 6h, w_{1/2} = 126); ¹⁹F NMR (CD₂Cl₂) δ -57.15 (s). Anal. Calcd for C₃₀H₂₁N₄F₁₈IMo: C, 35.95; H, 2.11; N, 5.59. Found: C, 36.25; H, 1.93; N, 5.50.

[N₃NF₁₈]MoN (2). Solid NaN₃ (649 mg, 9.977 mmol) was added in one portion to a stirred solution of **1** (5.000g, 4.988 mmol) in 60 mL THF. Within two hours the mixture turned purple and was allowed to stir overnight. THF was removed *in vacuo* and the dark residue was taken up in CH₂Cl₂, filtered through Celite, concentrated to ca. 125 mL, and stored at -40°C. Fine canary yellow needles were collected on a frit, washed with several portions of pentane, and dried *in vacuo*; yield 3.671 g (83%): ¹H NMR (CD₂Cl₂) δ 7.96 (s, 6, H_{ortho}), 7.54 (s, 3, H_{para}), 4.04 (t, 6), 3.18 (t, 6); ¹³C{H} NMR (CD₂Cl₂) δ 160.82, 131.86 (q, C_{meta}, J_{CF} = 33 Hz), 124.13 (q, CF₃, J_{CF} = 273 Hz), 121.37, 117.09, 57.09, 51.08; ¹⁹F NMR (CD₂Cl₂) δ -63.72 (s). Anal. Calcd for C₃₀H₂₁N₅F₁₈Mo: C, 40.51; H, 2.38; N, 7.87. Found: C, 40.86; H, 2.03; N, 8.03.

{[N₃NF₁₈]MoNTMS}OTf (3). To a stirred amber solution of **2** (2.500 g, 2.811 mmol) in 70 mL CH₂Cl₂ at -40°C was added dropwise TMSOTf (937 mg, 4.217 mmol) in 3 mL CH₂Cl₂. The solution was stirred for 2.5 hours during which it darkened and became viscous as the yellow product precipitated. Solvents were removed *in vacuo* and the bright yellow residue was slurried in Et₂O, collected on a frit, washed with several portions of Et₂O followed by pentane, and dried *in vacuo*; yield 2.840 g (91%): ¹H NMR (CD₃CN) δ 7.91 (s, 6, H_{ortho}), 7.88 (s, 3, H_{para}), 4.31 (t, 6), 3.50 (t, 6), -0.09 (s, 9, SiMe₃); ¹³C{H} NMR (CD₃CN) δ 162.82, 133.14 (q, C_{meta}, J_{CF} = 33 Hz), 125.28, 124.19 (q, CF₃, J_{CF} = 272 Hz), 121.16, 64.02, 54.10, -1.99; ¹⁹F NMR (CD₃CN) δ -62.94 (s, 18, CF₃), -78.87 (s, 3, OTf). Anal. Calcd for

$C_{34}H_{30}N_5F_{21}MoO_3SSi$: C, 36.73; H, 2.72; N, 6.30. Found: C, 36.46/36.66; H, 2.71/2.62; N, 6.17/6.35.

[N₃N₁₈]MoI(NTMS) (4). From **1**: A stirred dark orange solution of **1** (2.186 g, 2.181 mmol) in 40 mL THF at -40°C was treated with TMSN₃ (377 mg, 3.271 mmol) in 2 mL THF. As the solution warmed to room temperature over two hours, a deep purple color developed. Solvents were removed *in vacuo* and the residue was taken up in Et₂O, filtered through Celite, concentrated, and stored at -40°C. The mother liquor was decanted from very soluble dark purple microcrystals which were dried *in vacuo*; yield 1.022 g (43%): ¹H NMR (C₆D₆) δ 7.48 (s, 9, H_{ortho} and H_{para}), 3.05 (b, 6, w_{1/2} = 25), 2.58 (b, 6, w_{1/2} = 90), -0.44 (s, 9, SiMe₃); ¹⁹F NMR (C₆D₆) δ -62.87 (s).

From **2**: A stirred yellow suspension of **2** (83 mg, 0.093 mmol) in 5 mL Et₂O was treated with TMSI (37 mg, 0.187 mmol) in 1 mL Et₂O whereupon a rapid color change to deep purple ensued. After 5 minutes the mixture was filtered through Celite and solvents were removed *in vacuo*. ¹H NMR (C₆D₆) shows that this is the same product as obtained from **1**.

From **3**: A stirred purple solution of **3** (50 mg, 0.045 mmol) in 5 mL THF was treated with TMSI (27 mg, 0.135 mmol) in 2 mL THF whereupon a deeper purple color developed. The solution was stirred for one day and then solvents were removed *in vacuo*. The residue was taken up in Et₂O, filtered through Celite, and stripped to dryness. ¹H NMR (C₆D₆) of the crude product shows that it is the same as in the preparation from **1**.

[N₃NF₁₈]Mo(Me)NTMS (5). A stirred dark purple solution of **3** (100 mg, 0.090 mmol) in 4 mL THF at -40°C was treated with MeMgCl (0.094 mmol, 3.0 M in THF) whereupon the color rapidly turned dark indigo. The mixture was stirred for 30 minutes after which solvents were removed *in vacuo*. The residue was extracted with Et₂O, filtered through Celite, and concentrated. The product was crystallized from Et₂O/pentane at -40°C as extremely soluble dark indigo needles which were dried *in vacuo*; yield 35 mg (40%): ¹H NMR (C₆D₆) δ 7.29 (s, 6, H_{ortho}), 7.21 (s, 3, H_{para}), 3.09 (m, 4), 2.62 (m, 2), 2.52 (m, 2), 2.03 (m, 4), 0.63 (b, 3, MoMe), -0.31 (s, 9, SiMe₃); ¹⁹F NMR (C₆D₆) δ -62.73 (s, 12), -63.08 (s, 6).

[N₃NF₁₈]MoNNMo[N₃NF₁₈] (6). To a dark orange solution of **1** (1.000g, 0.998 mmol) in 50 mL THF was added Mg powder (25 mg, 1.048) in one portion. The color of the mixture gradually turned blue, then purple. After the mixture was stirred overnight, it was filtered through Celite and THF was removed *in vacuo*. The dark residue was dissolved in CH₂Cl₂/pentane and stored at -40°C. The mother liquor was decanted from purple blocks which were washed with pentane and dried *in vacuo*; yield 444 mg (50%): ¹H NMR (CD₂Cl₂) δ 5.44 (b, 12, w_{1/2} = 304, H_{ortho}), 0.38 (b, 12 w_{1/2} = 27, H_{para}); ¹⁹F NMR (CD₂Cl₂) δ -41.85 (b,18), -61.96 (b,18). Anal. Calcd for C₆₀H₄₂N₁₀F₃₆Mo₂: C, 40.51; H, 2.38; N, 7.87. Found: C, 40.76; H, 2.41; N, 7.79.

{[N₃NF₁₈]MoNN}[Na(15-crown-5)₂] (7b). A dark orange solution of **1** (154 mg, 0.154 mmol) in 7 mL THF was treated with Na/Hg (3.46 g, 0.768 mmol, 0.51% amalgam) and the mixture was stirred vigorously for two hours during which the color changed to dark blue (ca. 7 minutes) and then to port-red. Excess Na/Hg was filtered on a bed of Celite on a frit and the filtrate was stripped to dryness, dissolved in 15 mL Et₂O, and filtered through Celite. The red solution was cooled to -40°C and, with stirring, was treated with 15-crown-5 (75 mg, 0.339 mmol) in 1 mL Et₂O whereupon the solution turned forest green. After allowing the solution to warm to room temperature over two hours, it was stored at -40°C. The mother liquor was decanted from a dark green microcrystalline solid which was washed with several portions of pentane and dried *in vacuo*; yield 100 mg (48%): ¹H NMR (toluene-*d*₈) δ 7.77 (s, 6, H_{ortho}), 7.35 (s, 3, H_{para}), 3.39 (t, 6), 3.12 (s, 40, 15-crown-5), 2.09 (t, 6); ¹³C{¹H} NMR (toluene-*d*₈) δ 137.46, 131.34 (q, C_{para}, J_{CF} = 33 Hz), 125.20 (q, CF₃, 272 Hz), 121.17, 109.50, 69.37 (OCH₂CH₂O), 55.16, 52.82; ¹⁹F NMR (toluene-*d*₈) δ -62.61 (s). IR (DME) 1850.2 cm⁻¹.

[N₃NF₁₈]MoNNTMS (8). Na/Hg (73.40 g, 15.96 mmol, 0.5% amalgam) was added to a vigorously stirred dark orange solution of **1** (4.000g, 3.99 mmol) in 250 mL THF. The color turned to blue within ca. 5 minutes, then to port-red over two hours. The red solution was decanted from excess Na/Hg, cooled to -40°C, and with stirring treated with TMSCl (867 mg, 7.98 mmol) in 3 mL Et₂O whereupon the color rapidly changed to dark yellow. After the mixture

was stirred for 1 hour at room temperature, all solvents were removed *in vacuo* and the residue was extracted with Et₂O, filtered through Celite, and stripped to dryness again. The crude product was crystallized from CH₂Cl₂ at -40°C as dark yellow shards; yield 3.517 g (90%): ¹H NMR (CD₂Cl₂) δ 7.49 (s, 6, H_{ortho}), 7.44 (s, 3, H_{para}), 4.03 (t, 6), 3.17 (t, 6), -0.59 (s, 9, SiMe₃); ¹³C{H} NMR (CD₂Cl₂) δ 159.76, 132.23 (q, C_{meta}, J_{CF} = 33 Hz), 124.31 (q, CF₃, J_{CF} = 271 Hz), 122.70, 115.45, 57.21, 53.71, -0.32 (Si(CH₃)₃); ¹⁹F NMR (CD₂Cl₂) δ -63.42 (s). IR (CH₂Cl₂) 1697.8 cm⁻¹. Anal. Calcd for C₃₂H₃₀N₆F₁₈MoSi: C, 40.58; H, 3.10; N, 8.61. Found: C, 40.53; H, 2.96; N, 8.44.

[[N₃NF₁₈]MoNNMe₂]OTf (9). MeOTf (3.487 g, 21.252 mmol) was added dropwise to a stirred orange solution of **8** (3.459 g, 3.542 mmol) in 75 mL toluene whereupon the color rapidly turned dark red. The solution was allowed to stir for 16 hours after which volatiles were removed *in vacuo*. The dark red residue was dissolved in CH₂Cl₂, filtered, and product was crystallized from CH₂Cl₂/pentane at -40°C as dark red crystals which were washed with 2 x 2 mL pentane and dried *in vacuo*; yield 2.576 g (67%): ¹H NMR (CD₂Cl₂) δ 7.47 (b, 3, H_{para}), 7.29 (b, 6, H_{ortho}), 4.20 (t, 6), 3.53 (t, 6), 2.77 (s, 6, N(CH₃)₂); ¹³C{H} NMR (CD₂Cl₂) δ 158.67, 132.54 (q, CCF₃, J_{CF} = 33 Hz), 123.91 (q, CCF₃, J_{CF} = 272 Hz), 120.91, 116.21, 57.75, 56.38, 42.89 (N(CH₃)₂); ¹⁹F NMR (CD₂Cl₂) δ -63.92, -78.88 (OTf). Anal. Calcd for C₃₃H₂₇N₆F₂₁MoO₃S: C, 36.53; H, 2.51; N, 7.75. Found: C, 36.07; H, 2.38; N, 7.34.

[N₃N]Mo(Me)NNMe₂ (10a). MeMgI (1.016 mmol, 3.0 M in Et₂O) was added dropwise to a stirred blood-red suspension of **9** (1.000 g, 0.924 mmol) in 15 mL Et₂O at -40°C. The color rapidly turned to deep purple and after three hours 1,4-dioxane (ca. 2 mL) was added and the mixture was stirred for an additional 30 minutes, then filtered and stripped to a purple solid to give pure **10a** in nearly quantitative yield. Analytically pure samples were obtained by crystallization from toluene/pentane at -40°C as dark blocks which were dried *in vacuo*; yield 495 mg (50%): ¹H NMR (C₆D₆) δ 7.43 - 7.15 (m, 8), 6.75, 3.10 (m, 4), 2.85 (m, 2), 2.57 (s, 6, N(CH₃)₂), 2.47 (m, 2), 2.37 (m, 2), 2.13 (m, 2), 0.37 (s, 3, MoCH₃); ¹³C{H} NMR (C₆D₆) δ 160.10, 158.18, 132.39 (m, C_{meta}), 124.85 (q, CF₃, J_{CF} = 272 Hz), 124.60 (q, CF₃, J_{CF} = 273

Hz), 118.62, 117.66, 112.55 (m), 111.65 (m), 63.64, 61.24, 58.54, 55.03, 41.38 (NN(CH₃)₂), 22.77 (MoCH₃); ¹⁹F NMR (C₆D₆) δ -62.90 (s, 12), -63.58 (s, 6). Anal. Calcd for C₃₃H₃₀N₆F₁₈Mo: C, 41.79; H, 3.19; N, 8.86. Found: C, 40.95; H, 3.04; N, 8.51.

[N₃N₁₈]Mo(Ph)NNMe₂ (10b). PhMgBr (0.711 mmol, 3.0 M in Et₂O) was added dropwise to a stirred suspension of **9** (700 mg, 0.647 mmol) in 15 mL Et₂O at -40°C. The resulting deep purple solution was stirred for 5 hours, treated with 1,4-dioxane (ca. 1 mL), stirred for an additional 30 minutes, and filtered. Volatiles were removed *in vacuo* to leave pure **10b** as a highly soluble purple solid in virtually quantitative yield. Analytically pure samples were obtained by crystallization from Et₂O/pentane at -40°C; yield 147 mg (22%): ¹H NMR (C₆D₆) δ 7.47, 7.25, 7.15 (m), 6.68, 3.18 (m, 4), 2.82 (m, 2), 2.52 (t, 2), 2.49 (s, 6), 2.27 (t, 2), 2.00 (m, 2); ¹³C{H} NMR (C₆D₆) δ 179.43, 159.84, 157.36, 139.97, 132.32 (q, C_{meta}, J_{CF} = 33 Hz), 131.85 (q, C_{meta}, J_{CF} = 33 Hz), 128.71, 126.61, 124.37 (q, CF₃, J_{CF} = 272 Hz), 124.12 (q, CF₃, J_{CF} = 272 Hz), 118.45, 117.62, 112.98, 111.47, 61.82, 60.72, 58.62, 56.09, 40.90 (NN(CH₃)₂). Anal. Calcd for C₃₈H₃₂N₆F₁₈Mo: C, 45.16; H, 3.19; N, 8.32. Found: C, 44.92; H, 3.24; N, 8.24.

Thermolysis of 10a and 10b. Purple solutions of each complex (ca. 20 mg, 20 mM) in 1 mL C₆D₆ were prepared in NMR tubes which were then flame-sealed and placed into heating baths at 50°C. The temperature was increased to 80, 90, and finally 100°C over three days. NMR spectra were collected at each temperature. Conversion to **2** was ca. 55% for **10a** and ca. 40% for **10b**.

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CHAPTER III

Organometallic Chemistry and α -Olefin Polymerizations

Involving Bis(amido)ether Complexes of Hf(IV)

INTRODUCTION

There is little doubt that the Group IV metallocene core is one of the most important types of early transition metal fragments, not in the least because of its ubiquitous role in most Ziegler-Natta olefin polymerization catalysts. These highly reactive species traditionally incorporate two simple Cp ligands (or its derivatives) which could be substituted for indenyl or fluorenyl. From initial studies on these early catalysts, it became clear that 14 electron cationic alkyl complexes, $[\text{Cp}_2\text{M-R}]^+$, are the active species responsible for polymer chain growth.^{1,2} Other important findings include the mechanisms of polymer chain termination and chain transfer and the factors which affect molecular weights and polymer microstructure.

The elucidation of these key parameters provide a foundation upon which to build other ligand frameworks which could mimic or improve upon the prevalent bis(cyclopentadienyl) motif. One of the earliest modifications commenced with the introduction of cyclopentadienyl rings linked to a pendant amido ligand, an arrangement suggested to render a metal more sterically accessible and even more Lewis acidic since an amido group can donate two electrons fewer than a cyclopentadienyl ligand.³ Catalytically active complexes which bear ancillary amido ligands have emerged more recently despite the fact that the potential dialkyl catalyst precursors, $[\text{TMS}_2\text{N}]_2\text{MR}_2$ ($\text{M} = \text{Zr}, \text{Hf}$; $\text{R} = \text{Me}$ or Et), were prepared nearly two decades ago by Andersen.⁴⁻⁶ Particular attention has been devoted to species which contain chelating diamido ligands,⁷⁻²² especially since recent findings suggest that highly active Group IV polymerization catalysts which contain diamido ligands are much more stable with respect to β -elimination and chain transfer than are metallocene-based catalysts. For example, propylene-bridged aryl-substituted diamido titanium complexes promote the living polymerization of neat α -olefins,²³⁻²⁵ while Baumann and Schrock recently reported the living polymerization of 1-hexene by " $\{[\text{NON}]\text{Zr-Me}\}^+$ " ($[\text{NON}]^{2-} = [(\text{tBu-}d_6)\text{N-}o\text{-C}_6\text{H}_4]_2\text{O}^{2-}$).²⁶

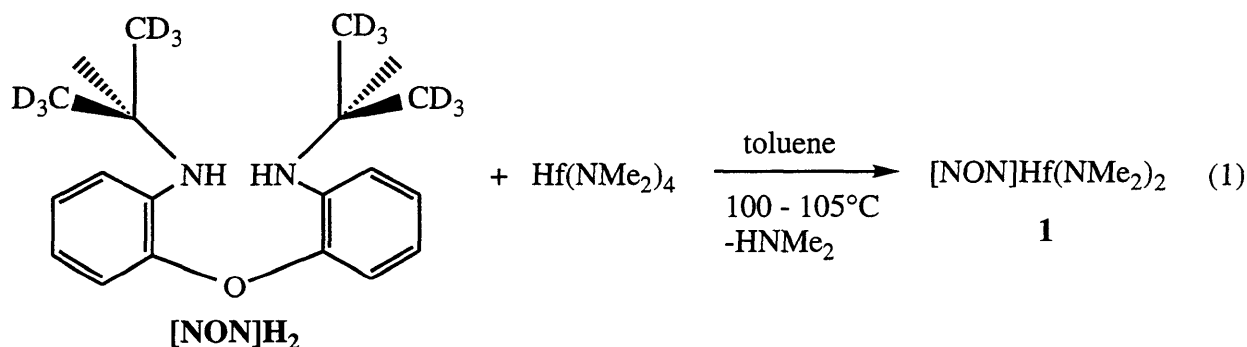
The relative stability of the latter catalyst (compared to metallocene-based catalysts whose initial activity is high but short-lived)¹ is believed to stem primarily from the $[\text{NON}]^{2-}$ framework which lacks β -hydrogens, consists of robust bonds, and incorporates a neutral O donor which

most likely stabilizes cationic alkyl species. The resulting well-defined catalysts also preclude the necessity for cocatalysts and offer promise for the preparation of block copolymers.²⁷

It remained to be seen whether more thermally robust hafnium catalysts could be prepared, a venture which was anticipated to be fruitful in view of the fact that M-C bond strengths are generally known to increase in the order for $M = \text{Ti} < \text{Zr} < \text{Hf}$.²⁸ This chapter therefore describes the investigation of the [NON]Hf core in terms of its potential as a suitable component in α -olefin polymerization catalysts and its utility in the preparation of unique organometallic species.

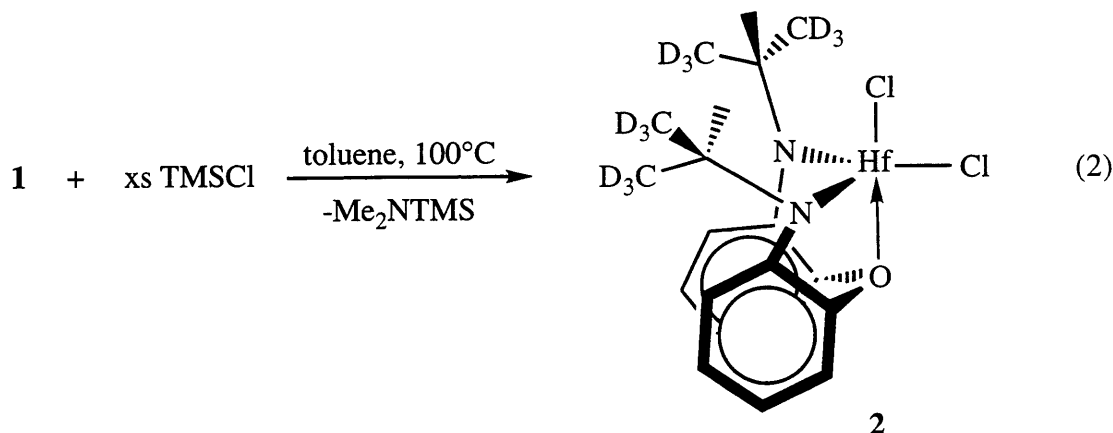
RESULTS

Neutral Dialkyl Complexes. The most convenient entry into Hf chemistry was found in the reaction between [NON]H₂ and Hf(NMe₂)₄ as a concentrated toluene solution at 100 - 105°C for 16 hours to give, upon removal of volatile components, [NON]Hf(NMe₂)₂ (**1**) in 82% yield (equation 1).²⁹ The ¹H NMR spectrum of crude **1** in C₆D₆ showed that it formed cleanly and thus was used without further purification. The methyl groups on the amide ligands resonate

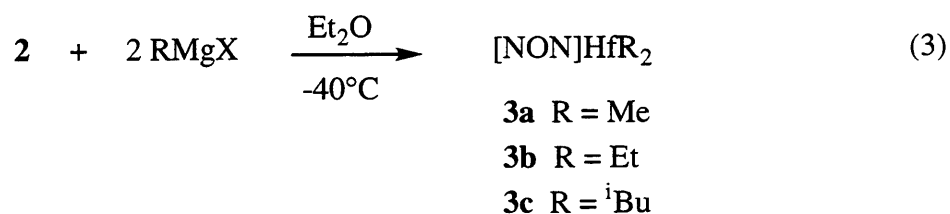


at 3.01 ppm and are equivalent on the NMR time scale. The reaction between **1** and excess TMSCl in toluene at 100°C for five hours gave cleanly, after removal of volatile components, light yellow [NON]HfCl₂ (**2**) in 90% yield (equation 2). Analytically pure samples could be obtained by crystallization from diethyl ether at -40°C, but the purity of crude **2** was sufficient for subsequent

syntheses. It is likely that **2** exists as a dimer in the solid state as suggested by the X-ray crystal structure of analogous $\{[\text{NON}]\text{ZrCl}\}_2(\mu\text{-Cl})_2$.³⁰

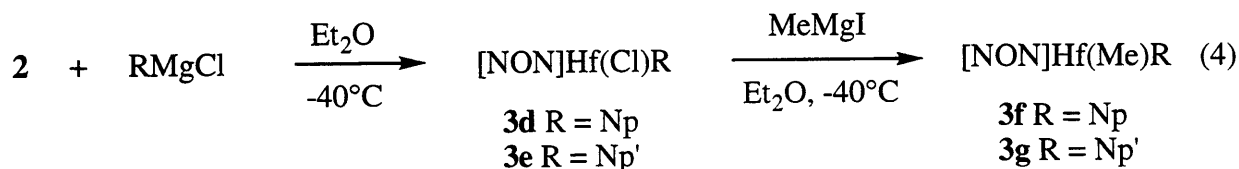


Dialkyl derivatives **3a-c** were prepared by treating **2** in diethyl ether at -40°C with the appropriate Grignard reagent and were crystallized in 70 - 80% yields from diethyl ether/pentane at -40°C (equation 3). In the reaction of **2** with at least one equivalent of NpMgCl , only

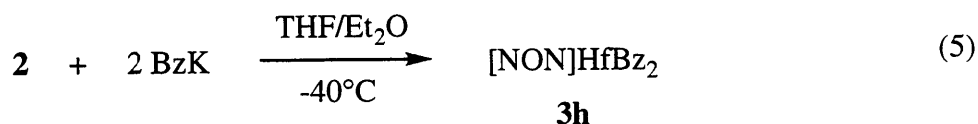


monoalkylation occurred to give $[\text{NON}]\text{Hf}(\text{Cl})\text{Np}$ (**3d**) in 87% yield from cold pentane, presumably because of the steric bulk around Hf (equation 4).⁶ Addition of 2 equivalents of the more aggressive nucleophile NpLi to **2** gave mixtures that contained crude $[\text{NON}]\text{HfNp}_2$ (by ^1H NMR), but this complex is evidently unstable as six attempts to prepare it in pure form were unsuccessful. However, the unsymmetric dialkyl complexes $[\text{NON}]\text{Hf}(\text{Me})\text{R}$ (**3f**, R = CH_2CMe_3 or Np; **3g**, R = $\text{CH}_2\text{CMe}_2(\text{Ph})$ or Np') could be prepared in good yields from the corresponding monochlorides and MeMgI as white crystals when crystallized from diethyl ether at -40°C .

Finally, dibenzyl complex **3h** was prepared by addition of 2 equivalents BzK to **2** in THF/diethyl ether (1:1) mixed solvent at -40°C in 61% yield as a highly crystalline white solid (equation 5).



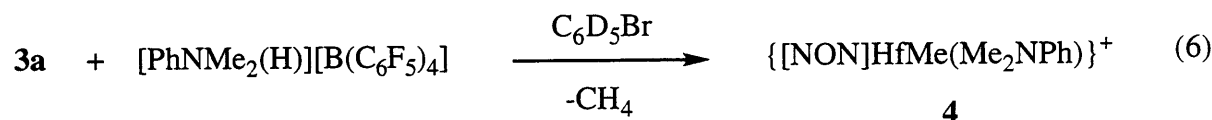
NMR spectra for the symmetric dialkyl derivatives show one set of resonances for the alkyl ligands, suggesting that in solution these complexes have C_{2v} symmetry which is most likely



achieved *via* a distorted trigonal bipyramidal molecule in which Hf is coplanar with the N-O-N manifold.²⁶ Surprisingly, diethyl complex **3b** and diisobutyl complex **3c** do not decompose at room temperature in the solid state and at least for several days in solution. Heating **3b** in neat PMe_3 at 100°C , however, induced decomposition to unidentifiable products over the course of one day. An olefin complex such as $[\text{NON}]\text{Hf}(\text{ethylene})(\text{PMe}_3)_2$ was not observed as might have been expected in view of the fact that $\text{Cp}_2\text{Hf}(\text{isobutylene})\cdot\text{PMe}_3$ may be prepared easily by a similar route.³¹

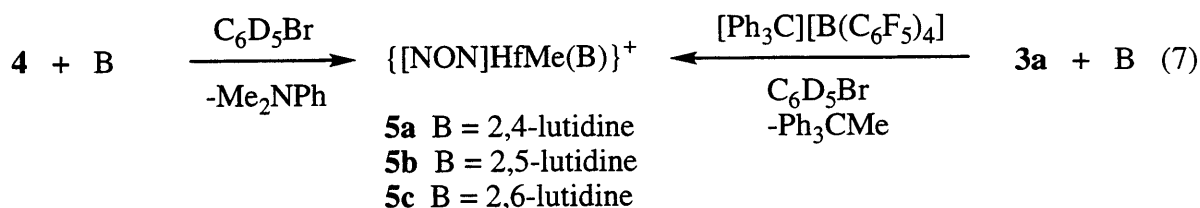
Solution Studies of Methyl Cations. Addition of an equivalent of $[\text{PhNMe}_2(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ to a $\text{C}_6\text{D}_5\text{Br}$ solution of **3a** at 22°C gave rise to the quantitative and clean formation of $\{[\text{NON}]\text{HfCH}_3(\text{Me}_2\text{NPh})\}^+$ (**4**) which is charge balanced by the relatively non-coordinating anion $\text{B}(\text{C}_6\text{F}_5)_4^-$ (equation 6). The ^1H NMR spectrum of **4** in $\text{C}_6\text{D}_5\text{Br}$ shows the methyl resonance at 0.89 ppm. A singlet at 2.79 for bound Me_2NPh and a much less intense resonance at 2.66 ppm for free Me_2NPh indicate that this base is almost completely bound at room temperature. The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of $\{[\text{NON}]\text{Hf}^{13}\text{CH}_3(\text{Me}_2\text{NPh})\}^+$ (**^{13}C -4**) contains a

methyl resonance at 64.90 ppm, downfield of that in neutral **3a** ($\delta_{\text{C}} = 56.32$). A variable temperature ^1H NMR experiment in which a solution containing **4** and one additional equivalent of



Me_2NPh showed that resonances for bound and free Me_2NPh began to coalesce at about 50°C , indicating that at elevated temperatures this base becomes labile (Figure 3.1). Remarkably, no decomposition of **4** was observed, even at 80°C for the duration of the NMR experiment and for several days at 22°C in solution.

Coordinated Me_2NPh in **4** was rapidly displaced by 2,4-, 2,5-, or 2,6-lutidine in $\text{C}_6\text{D}_5\text{Br}$ to give immediately pale yellow **5a-c** and free Me_2NPh (equation 7). Complexes **5a-c** may also be independently generated in $\text{C}_6\text{D}_5\text{Br}$ *via* abstraction of one methyl group from **3a** by an equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in the presence of the appropriate lutidine. The NMR spectra of



5a-c show that the ^1H chemical shifts of the sharp Hf- CH_3 resonances ($\delta_{\text{H}} = 0.64$) are virtually independent of the base, as are the ^{13}C chemical shifts for the isotopically enriched methyl groups in the ^{13}C -**5a-c** derivatives ($\delta_{\text{C}} = 62 - 66$; see Experimental section). The ^1H NMR spectrum of **5a** and one additional equivalent of 2,4-lutidine at 22°C showed one set of resonances for the 2,4-lutidine ligand, indicating that at this temperature there is rapid exchange between free and bound base. However, distinct resonances for free 2,4-lutidine and **5a** appeared at approximately -10°C . As was expected in an analogous experiment with **5b** and the more sterically demanding 2,5-

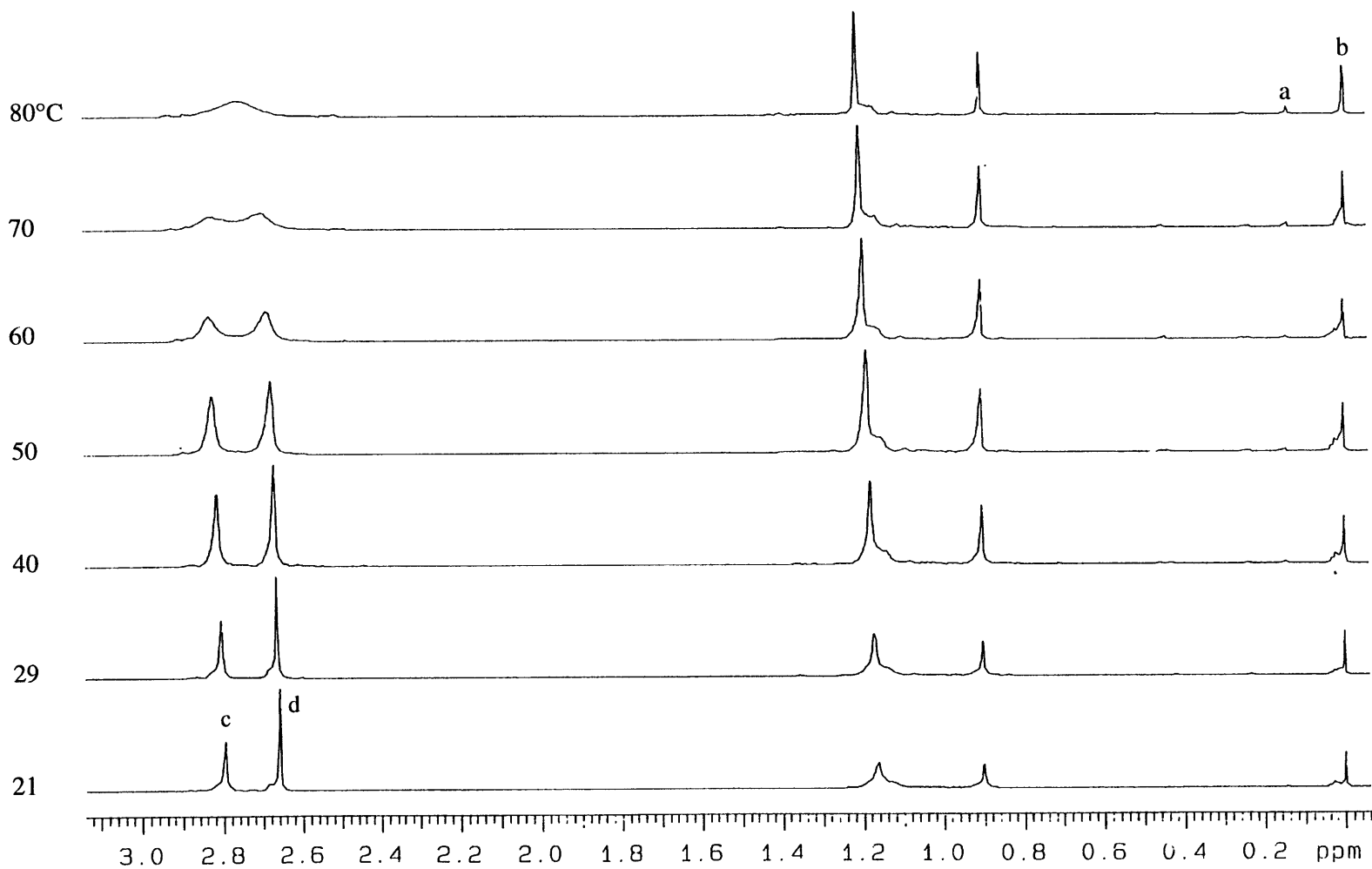
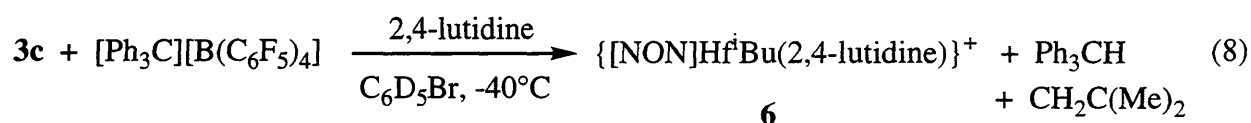


Figure 3.1. Variable Temperature 300 MHz ^1H NMR Spectra of $\{[\text{NON}]\text{HfCH}_3(\text{Me}_2\text{NPh})\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**4**) in $\text{C}_6\text{D}_5\text{Br}$ in the presence of PhNMe_2 . ^a CH_4 ; ^b Me_4Si internal reference; ^c Coordinated Me_2NPh ; ^d Free Me_2NPh .

lutidine ligand, the ^1H NMR spectra showed only one set of broad lutidine resonances at all temperatures down to -35°C .

A cationic isobutyl complex related to lutidine adducts **5a-c** was synthesized by treating diisobutyl complex **3c** with an equivalent each of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and 2,4-lutidine in $\text{C}_6\text{D}_5\text{Br}$ at -40°C (equation 8). The light yellow product is proposed to be the cation $\{[\text{NON}]\text{Hf}^i\text{Bu}(2,4\text{-lutidine})\}^+$ (**6**). The ^1H NMR spectrum of **6** shows the presence of isobutylene ($\delta_{\text{H}} = 4.68$ and 1.61) and a singlet for Ph_3CH ($\delta_{\text{H}} = 5.44$). Consistent with these findings are resonances for one coordinated isobutyl group, but they are partially obscured by broad signals arising from bound



2,4-lutidine. Cation **6** is relevant because it serves as a model for the growing polymer chain (P) in a catalytically active base adduct, $\{[\text{NON}]\text{HfCH}_2\text{CH}(\text{Me})\text{P}(\text{S})\}^+$ (S = chlorobenzene or $\text{C}_6\text{D}_5\text{Br}$).

Polymerization of 1-hexene. Preliminary experiments revealed that rapid polymerization of 1-hexene could be effected by **4** in $\text{C}_6\text{D}_5\text{Br}$ at 22°C . More detailed investigations into the catalytic activity of **4** were attractive since it remained catalytically active even after standing at 22°C for one day.

Poly(1-hexene) was produced under various reaction conditions by rapid addition of 1-hexene to vigorously stirred solutions of **4** in chlorobenzene (see Experimental section for a representative procedure). Molecular weights (M_n) and polydispersity indices (PDI) of the polymers were determined by GPC analysis. Table 3.1 lists these data and the relevant experimental parameters employed in these studies. As indicated by entries (2) and (5), polymers prepared at about 22°C gave $M_n(\text{found})$ two to three times greater than $M_n(\text{calc})$ ($M_n(\text{calc}) = M_n(\text{found})$ for a living polymerization). Reasonable control over the polymer molecular weights

was found in polymerizations performed at 50°C employing no more than 150 equivalents of 1-hexene (entries 1, 3, and 4), but $M_n(\text{found})$ dropped below $M_n(\text{calc})$ in the attempts to prepare longer polymers (entries 6 and 7). GPC traces of the polymers revealed unimodal distributions of molecular weights and narrow polydispersities, both indicating single-site catalysis. No poly(1-hexene) was isolated in polymerizations at 22°C to which additional Me_2NPh (3 equiv.) had been added.

Table 3.1. Polymerization of 1-hexene by **4** in Chlorobenzene.^a

Entry	1-hexene (equiv)	Time ^b (min)	Temp (°C)	PhCl ^c (mL)	$M_n(\text{calc})$ (g/mol)	$M_n(\text{found})$ (g/mol)	PDI
(1)	50	72	50	10	4208	7900	1.53
(2)	100	100	21	10	8416	24600	1.20
(3)	150	93	50	10	12624	14300	1.74
(4)	150	64	50	30	12624	10200	1.49
(5)	200	95	22	10	16832	35000	1.19
(6)	250	58	50	20	21040	13000	1.33
(7)	400	465	50	20	33664	10600	1.30

^a Polymer yields in each case were at least 97%. ^b Time was that required for complete consumption of 1-hexene. ^c Solvent volume excludes contribution from 1-hexene.

These data indicate that the role of Me_2NPh in polymerizations may be important and, coupled with the known solution behavior of catalyst **4** (Figure 3.1), prompted further investigation into the effect of temperature upon the polymerizations of 1-hexene. Therefore, averaged values between two runs for $M_n(\text{found})$ and PDI were determined for polymers prepared from 100 equivalents of 1-hexene and **4** in chlorobenzene at 10 °C intervals between 40 and 80°C (Figure 3.2). In each case the yields of poly(1-hexene) were essentially quantitative. It is clear that at 40°C $M_n(\text{found})$ is much greater than $M_n(\text{calc})$, but approaches the expected value (8416 g/mol) for a uniform polymerization at temperatures between 50 and 60°C, then continues to

decrease as the temperature is increased. In contrast, the relatively low values for PDI at 40°C increase smoothly to almost 2 at 80°C, indicating single-site catalysis at all temperatures investigated. No olefinic resonances were observed in the ^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectra of poly(1-hexene) prepared in these experiments.

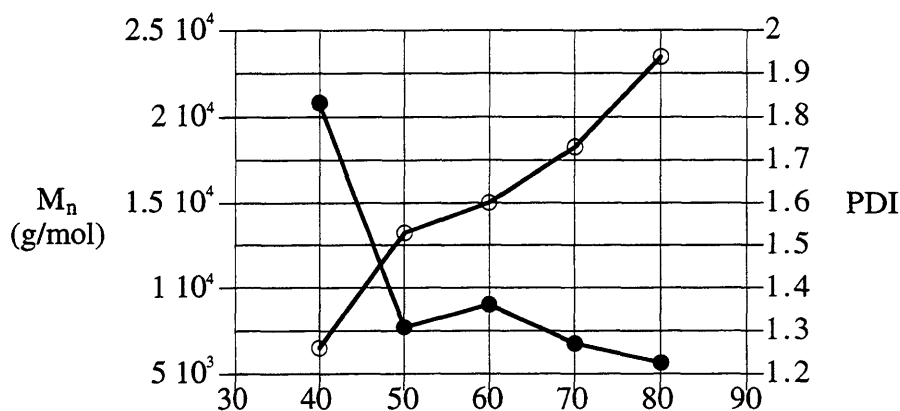


Figure 3.2. Plots of M_n (●) and PDI (○) versus T for poly(1-hexene).

Additional insight into the polymerization of 1-hexene was gained by treating ^{13}C -4 with two equivalents of 1-hexene in $\text{C}_6\text{D}_5\text{Br}$ at 22°C. The complete consumption of 1-hexene was confirmed by ^1H NMR. The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of the resulting solution showed that it contained mostly unreacted ^{13}C -4 ($\delta_{\text{C}} = 64.91$) and several less intense resonances (Figure 3.3). Six of these were assigned to poly(1-hexene) by comparison to the $^{13}\text{C}\{\text{H}\}$ NMR spectra of poly(1-hexene) produced by 4 on a preparative scale and from published chemical shifts.^{32,33} Several closely spaced resonances centered at 20 ppm were assigned to the terminal $^{13}\text{CH}_3$ end groups.³⁴ After 20 more equivalents of 1-hexene was added to the same sample and allowed to polymerize to completion, the $^{13}\text{C}\{\text{H}\}$ NMR spectrum still showed the presence of unreacted ^{13}C -4 and more intense resonances arising from poly(1-hexene). These data shed some light onto the mechanism of polymerization. First, it appears that the rate of propagation (k_p) is greater than the rate of initiation (k_i) if it is assumed that 1-hexene mixes rapidly with ^{13}C -4 before significant initiation occurs. (Unfortunately, detailed kinetic investigations which might yield definitive values

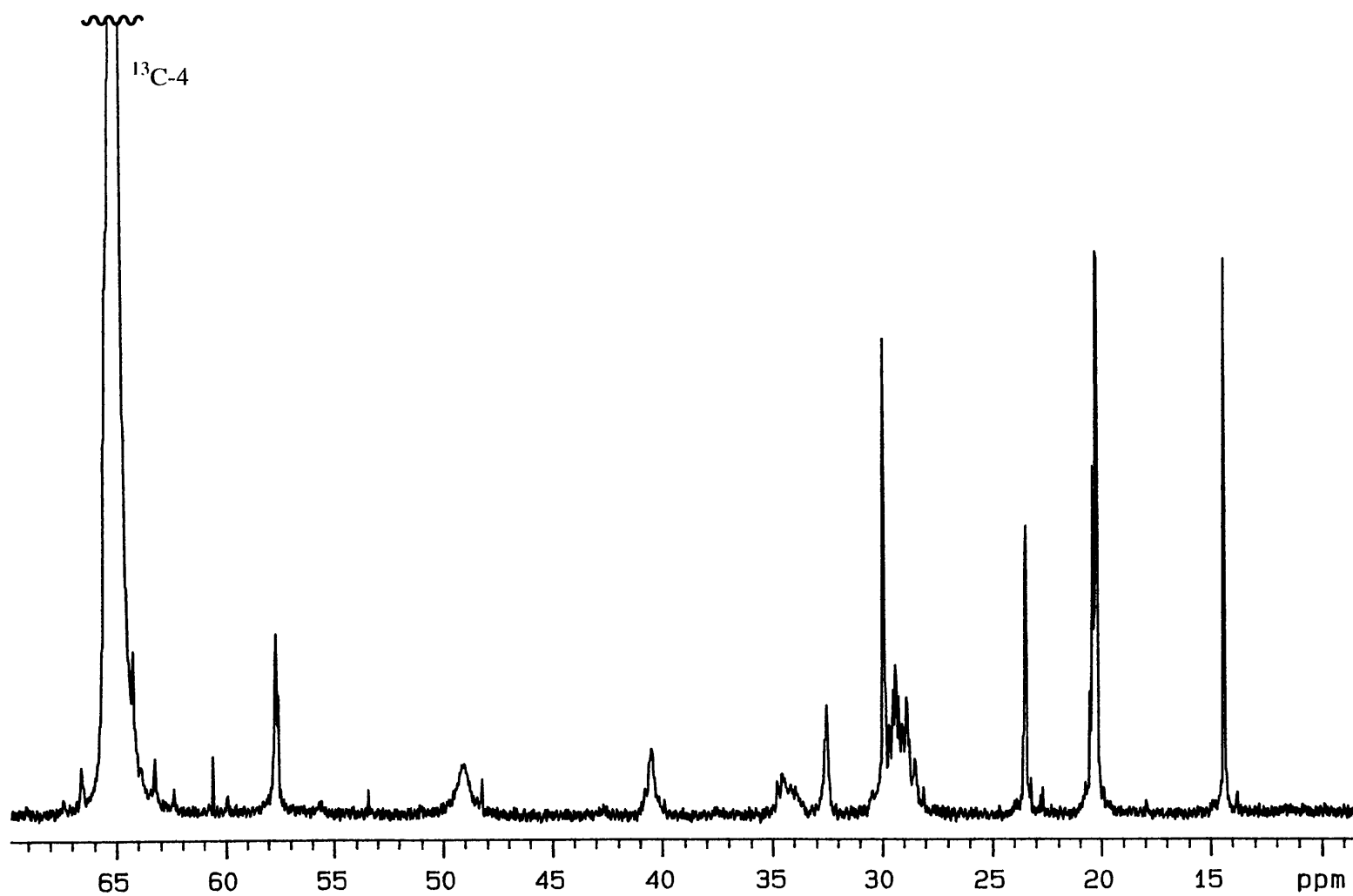
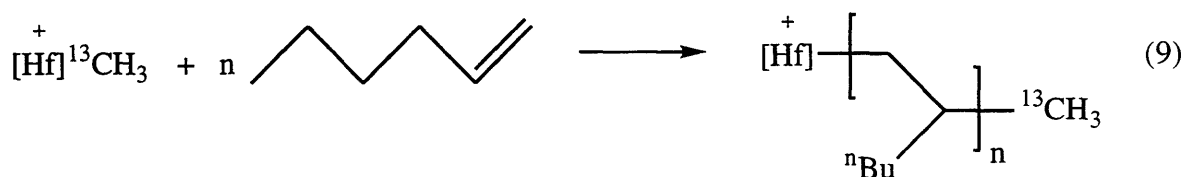


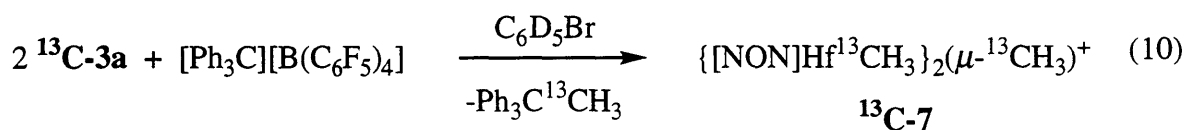
Figure 3.3. 125.80 MHz $^{13}\text{C}\{\text{H}\}$ NMR Spectrum of $^{13}\text{C-4}$ in $\text{C}_6\text{D}_5\text{Br}$ After Consumption of Two Equivalents of 1-Hexene.

for k_p and k_i were prevented by the fact that unreacted $^{13}\text{C-4}$ persists even after the consumption of 200 equivalents 1-hexene at which point solutions are prohibitively viscous for NMR analyses.) This result would be expected since Me_2NPh is presumed to be most strongly bound in the initiator which possesses a less congested coordination site than that for the propagating species. Second, 1-hexene evidently inserts into the $\text{Hf-}^{13}\text{CH}_3$ bond in a 1,2 manner as shown in equation 9. A 2,1 manner of addition would give a species in which the $^{13}\text{CH}_3$ group would be bound to a

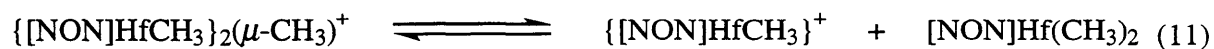


secondary carbon and the chemical shift for that $^{13}\text{CH}_3$ group would be expected to fall in the range of 10-12 ppm.³⁵ The $^{13}\text{C}\{\text{H}\}$ NMR spectra in labeling experiments described here and for poly(1-hexene) prepared under the conditions mentioned previously show no resonances in this region.

Evidence for a Bimetallic Cation. The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of $^{13}\text{C-3a}$ contains a resonance for the methyl carbon at 56.45 ppm in $\text{C}_6\text{D}_5\text{Br}$. Upon addition of one-half equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ a rapid color change to pale yellow ensued and the resulting $^{13}\text{C}\{\text{H}\}$ NMR spectrum at 24°C showed a sharp resonance at 30.20 ppm for $\text{Ph}_3\text{C}^{13}\text{CH}_3$ and very broad $\text{Hf}^{13}\text{CH}_3$ resonances between 45 and 65 ppm for what is proposed to be the methyl-bridged bimetallic cation $^{13}\text{C-7}$ (equation 10). The ^1H NMR spectrum for an analogous experiment with **3a** revealed a very broad Hf-CH_3 signal centered at 0.68 ppm for **7**. The addition of one equivalent of 2,4-lutidine to $^{13}\text{C-7}$ in $\text{C}_6\text{D}_5\text{Br}$ at 22°C rapidly generated $\{[\text{NON}]\text{Hf}^{13}\text{CH}_3\}_2(2,4-$



lutidine)}⁺ (**5a**; $\delta_C = 62.28$ ppm) and neutral **¹³C-3a** ($\delta_C = 56.45$ ppm). These data suggested that **¹³C-7** may be fluxional and therefore prompted further investigation into the dynamic solution behavior of this species. Upon cooling a sample of **¹³C-7** in C₆D₅Br to -30°C, the ¹³C{¹H} NMR spectrum displayed three broad ¹³CH₃ resonances (Figure 3.4). The first resonance at 62.66 ppm might be ascribed to a base-free methyl cation, {[NON]Hf¹³CH₃}⁺, based on a comparison to the ¹³CH₃ chemical shifts in **¹³C-4** ($\delta_C = 64.91$) and **5a-c**. Resonances at 55.49 and 48.17 ppm were assigned to the terminal and bridging methyl ligands, respectively, in **¹³C-7**. These assignments are in accord with the general trend that ¹³C chemical shifts for bridging methyl ligands occur upfield of those for terminal methyl ligands in analogous metallocene cations.³⁶⁻⁴¹ Carrying out a similar experiment with an excess of **¹³C-3a** (Hf:B = 3) gave rise to a ¹³C{¹H} NMR spectrum which showed at 22°C only a very broad signal at 56.64 ppm. At -30°C, the spectral features were nearly identical to those for the -30°C spectrum shown in Figure 3.4 except that a resonance centered at 56.71 was more intense. Increasing the concentration of **¹³C-3a** (Hf:B = 7) gave rise to ¹³C{¹H} spectra in which only one broad resonance at about 56.5 ppm was observed at each temperature down to -35°C. These results might be interpreted in terms of a solution equilibrium between [NON]Hf(CH₃)₂, {[NON]HfCH₃}⁺, and {[NON]HfCH₃}₂(μ-CH₃)⁺ (equation 11). Figure 3.4 indicates that for stoichiometric quantities of **¹³C-3a** (Hf:B = 2), this equilibrium does not lie far (at least qualitatively) from unity at -30°C. Signals for **¹³C-7**



in the experiments incorporating higher concentrations of **¹³C-3a** could not be discerned from the other broad resonances. An attempt to isolate **7** by the reaction of [Ph₃C]OTf with **3a** in C₆D₅Br gave what is probably neutral [NON]Hf(Me)OTf (by ¹H NMR) while no reaction of **3a** was observed with [Ph₃C][BPh₄],⁴² presumably because of the very poor solubility of [Ph₃C][BPh₄] in C₆D₅Br. Exchange of methyl groups between neutral and cationic Hf species *via* {[NON]HfCH₃}₂(μ-CH₃)⁺ might be expected on the basis of these findings. To test this

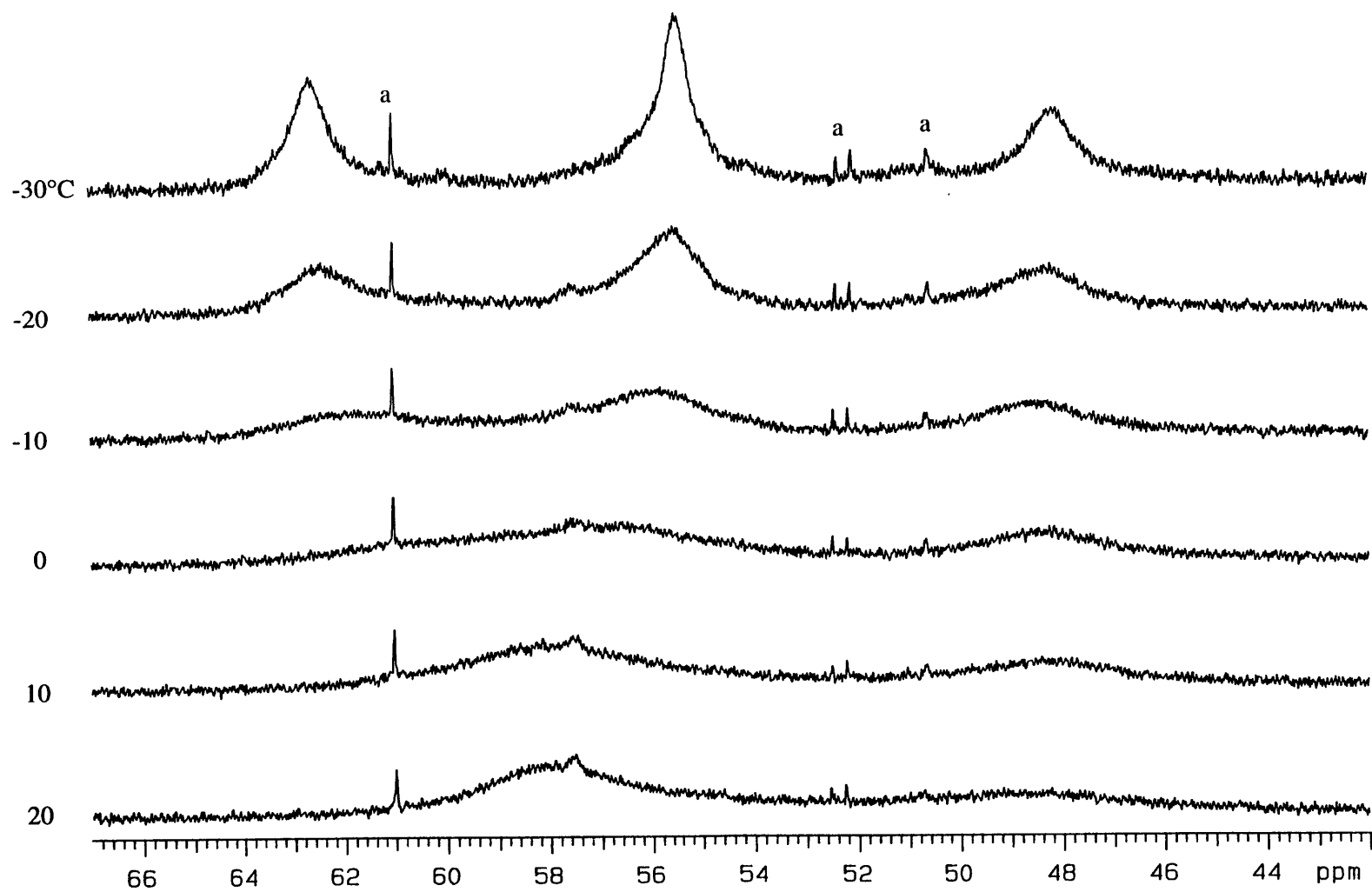
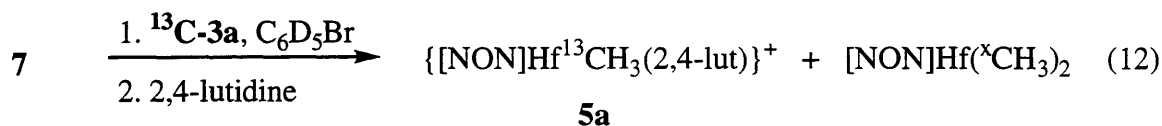


Figure 3.4. Variable Temperature 125.80 MHz $^{13}\text{C}\{\text{H}\}$ Spectra of $\{([\text{NON}]\text{Hf}^{13}\text{CH}_3)_2(\mu\text{-}^{13}\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (^{13}C -7) in $\text{C}_6\text{D}_5\text{Br}$.
^a Spectrometer artifacts.

proposal, a C₆D₅Br solution of **7** (generated *in situ* from [Ph₃C][B(C₆F₅)₄] and two equivalents of **3a**) was allowed to equilibrate with one equivalent of ¹³C-**3a** for 2 hours (equation 12). After quenching with one equivalent of 2,4-lutidine, the ¹³C{H} NMR spectrum (for 128 transients) showed a sharp resonance at 61.98 ppm arising from {[NON]Hf¹³CH₃(2,4-lut)}⁺ (**5a**) and one at 56.44 ppm from the ¹³C labeled isotopomers of **3a**. A very weak resonance was found at 30.20 ppm, possibly arising from unlabeled Ph₃CCH₃. Evidently ¹³CH₃ abstraction from neutral

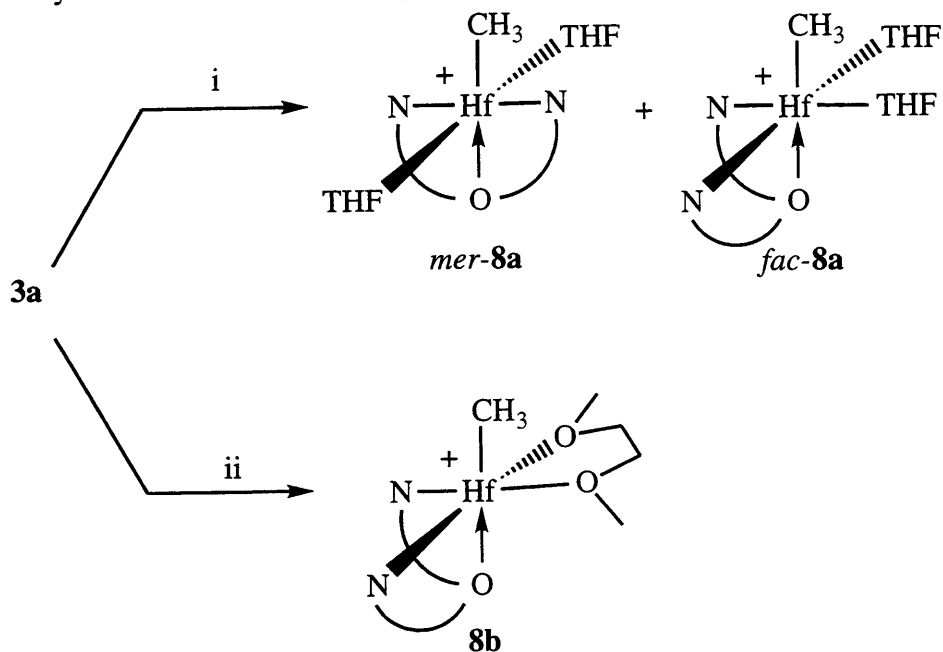


¹³C-**3a** occurred exclusively by {[NON]HfCH₃}⁺. Similar ¹³C isotopic scrambling between cationic and neutral thorium complexes *via* a bridging methyl bimetallic cation related to ¹³C-**7** was observed by Marks *et. al.*⁴¹

Isolation of Base Stabilized Alkyl Cations. Several base-stabilized methyl cations were prepared *via* oxidative cleavage of Hf-C bonds (Scheme 3.1). Treatment of **3a** with one equivalent of [Cp'₂Fe]BPh₄ in toluene and 2.2 equivalents of THF gave {[NON]HfCH₃(THF)₂}BPh₄ (**8a**) in 62% yield as colorless crystals from cold dichloromethane (Cp' = MeC₅H₄). The ¹H and ¹³C{H} NMR spectra of **8a** in CD₂Cl₂ showed that it contains two molecules of coordinated THF and that it exists in solution as an equimolar mixture of the *mer* and *fac* isomers. The ¹H NMR spectrum contains two methyl resonances of equal intensity at 0.72 (*mer*) and 0.55 ppm (*fac*) while two [NON]²⁻ ^tBu signals appeared at 1.61 (*mer*) and 1.40 ppm (*fac*; Figure 3.5). Lowering the temperature to -40°C did not affect the relative intensities of each set of resonances, but dissolving **8a** in C₆D₅Br changed the *mer/fac* ratio to 2.4. Unambiguous assignments of these resonances to each isomer were determined by a comparison of the chemical shifts to those of the related DME complex {[NON]HfCH₃(DME)}BPh₄ (**8b**), prepared in 63% yield. The ¹H and ¹³C{H} NMR spectra of **8b** in CD₂Cl₂ showed one [NON]²⁻ ^tBu resonance and a symmetric DME ligand, indicating that this complex has a mirror plane which passes

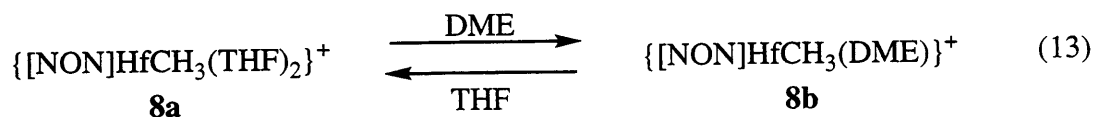
between the $[\text{NON}]^{2-}$ amido nitrogens. Furthermore, the ^1H NMR spectrum revealed one Hf-CH_3 resonance at 0.51 ppm which corresponds to that found in *fac*-**8a** (see Figure 3.5).

Scheme 3.1. Synthesis of Hafnium Methyl Cations.^a



^a All reactions were carried out in toluene at 22°C employing the following reagents: (i) $[\text{Cp}'_2\text{Fe}]\text{BPh}_4$, 2.2 equiv. THF; (ii) $[\text{Cp}'_2\text{Fe}]\text{BPh}_4$, 1.2 equiv. DME.

The lability of bases in **8** and **9** was probed by adding a slight excess of DME to a dichloromethane solution of **8a** at 22°C which resulted in the quantitative formation of **8b** (equation 13). In turn, dissolution of **8b** in THF and cooling to -40°C gave back crystalline **8a**.



Furthermore, catalytically active N,N-dimethylaniline adduct **4** readily liberated Me_2NPh upon treatment with two equivalents of THF in $\text{C}_6\text{D}_5\text{Br}$ to give the cation in **8b**. Not surprisingly, **8a** and **8b** did not polymerize 1-hexene in CD_2Cl_2 at 22°C over the course of 2 days.

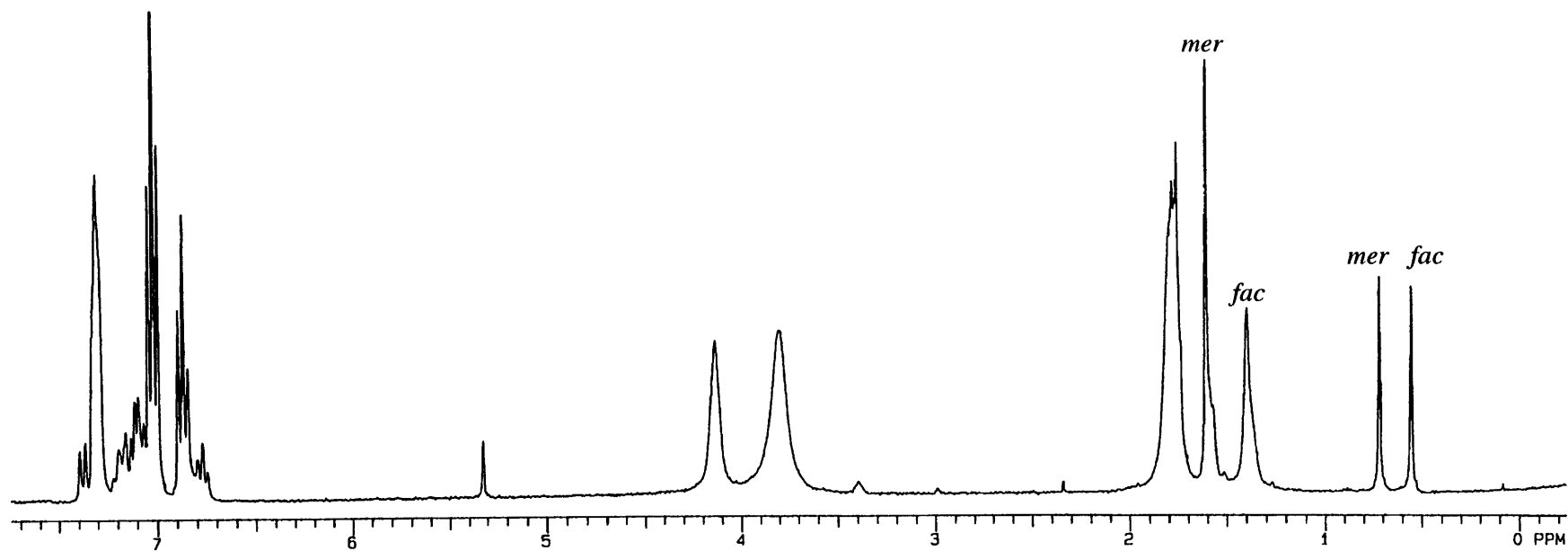
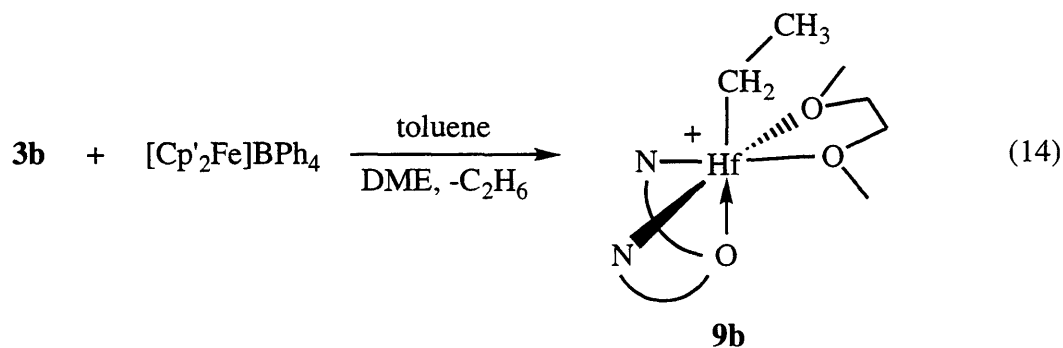


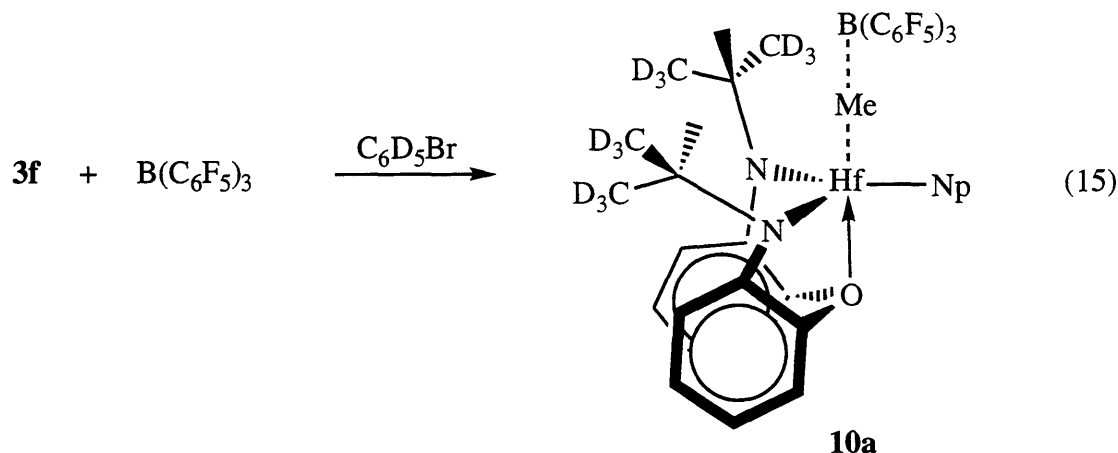
Figure 3.5. 500 MHz ^1H NMR Spectrum of $\{[\text{NON}]\text{HfMe}(\text{THF})_2\}\text{BPh}_4$ (8a) in CD_2Cl_2 at 22°C.

These findings suggested that complexes which contain alkyl ligands bearing β -protons might also be in the offing. Thus diethyl complex **3b** reacted smoothly with $[\text{Cp}'_2\text{Fe}]\text{BPh}_4$ in toluene/THF to afford, after crystallization from $\text{CH}_2\text{Cl}_2/\text{THF}$ at -40°C , ivory crystals of $\{[\text{NON}]\text{HfEt}(\text{THF})_2\}\text{BPh}_4$ (**9a**) in 49% yield. The ^1H NMR spectrum of **9a** in CD_2Cl_2 consists of very broad signals arising from labile THF ligands in what appears to be two isomers by comparison to the ^1H NMR spectrum of **8a**. A well-resolved triplet at 1.66 ppm was assigned to an ethyl group in one isomer. The related DME adduct was prepared in a similar manner by addition of $[\text{Cp}'_2\text{Fe}]\text{BPh}_4$ and one equivalent of DME to **3b** in toluene to give $\{[\text{NON}]\text{HfEt}(\text{DME})\}\text{BPh}_4$ (**9b**) which could be isolated as a microcrystalline solid when crystallized from cold dichloromethane/DME (equation 14). Isolated yields were poor (typically 20 - 25%) due to the very high solubility of **9b** in dichloromethane. The ^1H and $^{13}\text{C}\{\text{H}\}$ NMR spectra of **9b** clearly indicate a facial arrangement of ligands and broadened resonances for the coordinated DME ligand. Key NMR data for **9b** (CD_2Cl_2 , 22°C) include resonances for H_β at



0.92 ppm (δ 0.97 in neutral **3b**) and C_β at 12.72 ppm (δ 14.14 in **3b**). These data are consistent with a normal and undistorted ethyl group.⁴³ Addition of a slight excess of THF to dichloromethane solutions of **9b** quantitatively generates **9a**. Complex **9b** is stable in the solid state if kept at -40°C but decomposes to unidentifiable products if left in dichloromethane solution at 22°C .

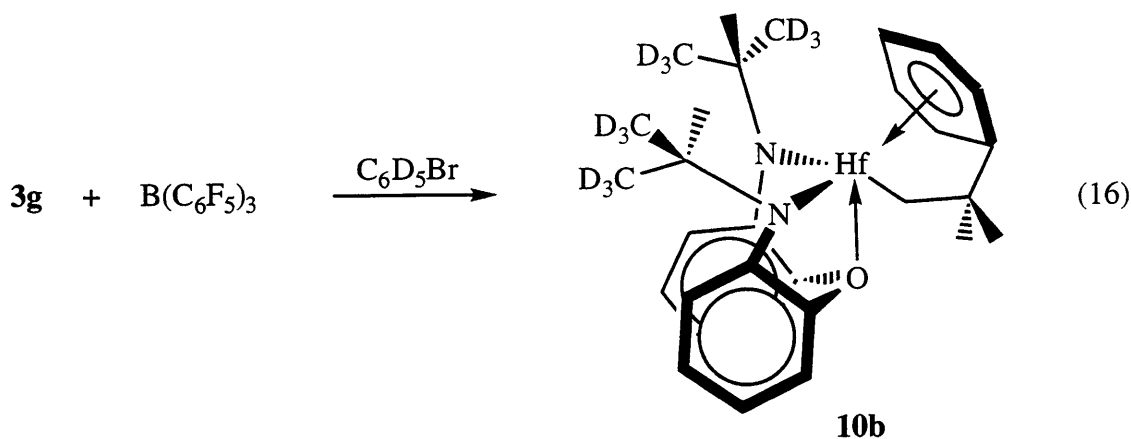
Cationic Complexes Which Contain Bulky Alkyl Groups. The strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ selectively abstracted a methyl group from **3f** in $\text{C}_6\text{D}_5\text{Br}$ at 22°C as shown in equation 15. The product is proposed to be the zwitterion $\{[\text{NON}]\text{HfR}\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (**10a**) based on analogous studies in metallocene chemistry.^{38,44-48} Anion coordination in **10a** is reflected in the downfield location of the $\text{Hf}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ resonance at δ_{H} 2.81. The difference in chemical shifts of the *meta*- and *para*-fluorines was suggested by Horton to indicate the degree



of anion coordination to a metal ($\Delta\delta(\text{F}_{\text{meta}}, \text{F}_{\text{para}}) < 3$ ppm indicates an uncoordinated anion).¹⁵⁻¹⁷ The value of $\Delta\delta(\text{F}_{\text{meta}}, \text{F}_{\text{para}})$ for **10a** is 4.72 ppm which confirms the presence of a coordinated $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anion. The X-ray crystal structure of the related zwitterion $\{[\text{NON}]\text{ZrMe}\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ showed that the axial methyl group is the one which is partially abstracted,²⁶ suggesting that the more bulky neopentyl group in **10a** probably occupies the equatorial site as shown in equation 15. Solutions of **10a** in either C_6D_6 or $\text{C}_6\text{D}_5\text{Br}$ are reasonably stable at 22°C , but gradually evolved isobutylene ($\delta_{\text{H}} = 4.75$ and 1.60) which most likely arises from β -methyl elimination. This rare behavior has been observed for only a few other cationic complexes containing neopentyl ligands.⁴⁹⁻⁵² The other expected product of β -methyl elimination, $\{[\text{NON}]\text{HfMe}\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$, could be identified (by ^1H NMR) by comparison to complex mixtures obtained from the reaction of **3a** with $\text{B}(\text{C}_6\text{F}_5)_3$. Complex **10a** polymerizes 1-hexene (200 equivalents, PhCl , 22°C , 6 hours) to give poly(1-hexene) in only 85% yield ($M_n =$

9345 g/mol and PDI = 1.38). No olefinic resonances were found in the ^1H - and $^{13}\text{C}\{\text{H}\}$ spectra of poly(1-hexene) prepared under these conditions. The significant decrease in catalytic activity of **10a** from that observed for **4** is a likely consequence of strong anion coordination to Hf in contrast to highly active metallocene based olefin polymerization catalysts activated with $\text{B}(\text{C}_6\text{F}_5)_3$.^{44,45,47,48,53}

Treatment of methyl(neophyl) complex **3g** with one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ in $\text{C}_6\text{D}_5\text{Br}$ at -40°C also resulted in selective methyl abstraction to give bright yellow **10b** (equation 16). Complex **10b** separates as an oil when prepared in toluene and attempts to isolate it yielded only oils which decomposed readily. Therefore it was characterized in solution by NMR.



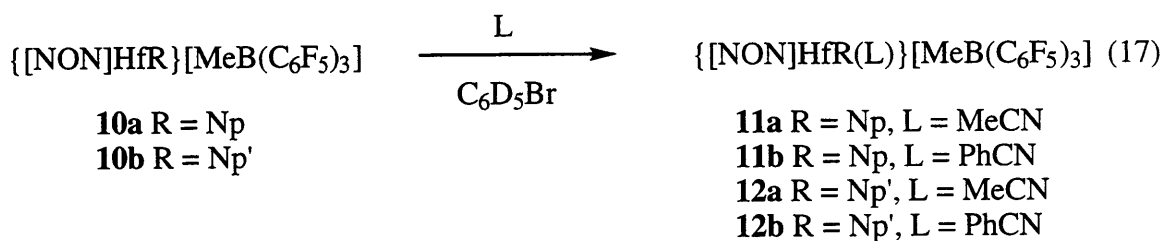
Spectroscopic data for **10b** are consistent with it being a rare Group IV d^0 arene complex. In contrast to **10a**, the $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anion in **10b** does not appear to be coordinated (free anion: $\delta_{\text{Me}} = 1.18$; $\Delta\delta(\text{F}_{\text{meta}}, \text{F}_{\text{para}}) = 2.61$ ppm). The ^1H NMR spectrum of **10b** in $\text{C}_6\text{D}_5\text{Br}$ at 22°C reveals broad arene resonances which are also shifted considerably downfield (δ_{H} 7.63 (H_{ortho}), 7.56 (H_{meta}), 7.34 (H_{para})) from those in neutral **3g**. No decoalescence of these resonances was observed at -30°C . Aliphatic signals for the neophyl ligand are also broad, possibly as a consequence of restricted rotation. The $^{13}\text{C}\{\text{H}\}$ NMR spectrum of neutral **3g** in $\text{C}_6\text{D}_5\text{Br}$ showed clearly the arene C_{ipso} as a sharp singlet at 153.94 ppm, but in **10b** it appeared downfield as a broad resonance at 156.65 ppm, consistent with arene coordination. Complicated resonances for

[NON]²⁻, MeB(C₆F₅)₃⁻, and C₆D₅Br solvent rendered other spectral assignments in the aromatic region more ambiguous, so similar comparisons for arene C_{ortho}, C_{meta}, and C_{para} could not be made. No significant changes in the ¹³C{H} NMR spectrum were observed upon cooling to -30°C.

Arene complexes of transition metals (especially for late metals) are well-known while those of the Group IV triad are exceedingly rare,⁵⁴⁻⁵⁹ especially for cationic complexes in which the arene is not derived from an anion. Presumably for d⁰ Group IV metals, π -backbonding from the metal to the arene ligand is severely attenuated. The X-ray crystal structures of toluene complexes [Me₅C₅HfMe₂(toluene)][MeB(C₆F₅)₃]⁶⁰ and [(1,3-(TMS)₂-C₅H₃)₂HfMe₂(toluene)][MeB(C₆F₅)₃]⁶¹ both show that toluene coordinates to Hf in η^6 fashion. These complexes also exhibit downfield ¹H and ¹³C chemical shifts for the toluene ligands which is typical for other complexes of this type.^{46,62} Spectroscopic data for **10b** is consistent with this trend, but in the absence of any structural data, the hapticity of the arene ligand cannot be unambiguously assigned and the possibility of intermolecular interactions cannot be ruled out. It should be noted that complex **10b** could be considered an 18 electron species if the [NON]Hf fragment allowed η^6 coordination of the neophyl ligand; at this stage there are no known cationic Group IV η^2 - or η^4 -arene complexes. It appears that the only other diamide complexes of Group IV metals containing arene ligands are [{Me₂Si(NCMe₃)₂}Zr(η^1 , η^6 -CH₂CH(R)CH₂Ph)][B(C₆F₅)₄] (R = H, Me)¹⁵ and the proposed [(Cy₂BNCH₂CH₂NBCy₂)MⁱBu(toluen)] [B(C₆F₅)₄] (M = Ti, Zr, Hf).⁷

Complexes **3f** and **3g** would be attractive precursors to sterically bulky cations related to **4**. However, several attempts to generate directly such a cation by abstraction of the methyl group in **3f** with [Ph₃C][B(C₆F₅)₄] unfortunately gave decomposition products, although Ph₃CMe was observed by ¹H NMR in the reaction mixtures. Furthermore, treatment of **3f** with [PhNMe₂(H)][B(C₆F₅)₄] led to protonation of the [NON]²⁻ ligand and only the gradual formation of CH₄ (see next section). The cleanest route was found by addition of nitriles to **10a** and **10b** in C₆D₅Br to generate deep yellow **11a,b** and **12a,b**, respectively, which were characterized

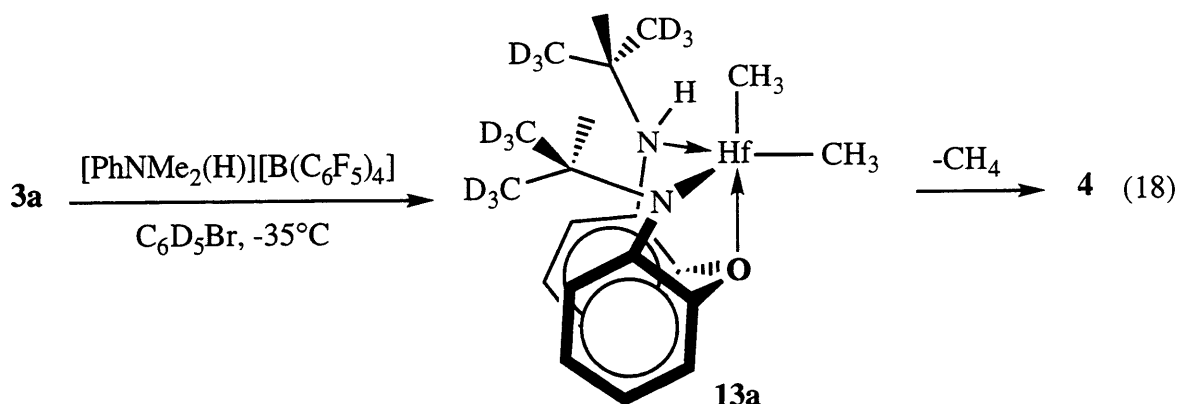
spectroscopically (equation 17). Coordination of acetonitrile ligands in **11a** and **12a** was evidenced in ^1H NMR spectra by broad methyl resonances at 1.90 and 1.72 ppm, respectively, whereas benzonitrile complexes **11b** and **12b** gave rise to complicated aromatic signals for which unambiguous assignments could not be made. Both ^{19}F and ^1H NMR spectra of all these nitrile



complexes indicate non-coordinated $\text{MeB}(\text{C}_6\text{F}_5)_3^-$ anions. Nitrile adducts **11** and **12** are stable in $\text{C}_6\text{D}_5\text{Br}$ at 22°C ; no evidence was found for β -methyl elimination in the neopentyl derivatives.

Intermediates in Protonolysis Reactions. The reaction of bulky ammonium reagents with Group IV dialkyls provides a general synthetic route to cationic alkyl complexes.⁴³ Protonolysis of a Hf-C bond is indeed the method of choice for preparing the olefin polymerization catalyst **4** as discussed in a previous section. This type of reaction is examined in greater detail here.

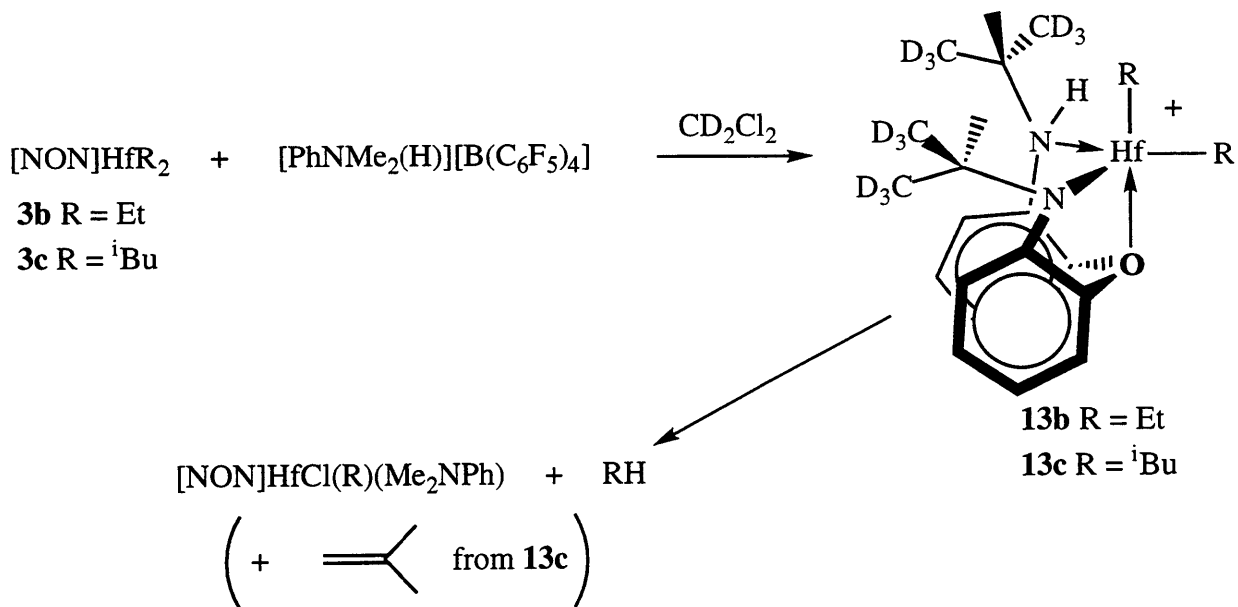
The reaction of **3a** with one equivalent of $[\text{PhNMe}_2(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ partially dissolved in $\text{C}_6\text{D}_5\text{Br}$ at -40°C led to the rapid dissolution of the sparingly soluble ammonium reagent (equation 18). Gas evolution (presumably CH_4 which is typical in similar experiments performed at 22°C)



was not observed. The ^1H NMR spectrum at -35°C indicated that the unsymmetric complex **13a** had formed by protonation of one amido nitrogen. Important spectral features for complex **13a** include two equally intense $[\text{NON}]^{2-} \text{tBu}$ resonances at 1.06 and 1.03 ppm and two Hf- CH_3 resonances at 0.55 and 0.53 ppm. The downfield location of a slightly broadened singlet at 4.33 ppm with relative intensity one was assigned to the N-H proton. The solution also contained free Me_2NPh (δ 2.53, -35°C). Over the course of several minutes, resonances for $\{[\text{NON}]\text{HfCH}_3(\text{Me}_2\text{NPh})\}^+$ (**4**) and CH_4 (δ 0.16) were observed to increase in intensity as those for **13a** gradually disappeared. The generation of **13a** was always accompanied by the formation of substantial amounts of **4**, even when performed at -40°C . No reaction was observed between **3a** and $[\text{Et}_3\text{NH}]\text{BPh}_4$ in CD_2Cl_2 , possibly because of the poor solubility of $[\text{Et}_3\text{NH}]\text{BPh}_4$ in this solvent.

In an analogous set of reactions, more stable "N-H" species could be prepared by protonating **3b** and **3c** by $[\text{PhNMe}_2(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ in cold CD_2Cl_2 to give **13b** and **13c**, respectively (Scheme 3.2). In contrast to the instability of **13a** at -35°C , **13b** persisted in solution for hours at 22°C . The ^1H NMR spectrum of **13b** includes a singlet at 4.64 ppm arising from the

Scheme 3.2. Protonation of Neutral Dialkyl Complexes.



N-H moiety and two sets of $[\text{NON}]^{2-}$ ^tBu and ethyl H_β resonances, respectively (Figure 3.6). The α -protons on the ethyl ligands are evidently rendered diastereotopic as indicated by two complex multiplets at 0.87 and 1.23 ppm, thereby furnishing additional proof that **13b** is an unsymmetrical molecule. The gradual liberation of ethane ($\delta_{\text{H}} = 0.85$) and the consumption of free Me_2NPh ($\delta_{\text{H}} = 2.92$) was observed over the course of hours as resonances appeared for what is presumed to be $[\text{NON}]\text{HfCl}(\text{Et})(\text{Me}_2\text{NPh})$ (see Experimental section for details).⁶³ This would be the product of formal chloride abstraction from CD_2Cl_2 by putative $\{[\text{NON}]\text{HfEt}(\text{Me}_2\text{NPh})\}^+$ which was not detected. When **13b** was generated and then allowed to decompose in $\text{C}_6\text{D}_5\text{Br}$ at 22°C , only ethane was readily identified by ^1H NMR; the identity of organometallic products could not be determined.

The ^1H NMR spectrum of **13c** in CD_2Cl_2 showed the N-H resonance at 4.89 ppm and that this molecule, like **13a** and **13b**, does not possess a plane of symmetry as indicated by four doublets at 1.03, 0.98, 0.81, and 0.66 ppm arising from the inequivalent methyl substituents on the isobutyl ligands. The methylene protons are diastereotopic and give rise to two multiplets at 1.22 and 1.10 ppm, respectively. Surprisingly, one of the two isobutyl methyne multiplets occurs downfield at δ 2.41 while the other one is at δ 1.52. As expected, cation **13c** decomposed in CD_2Cl_2 *via* isobutane elimination. A doublet for the isobutane methyl substituents ($\delta_{\text{H}} = 0.70$) increased in intensity with concomitant and clean formation of a neutral complex, presumably $[\text{NON}]\text{HfCl}(\text{iBu})(\text{Me}_2\text{NPh})$, over the course of one day. Resonances for isobutylene were also found. Its origin and the fate of the $\text{B}(\text{C}_6\text{F}_5)_4^-$ anion in these reactions were not determined.

Deuteration of **3b** with $[\text{PhNMe}_2(\text{D})][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 gave cleanly **D-13b** whose ^1H NMR spectrum is nearly identical to that shown in Figure 3.6 for **13b**. Since the total amount of deuterium present in $[\text{PhNMe}_2(\text{D})][\text{B}(\text{C}_6\text{F}_5)_4]$ as N-D was only 50% (see Experimental section for details), a N-H resonance that appeared at 4.64 ppm integrated to slightly less than one proton. Integration error or perhaps proton exchange processes with solvent are possible reasons why this resonance did not also integrate to 0.5. Most importantly, however, the ^2H NMR spectrum of **D-13b** generated in dichloromethane contained a broad N-D signal at 4.56 ppm. As anticipated,

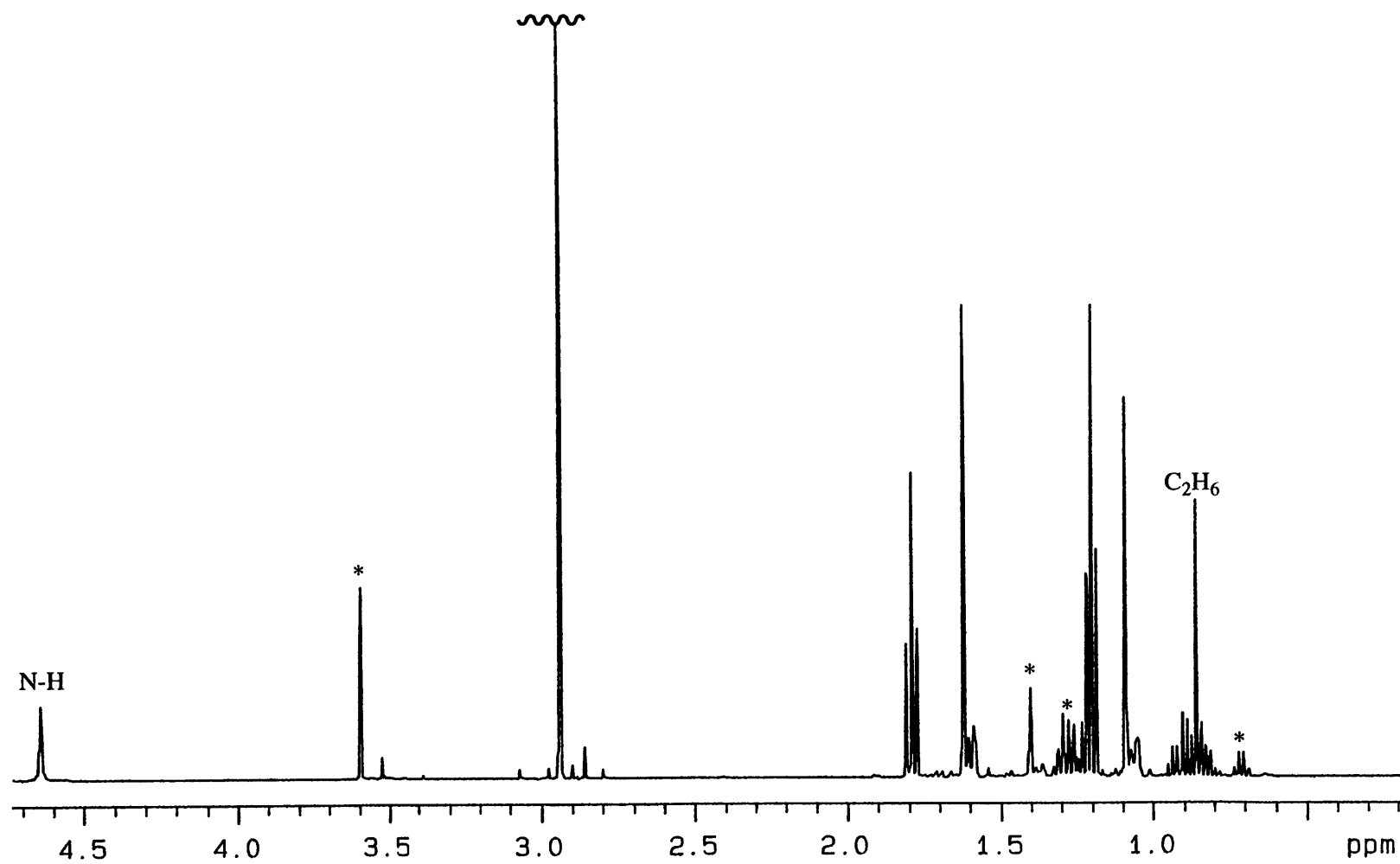


Figure 3.6. 500 MHz ^1H NMR Spectrum of **13b** in CD_2Cl_2 at 22°C . * Resonances for $[\text{NON}]\text{HfCl}(\text{Et})(\text{Me}_2\text{NPh})$.

two $[\text{NON}]^2\text{-}^t\text{Bu}$ resonances also appeared at 1.53 and 1.38 ppm. Solutions of **D-13b** gradually decomposed to $[\text{NON}]\text{HfCl}(\text{Et})(\text{Me}_2\text{NPh})$ and ethane over two days. A 500 MHz ^1H NMR spectrum of the reaction mixture in CD_2Cl_2 revealed a multiplet at 0.85 ppm, suggesting that deuterium had been incorporated into ethane. This region in the ^2H NMR spectrum is partially obscured by the ^tBu resonance from $[\text{NON}]\text{HfCl}(\text{Et})(\text{Me}_2\text{NPh})$ at 1.29 ppm, but a small shoulder at δ 0.83 may arise from CH_2DCH_3 .

In an analogous set of experiments, the diisobutyl complex (**3c**) was deuterated with one equivalent of $[\text{PhNMe}_2(\text{D})]\text{B}(\text{C}_6\text{F}_5)_4$ to give **D-13c**. The ^1H NMR spectrum of **D-13c** in CD_2Cl_2 is identical in every respect to that for **13c** except for the N-H resonance at δ 4.49 which integrated to less than one proton. This is corroborated by the presence of a broad N-D resonance at δ 4.38 in the ^2H NMR spectrum. Upon standing at 22°C for two days, **D-13c** decomposed to $[\text{NON}]\text{HfCl}(^i\text{Bu})(\text{Me}_2\text{NPh})$, isobutylene, and isobutane as confirmed by ^1H NMR. Evidence in the ^2H NMR spectrum for deuterium incorporation into the latter two products include a weak resonance at δ_{D} 1.65 for $\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{D})(\text{CH}_3)$ while a triplet at δ_{D} 0.79 ($J_{\text{HD}} = 7.5$ Hz) indicates the evolution of $\text{CH}(\text{CH}_3)_2(\text{CH}_2\text{D})$. Since both of these resonances are partially obscured by the broad $[\text{NON}]^2\text{-}^t\text{Bu}$ signal at 1.30 ppm and since there was a low initial concentration of "D⁺" (see Experimental section), these spectral assignments are tenuous at this stage.

DISCUSSION

The ease with which **2** was alkylated allowed the preparation of a variety of neutral dialkyl complexes. Complexes **3b** and **3c** which both contain β -protons are remarkably stable toward β -elimination. In contrast, there are only a few (cyclopentadienyl)hafnium complexes reported so far which contain two^{31,64-66} or even three⁶¹ alkyl ligands with β -protons. Stable Group IV complexes containing both alkyl and amido ligands emerged nearly three decades ago when Bürger prepared the thermally robust monoalkyl complexes of the type $(\text{R}_2\text{N})_3\text{TiR}'$ ($\text{R} = \text{Me}, \text{Et}$; $\text{R}' = \text{Et}, ^n\text{Pr}, ^i\text{Pr}, ^n\text{Bu}$).^{67,68} It would appear that decomposition (by β -elimination or other pathways) of highly electrophilic amido complexes can be attenuated significantly if large amido substituents are

employed. For example, sterically demanding amido ligands were cited as the reason for the thermal stability of $[\text{TMS}_2\text{N}]_2\text{HfEt}_2$ which was reported by Andersen to melt at 65°C without decomposition.⁵ More recent examples of complexes bearing alkyl groups with β -protons and bulky amido ancillary ligands include $[\text{Cy}_2\text{BNCH}_2\text{CH}_2\text{NBCy}_2]\text{MR}_2$ (Cy = cyclohexyl; M = Zr, Hf; R = Et, $i\text{Bu}$, $n\text{Bu}$)⁷ and $[(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{O}]\text{Zr}^i\text{Bu}_2$.¹⁴ Therefore, it is reasonable that in **3b** and **3c** the relatively bulky $[\text{NON}]^{2-}$ ligand may also prevent the close approach of an alkyl β -proton to Hf, a circumstance that would disfavor β -elimination.

Only dimethyl complex **3a** served as a precursor to a monoalkyl cation with practical catalytic activity. The variable temperature NMR solution studies of cation **4** and a recent proposal that the base-free species $\{[\text{NON}]\text{ZrMe}\}^+$ is an active catalyst³⁰ suggest that base adduct **4** may be a resting state of the catalyst. Other related catalytically active complexes containing coordinated N,N-dimethylaniline have been reported^{14, 16} such as $\{[\text{TMSN}(\text{CH}_2\text{CH}_2\text{NTMS})_2]\text{ZrMe}(\text{Me}_2\text{NPh})\}^+$,¹⁷ and it is likely that the complexes formed upon dissociation of base are the active species. Base-free cations such as the Zr species mentioned above might be implied by the finding that N,N-dimethylaniline in **4** could be readily displaced by the more aggressive lutidine ligands to give catalytically inactive complexes **5a-c**. Alternatively, exchange between free and bound base lutidines in **5a** and **5b** could occur *via* bis(lutidine) adducts " $\{[\text{NON}]\text{HfMe}(\text{lutidine})_2\}^+$ " which would be analogous to bis(THF) complexes **8a** and **9a**. At this stage, it appears that dissociation of a base from cations of the type $\{[\text{NON}]\text{HfR}(\text{L})\}^+$ is required to generate catalytically active species.

The temperature dependent competition between N,N-dimethylaniline and 1-hexene for Hf in **4** plays an important role in polymerizations. The high molecular weights of poly(1-hexene) produced at low temperatures and the results from a ^{13}C labeling study (Figure 3.3) indicated that initiation is not uniform. Evidently the exchange between free and bound N,N-dimethylaniline at higher temperatures becomes rapid enough such that 1-hexene competes favorably for Hf, as indicated by the sharp decrease in poly(1-hexene) molecular weights (Figure 3.2). The narrow polydispersities and unimodal GPC traces are indicative of single-site catalysis while close

inspection of $^{13}\text{C}\{\text{H}\}$ NMR spectra of these polymers showed that they are atactic. The latter result would be expected since **4** is not chiral. Furthermore, the rate of "flipping" of the $[\text{NON}]^2-$ ligand may be more rapid than the rate of olefin insertion into a Hf-alkyl bond, thereby equilibrating both faces to which an olefin may bind in a base-free propagating species.

Base-free Group IV cations bearing small alkyl groups are, in general, too electrophilic to exist as discrete species and may therefore satisfy their electron deficiency by coordination of neutral dialkyl complexes to form bridging alkyl bimetallic cations.⁶⁹ The first evidence for this kind of interaction was found by Watson in the bridging methyl Lu dimer, $(\text{Me}_5\text{C}_5)_2\text{Lu}(\mu\text{-Me})\text{MeLu}(\text{Me}_5\text{C}_5)_2$,⁷⁰ which is an isoelectronic analog of the first stable Group IV examples reported by Bochmann in 1994.³⁷ Whereas sharp ^1H and ^{13}C signals for bridging and terminal alkyl groups can be readily distinguished at low temperatures for fluxional species such as $\{[(\text{Me}_5\text{C}_5)_2\text{ThMe}]_2(\mu\text{-Me})\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ ³⁸ or even $[(\text{Cp}_2\text{HfEt})_2(\mu\text{-Et})][\text{B}(\text{C}_6\text{F}_5)_4]$,⁶⁶ spectral assignments for the bimetallic cation **7** were rendered more ambiguous since it is highly fluxional in $\text{C}_6\text{D}_5\text{Br}$, even at -30°C , and separates as an oil from solvents with lower melting points such as toluene. The only other example of a non-metallocene bridging methyl bimetallic cation, reported by Horton in 1996, is $\{[\text{TMSN}(\text{CH}_2\text{CH}_2\text{NTMS})_2\text{ZrMe}]_2(\mu\text{-Me})\}[\text{B}(\text{C}_6\text{F}_5)_4]$.¹⁷ Complexes such as **7** have been proposed to be models for the temporary inactive resting stages of polymerization catalysts.³⁷ This proposal agrees well with the results from scouting experiments in which $\text{C}_6\text{D}_5\text{Br}$ solutions of **7** were treated with 1-hexene to produce poly(1-hexene) of very high molecular weight. This is the anticipated result since the concentration of catalytically active $\{[\text{NON}]\text{HfR}\}^+$ is attenuated by the formation of **7** ($\text{R} = \text{Me}$ or growing polymer chain).

The majority of mononuclear Group IV alkyl cations exist as complexes of the general form $[\text{Cp}_2\text{MR}(\text{L})]^+$ whereas those which contain alkyl groups bearing β -protons are usually unstable toward β -hydride or, in rarer cases, β -methyl elimination ($\text{Cp} = \text{cyclopentadienyl derivative}$; $\text{M} = \text{Zr or Hf}$; $\text{R} = \text{H, Me, or Bz}$; and $\text{L} = \text{neutral base}$).⁴³ The paucity of hafnium alkyl cations, however, is offset by a few notable examples. The isolable $[\text{Cp}^*_2\text{Hf}(\text{Me})\text{THT}]\text{BPh}_4$ reported by Teuben oligomerizes propene but polymerizes ethylene^{71,72} whereas the catalytic activity of

$[(C_5H_4SiMe_3)_2HfMe][B(C_6F_5)_4]$ reported by Bochmann shows a pronounced dependence upon solvent and anion coordination.⁷³ Buchwald reported the synthesis of a rare monomeric hafnium hydride $[(EBTHI)HfH(PhNMe_2)][Co(C_2B_9H_{11})_2]$ which is useful for the asymmetric hydrogenation of olefins.⁷⁴ The first reports of cationic higher alkyl hafnocene complexes appeared in 1994 for $[(C_5Me_5)_2Hf(^iBu)L][BPh_4]$ and $[(C_5H_4Me)_2Hf(^nBu)L][B(3,5-(CF_3)_2C_6H_3)_4]$, but these readily decompose *via* β -elimination in the absence of excess L and at higher temperatures (L = THF or PMe_3).⁶⁵ Bochmann *et. al* reported the synthesis of several hafnium cations, $[Cp''HfEt_2(\eta^6\text{-toluene})][EtB(C_6F_5)_3]$ and $\{[Cp''HfEt(\eta^6\text{-toluene})]_2(\mu\text{-}C_2H_4)\}[EtB(C_6F_5)_3]$, which are stabilized by coordination of toluene ($Cp'' = 1,3\text{-(TMS)}_2\text{-}C_5H_3$).⁶¹ Finally, more recent studies of bis(borylamido) complexes of hafnium showed that it is possible to prepare relatively electron deficient cations of the type $\{[Cy_2BNCH_2CH_2NBCy_2]HfR(B)\}[B(C_6F_5)_4]$ (Cy = cyclohexyl; R = Et, ^iBu , ^nHex ; B = toluene or C_6D_5Cl).⁷ Thus **8** and **9** together represent a modest contribution to the small but growing number of isolable hafnium alkyl cations. The presence of both *fac*- and *mer*-**8a** in solution demonstrates the flexibility of the $[NON]^{2-}$ ligand. For example, while it appears that coordination of only one base such as N,N-dimethylaniline in **4** yields a pseudo-TBP cationic complex, further folding of the $[NON]^{2-}$ ligand may allow coordination of two stronger bases such as THF (as in **8a**), 2,4-lutidine, (as suggested for **5a** by variable temperature NMR studies), or one molecule of DME (as in **8b** and **9b**). The coordination wedge of Group IV metallocene alkyl cations allows the coordination of only one base such as THF,^{43,65,75-78} but the moderate steric bulk presented by diamide ligand motifs as in complexes **8** and **9** facilitates the coordination of two bases.¹⁵ These complexes are related to the proposed bis(alkene) adducts implicated by some in the propagation and chain-transfer steps of α -olefin polymerization.^{2,79,80} Complexes in which the $N_{eq}\text{-Hf-}N_{eq}$ angle approaches 180° , presumably as in *mer*-**8a** and **-9a** and as shown in the X-ray crystal structure of related $\{[(TMSN\text{-}o\text{-}C_6H_4)_2O]HfMe(THF)_2\}BPh_4$,³⁰ should be compared to the proposed solution structure of neutral $[NON]HfR_2$ complexes in which the R groups rapidly equilibrate *via* a planar $[NON]^{2-}$ manifold. Since complexes **8a** and **9a** are readily interconverted

by addition of the appropriate base, probably by a dissociative mechanism, and since the 1:1 *mer/fac*-**8a** ratio in CD₂Cl₂ is constant over a 60 C° temperature range, it therefore appears that there exists little, if any, preference for the [NON]²⁻ ligand to adopt either a planar or "folded" geometry. The stability of ethyl cation **9b** might be explained by stronger Hf-O(DME) π -bonding over agostic Hf...H β interactions,⁴³ even though β -agostic interactions are believed to be most efficient in ethyl complexes.^{81,82}

In 1986 Bochmann and coworkers reported the preparation of [Cp₂TiCH₃(NH₃)]X from Cp₂Ti(CH₃)₂ and [NH₄]X (X = PF₆⁻, ClO₄⁻).⁸³ A few years later Hlatky and Turner reported that the reaction of (Me₅C₅)₂Zr(CH₃)₂ with [(ⁿBu)₃NH][BPh₄] yielded the zwitterionic complex [(Me₅C₅)₂Zr]⁺[C₆H₄BPh₃]⁻ *via* initial Zr-CH₃ bond protonolysis followed by subsequent BPh₄⁻ C_{aryl}-H bond activation.⁸⁴ The use of bulky ammonium reagents to deliver protons to M-C bonds has since been established as a general route to the synthesis of 16-electron [Cp₂MR(L)]⁺ and base-free 14-electron [Cp₂MR]⁺ complexes. Sterically less demanding proton sources such as dialkyl ammonium hydrohalides ([R₂NH₂]X; X = Cl, I) have been widely employed for the preparation of metal halide complexes M-X *via* cleavage of M-NR₂ bonds.^{85,86} In some cases this approach has led to the protonolysis of chelating amido ligands.^{12,87} It was therefore completely unanticipated that the reactions of dialkyl complexes **3a-c** with Me₂NPh(H)⁺ resulted in neither initial M-C nor M-NR₂ protonolysis, but rather protonation of one [NON]²⁻ amide to give coordinated amine functionalities in cations **13a-c**. It should be noted that a zirconium(IV) species reported by Piers⁸⁸ and a titanium(III) complex recently mentioned by Hughes⁸⁹ retain coordinated amine ligands generated by the addition of protons to M-NR₂ bonds, but these complexes are neutral and do not also contain η^1 -hydrocarbyl ligands. It appears that the *stepwise* protonolysis of M-C bonds *via* the observable and clean generation of **4** from **13a** and the putative species {[NON]HfR(Me₂NPh)}⁺ from **13b** (R = Et) and **13c** (R = ⁱBu) is without precedent.

The mechanism (or mechanisms) is not known by which a proton is delivered to metal-carbon bonds in transition metal complexes, but a few aspects may be considered at this stage. First, it seems that ligand motifs play significant roles in protonolysis reactions. The judicious

choice of bulky amido substituents was suggested by McConville to kinetically protect the ancillary ligand amides from protonolysis in $[\text{RN}(\text{CH}_2)_3\text{NR}]\text{Zr}(\text{NMe}_2)_2$ ($\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$)^{9,12} whereas the steric accessibility of an amido ligand in a Zr (IV) species mentioned above probably rendered it more susceptible to attack by a proton source.⁸⁸ In contrast, addition of protons to Group IV metallocene complexes which also contain amido ligands usually do not decompose by yielding free cyclopentadienes. Interestingly, the reactions of homoleptic metal amides $\text{M}(\text{NR}_2)_4$ with a range of cyclopentadienes (and their analogs) is a well-known synthetic route to complexes of the type $\text{Cp}_2\text{M}(\text{NR}_2)_2$.^{85,86,88,90-94} The relative basicity of the amido nitrogens in $[\text{NON}]\text{HfR}_2$ complexes is more than likely an important factor. For example, a qualitative comparison of pK_a values indicates that proton transfer from $[\text{Me}_2\text{NPh}(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ (as in $[\text{Me}_2\text{NPh}(\text{H})]\text{Cl}$, $\text{pK}_a \approx 5$)^{95,96} to the $[\text{NON}]^{2-}$ N_{eq} atoms in **3a-c** (approximately $[\text{tBuN}(\text{H})_2\text{Ph}]\text{Cl}$ for **13a-c**; $\text{pK}_a \approx 7$)⁹⁷ would be expected, thereby giving complexes **13a-c** which are poised for alkane elimination. Thus ancillary amido ligands could affect the ease with which M-C or other M-NR₂ bonds in a given complex can be cleaved. Second, the free N,N-dimethylaniline generated in these protonolysis reactions might serve to shuttle protons from $[\text{NON}]^{2-}$ N_{eq} atoms to hafnium-carbon bonds. The qualitative difference in rates observed for alkane elimination between **13a** (minutes at -30°C) and more sterically encumbered **13b** and **13c** (hours at 22°C) is consistent with this proposal. Finally, perhaps an added proton may migrate between the two amido nitrogens in **13a-c** *via* symmetric " $\text{N}_{\text{eq}}\cdots\text{H}\cdots\text{N}_{\text{eq}}$ " intermediates. The available data, however, indicates that such species, if formed at all, are most likely short-lived since only unsymmetric species are observed by NMR.

CONCLUSION

As predicted at the commencement of this study, the $[\text{NON}]\text{Hf}$ fragment gave rise to a very robust catalyst for the controlled polymerization of 1-hexene. The 14 electron alkyl cations of the type $\{[\text{NON}]\text{Hf-R}\}^+$ were shown to coordinate bases to a degree such that uniform initiation is evidently not attainable. This is most likely a consequence of the stronger Hf-(ligand) bonds by

comparison to analogous Zr species. The increased electrophilicity of the cationic Hf alkyl complexes, however, has made possible the observation of several unusual species that partially satisfy their electron deficiency by coordination of a variety of ligands: a neutral dimethyl to form a bimetallic bridging methyl complex; donor ligands to stabilize neopentyl, ethyl and isobutyl complexes; or an aromatic ring to furnish a rare arene complex. Furthermore, the reactions between neutral dialkyl complexes and protons discussed in the last section have provided a rare glimpse into the mechanism of protonolysis. Partial protonation of chelating polyamido ligands is apparently emerging as an important theme, not only in this current work but also in the chemistry of several triamidoamine Re complexes discussed in Chapter I. There is little reason to suppose that this theme is not also expressed in the chemistry of other transition metal complexes, especially those which contain Group IV metals and sterically accessible amido nitrogen atoms.

EXPERIMENTAL

General Procedures. All air sensitive manipulations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or when using Schlenk techniques. Pentane, diethyl ether, and tetrahydrofuran were purified by sparging with nitrogen and passing through scrubbing columns;⁹⁸ 1,2-dimethoxyethane, toluene, and 1,4-dioxane were distilled from sodium; dichloromethane was distilled from CaH₂. Deuterated solvents were purified in a manner similar to that for protio solvents, degassed by three freeze-pump-thaw cycles, and vacuum transferred to solvent storage flasks until use. [(^tBu-*d*₆)NH-*o*-C₆H₄)₂O ([NON]H₂);²⁶ NpMgCl;⁹⁹ [(MeC₅H₄)₂Fe]BPh₄;⁷⁶ B(C₆F₅)₃, and Li[B(C₆F₅)₄],¹⁰⁰ were prepared by published methods. Np'MgCl was prepared in a manner analogous to that for NpMgCl. [PhNMe₂(H)][B(C₆F₅)₄] and [Ph₃C][B(C₆F₅)₄] (recrystallized from dichloromethane/pentane at -40°C) were received as gifts from Exxon Chemical. Other reagents were purchased from commercial sources and used as received.

NMR operating frequencies and reference standards are as follows: ¹H (500 or 300 MHz, SiMe₄ = 0 ppm), ¹³C (125.80 or 75.4 MHz, SiMe₄ = 0 ppm), ¹⁹F (470 or 282.2 MHz, CFCl₃ =

0 ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal reference. Fluorine spectra were referenced externally. Chemical shifts are reported in ppm and coupling constants are in hertz. Fluorine spectra were referenced externally. Multiplicities in fluorine spectra are quantified as "J", a pseudo coupling constant. Chemical shifts are reported in ppm and coupling constants are in hertz. All spectra were acquired at ~22°C unless otherwise noted.

Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratory or by Microlytics (South Deerfield, MA), E + R Microanalytical Laboratory, Inc. (Corona, NY), or Schwarzkopf Microanalytical Laboratory (Woodside, NY).

GPC analyses were performed on a system equipped with two Alltech columns (Jordi-Gell DVB mixed bed - 250 mm x 10 mm (i.d.)). The solvent was supplied at a flow rate of 1.0 mL/min with a Knauer HPLC pump 64. HPLC grade CH₂Cl₂ was continuously dried and distilled from CaH₂. A Wyatt Technology mini Dawn light scattering detector coupled to a Knauer differential-refractometer was employed. The differential refractive index increment, dn/dc, was determined assuming that all polymer that was weighed for the run (usually ~5 mg to ± 0.1 mg) eluted from the column. In order to minimize polymer weighing error the average value for dn/dc (0.049 mL/g) from 18 runs (0.045 to 0.053 mL/g) was employed and the molecular weights recalculated.

[NON]Hf(NMe₂)₂ (1). [NON]H₂ (22.867 g, 0.070 mol) and Hf(NMe₂)₄ (25.000 g, 0.070 mol) were dissolved in 30 mL toluene, then slowly heated. Rapid gas evolution was observed whereupon the microcrystalline product precipitated from solution. The resulting mixture was kept at 100 - 105°C for 16 hours, cooled to 22°C, after which volatile components were removed *in vacuo*. The white microcrystalline solid was slurried in 40 mL pentane, collected on a frit, washed with several portions of pentane, and dried *in vacuo*; yield 33.90 g (82%): ¹H NMR (C₆D₆) δ 7.06 (m, 2, Ar), 6.97 (m, 2, Ar), 6.90 (m, 2, Ar), 6.56 (m, 2, Ar), 3.01 (s, 12, NMe₂), 1.34 (s, 6, ^tBu); ¹³C{H} NMR (C₆D₆) δ 147.73, 145.30, 125.79, 123.28, 118.51, 117.91,

57.18 ($C(CD_3)_2CH_3$), 43.33 ($N(CH_3)_2$), 32.23 ($C(CD_3)_2CH_3$), 31.69 (m, $C(CD_3)_2CH_3$). Anal. Calcd for $C_{24}H_{26}N_4D_{12}OHf$: C, 48.93; H, 6.50; N, 9.51. Found: C, 49.08; H, 6.54; N, 9.51.

[NON]HfCl₂ (2). **1** (33.90 g, 57.54 mmol) and TMSCl (25.005 g, 230.16 mmol) were dissolved in 125 mL toluene in a 250 mL round-bottom Shlenk flask. The stirred mixture was heated to 100°C whereupon all solids dissolved. After 16 hours, the solution was cooled to 22°C and volatile components were removed *in vacuo*. The pale yellow solid was slurried in 100 mL pentane, collected by filtration, washed with 2 x 30 mL pentane, and dried *in vacuo*; yield 31.445 g (96%). Analytically pure samples were recrystallized from Et₂O at -40°C: ¹H NMR (C_6D_6) δ 6.80 (m, 6, Ar), 6.53 (m, 2, Ar), 1.31 (s, 6, ^tBu); ¹³C{H} NMR (C_6D_6) δ 146.89 (b), 140.71, 127.58 (b), 123.31 (b), 121.74, 118.81 (b), 57.79 ($C(CD_3)_2CH_3$), 31.01 ($C(CD_3)_2CH_3$), 30.46 (m, $C(CD_3)_2CH_3$). Anal. Calcd for $C_{20}H_{14}N_2Cl_2D_{12}HfO$: C, 42.00; H, 4.58; N, 4.90; Cl, 12.40. Found: C, 42.16; H, 4.60; N, 4.86; Cl, 12.81.

[NON]HfMe₂ (3a). A stirred pale yellow solution of **2** (10.413 g, 18.21 mmol) in 100 mL Et₂O at -40°C was treated with MeMgI (38.24 mmol, 3.0 M in Et₂O) whereupon MgClI precipitated immediately. The mixture was allowed to warm to 25°C over 1 hour after which 1,4-dioxane (ca. 5 mL) was added and the mixture was stirred for an additional 50 minutes. The mixture was filtered through Celite and the filtrate was stripped to dryness. The crude material was crystallized from Et₂O at -40°C as colorless prisms which were dried *in vacuo*; yield 7.405 g (77%): ¹H NMR (C_6D_6) δ 6.94 - 6.83 (m, 6, Ar), 6.54 (m, 2, Ar), 1.36 (s, 6, ^tBu), 0.65 (s, 6, Me); ¹³C{H} NMR (C_6D_6) δ 126.66, 123.15, 119.93, 119.15, 57.01. Anal. Calcd for $C_{22}H_{20}N_2D_{12}HfO$: C, 49.76; H, 6.07 N, 5.27. Found: C, 49.62/49.66; H, 5.97/5.90; N, 5.18/5.21.

[NON]Hf(¹³CH₃)₂ (¹³C-3a). This complex was prepared in an analogous manner to **3a** from **2** (1.430 g, 2.50 mmol) and ¹³CH₃MgI (5.00 mmol, 1.54 M in Et₂O; prepared from equimolar amounts of ¹³CH₃I and Mg in Et₂O) in 17 mL Et₂O at -40°C; yield 670 mg (50%). ¹H NMR (C_6D_6) δ 6.94 - 6.83 (m, 6, Ar), 6.54 (m, 2, Ar), 1.36 (s, 6, ^tBu), 0.65 (d, 6, ¹J_{CH} = 111.6, Me).

[NON]HfEt₂ (3b). EtMgBr (7.280 mmol, 3.0M in Et₂O) was added dropwise to a stirred pale yellow suspension of **2** (2.000 g, 3.467 mmol) in 60 mL Et₂O at -40°C whereupon MgBrCl precipitated gradually. The mixture was allowed to warm to 25°C over 2 hours after which 1,4-dioxane (ca. 2 mL) was added and the resulting mixture was stirred for an additional 10 minutes, filtered through Celite, and the filtrate stripped to dryness. The residue was dissolved in Et₂O (7 mL) and stored at -40°C. Colorless crystals were separated from the mother liquor, washed quickly with pentane, and dried *in vacuo*; yield 1.535 g (79%): ¹H NMR (C₆D₆) δ 7.01 - 6.80 (m, 6), 6.55 (m, 2), 1.78 (t, 6, CH₂CH₃), 1.36 (s, 6, ^tBu), 0.97 (q, 4, CH₂CH₃); ¹³C{H} NMR (C₆D₆) δ 148.08, 142.82, 126.59, 123.43, 120.02, 119.30, 70.26 (CH₂CH₃), 56.92, 31.47, 30.02, 14.14 (CH₂CH₃). Anal. Calcd for C₂₄H₂₄N₂D₁₂HfO: C, 51.56; H, 8.65 N, 5.01. Found: C, 51.72; H, 6.74; N, 5.35.

[NON]Hf^{*i*}Bu₂ (3c). A stirred pale yellow suspension of **2** (3.000 g, 5.200 mmol) in 50 mL Et₂O at -40°C was treated with ^{*i*}BuMgCl (10.400 mmol, 2.0 M in Et₂O) whereupon MgCl₂ precipitated gradually. The mixture was allowed to warm to 25°C over 2 hours after which 1,4-dioxane (ca. 3 mL) was added and the mixture was stirred for an additional 30 minutes, filtered through Celite, and the filtrate was stripped to dryness. The crude product was dissolved in pentane (30 mL), filtered, concentrated and stored at -40°C. Large colorless prisms were separated from the mother liquor and dried *in vacuo*; yield 2.493 g (78%): ¹H NMR (C₆D₆) δ 7.02 - 6.85 (m, 6, Ar), 6.56 (m, 2, Ar), 2.43 (m, 2, CH₂CHC(CH₃)₂), 1.37 (s, 6, ^tBu), 1.16 (d, 12, CH₂CHC(CH₃)₂), 1.02 (d, 4, CH₂CHC(CH₃)₂, J_{HH} = 6.9); ¹³C{H} NMR (C₆D₆) δ 148.29, 142.77, 126.64, 123.73, 120.18, 119.48, 92.22, 31.57, 31.35, 30.81 (m, CD₃), 29.84. Anal. Calcd for C₂₈H₃₂N₂D₁₂HfO: C, 54.66; H, 7.21 N, 4.55. Found: C, 54.85; H, 7.39; N, 4.48.

[NON]Hf(Cl)Np (3d). A stirred suspension of **2** (3.282 g, 5.690 mmol) in 50 mL Et₂O at -40°C was treated dropwise with NpMgCl (5.690 mmol, 3.16 M in Et₂O) and was allowed to warm to room temperature over 2 hours during which a white precipitate gradually formed. 1,4-dioxane (ca. 3 mL) was added and the mixture was stirred for another 15 minutes and then filtered through Celite. The filtrate was stripped to dryness, dissolved in Et₂O/pentane, and filtered again.

The filtrate was stored at -40°C . Colorless crystals of the product were collected, washed with pentane, and dried *in vacuo*; yield 3.002 g (87%): ^1H NMR (C_6D_6) δ 6.90 (m, 4), 6.81 (m, 2), 6.51 (m, 2), 1.38 (m, 14, ^tBu), 1.34 (s, 2, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 1.10 (s, 9, $\text{CH}_2\text{C}(\text{CH}_3)_3$); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ 146.31, 141.90, 127.42, 123.11, 120.01, 118.54, 92.13 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 57.10 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 56.95 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 35.28 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 31.41 (s, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 30.88 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$). Anal. Calcd. for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{ClD}_{12}\text{HfO}$: C, 49.42; H, 6.14; N, 4.61. Found: C, 49.28; H, 6.25; N, 4.51.

[NON]Hf(Cl)Np' (3e). A stirred suspension of **2** (3.000g, 5.200 mmol) in 50 mL Et_2O at -40°C was treated dropwise with NpMgCl (5.72, 1.3 M in Et_2O) and allowed to stir for 16 hours. 1,4-dioxane (2 mL) was added and the mixture was stirred for an additional 15 minutes, filtered through Celite, and then stripped to a white solid which was pure **3e** by ^1H NMR. Analytically pure samples were obtained as colorless crystals from pentane at -40°C ; yield 2.678 g (78%): ^1H NMR (C_6D_6) δ 7.32 (m, 2), 7.22 (m, 2), 7.09 (m, 1), 6.88 (m, 6), 6.52 (m, 2), 1.70 (s, 2, $\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 1.47 (s, 6, $\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 1.31 (s, 6, ^tBu); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ 154.44, 146.34, 141.81, 128.39, 127.03, 125.77, 125.22, 122.79, 119.74, 118.27, 91.47 ($\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 56.63 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 41.01 ($\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 34.18 ($\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 31.06 ($\text{C}(\text{CD}_3)_2\text{CH}_3$), 30.54 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$). Anal. Calcd. for $\text{C}_{29}\text{H}_{27}\text{N}_2\text{ClD}_{12}\text{HfO}$: C, 52.96; H, 5.98; N, 4.26. Found: C, 53.63; H, 6.28; N, 4.35.

[NON]Hf(Me)Np (3f). A stirred solution of **3d** (1.354 g, 2.228 mmol) in 15 mL Et_2O at -40°C was treated dropwise with MeMgI (2.340 mmol, 3.0 M in Et_2O) and allowed to stir at room temperature for 16 hours. 1,4-dioxane (1 mL) was added and the mixture was stirred for an additional 30 minutes, filtered through Celite, and then stripped to dryness. The crude product was taken up in pentane, filtered again through Celite, and crystallized -40°C as small white crystals; yield 949 mg (73 %): ^1H NMR (C_6D_6) δ 6.95 (m, 4), 6.84 (m, 2), 6.54 (m, 2), 1.38 (s, 6, ^tBu), 1.24 (s, 2, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 1.06 (s, 9, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 0.82 (s, 3, HfCH_3); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ 147.47, 142.81, 126.71, 123.29, 119.78, 119.26, 95.12 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 62.68

(HfMe), 56.95 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 56.60 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 35.65 ($\text{CH}_2\text{C}(\text{CH}_3)_3$), 31.43 ($\text{C}(\text{CD}_3)_2\text{CH}_3$), 31.18 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$).

[NON]Hf(Me)Np' (3g). A stirred solution of **3e** (2.365 g, 3.596 mmol) in 50 mL Et_2O at -40°C was treated dropwise with MeMgI (4.185 mmol, 3.0 M in Et_2O) and allowed to stir at room temperature for 16 hours. 1,4-dioxane (2 mL) was added and the mixture was stirred for an additional 30 minutes, filtered through Celite, and then stripped to dryness. The crude product was crystallized from Et_2O at -40°C as a white microcrystalline solid; yield 1.442 mg (62 %): ^1H NMR (C_6D_6) δ 7.41 (m, 2), 7.25 (t, 2), 7.10 (t, 1) 6.95 (m, 4), 6.86 (d, 2), 6.55 (m, 2), 1.55 (s, 2, $\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 1.37 (s, 6, $\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 1.31 (s, 6, ^tBu), 0.41 (s, 3, HfCH₃); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ 154.70, 147.88, 143.11, 128.81, 126.62, 126.02, 125.62, 123.16, 119.82, 119.30, 93.87 ($\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 64.01 (HfCH₃), 56.57 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 41.47 ($\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 35.10 ($\text{CH}_2(\text{CH}_3)_2\text{Ph}$), 31.32 ($\text{C}(\text{CD}_3)_2\text{CH}_3$), 3.077 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$).

[NON]HfBz₂ (3h). To a stirred solution of **2** (2.000 g, 3.50 mmol) in 20 mL Et_2O /20 mL THF was added solid BzK (957 mg, 7.35 mmol) in one portion whereupon KCl precipitated immediately. The mixture was stirred for 10 minutes, then stripped to a sticky solid which was dissolved in Et_2O , filtered through Celite, concentrated to 15 mL, and stored at -40°C . The product was collected as colorless crystals which were dried *in vacuo*; yield 1.562 g (61%): ^1H NMR (C_6D_6) δ 7.18 (m, 4), 6.91 - 6.78 (m, 12), 6.53 (m, 2), 2.40 (s, 4, CH_2Ph), 1.15 (s, 6, ^tBu); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ 148.01, 147.81, 128.81, 127.93, 126.88, 123.73, 122.46, 120.82, 119.55, 83.39, 30.86, 30.70 (m). Anal. Calcd. for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{D}_{12}\text{HfO}$: C, 59.77; H, 5.90; N, 4.10. Found: C, 59.79; H, 5.85; N, 4.17.

{[NON]HfCH₃(PhNMe₂)}[B(C₆F₅)₄] (4). Solid **3a** (15 mg, 0.028 mmol) and [PhNMe₂(H)][B(C₆F₅)₄] (22 mg, 0.028 mmol) were gradually dissolved in 0.7 mL $\text{C}_6\text{D}_5\text{Br}$ by stirring for 30 minutes to give a pale lime solution: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 6.8 - 7.3 (m, 14, Ar), 2.79 (s, 6, Me₂NPh), 1.15 (s, 6, ^tBu), 0.89 (s, 3, HfCH₃).

{[NON]Hf¹³CH₃(PhNMe₂)}[B(C₆F₅)₄] (¹³C-4) was prepared in analogous manner from **¹³C-3a** (15 mg, 0.028 mmol) and [PhNMe₂(H)][B(C₆F₅)₄] (22 mg, 0.028 mmol):

^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 6.8 - 7.3 (m, 14, Ar), 2.79 (s, 6, Me_2NPh), 1.15 (s, 6, ^tBu), 0.89 (d, 3, HfCH_3 , $J_{\text{CH}} = 111$ Hz); $^{13}\text{C}\{\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 64.91 (HfCH_3).

[[NON]HfCH₃(2,4-lutidine)][B(C₆F₅)₄] (5a). Solid **3a** (15 mg, 0.028 mmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (26 mg, 0.028 mmol) were dissolved in 0.7 mL $\text{C}_6\text{D}_5\text{Br}$ in an NMR tube at 25°C to give an orange solution. Then 2,4-lutidine (3 mg, 0.028 mmol) was syringed into the NMR tube whereupon the solution rapidly turned yellow: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 8.39 (br, 1, 2,4-lut), 7.29 - 6.66 (m, Ar), 2.21 (br, 3, Me_{ortho}), 2.03 (s, 3, Ph_3CCH_3), 1.96 (s, 3, Me_{para}), 1.14 (s, 6, ^tBu), 0.63 (s, 3, HfMe); $^{13}\text{C}\{\text{H}\}$ NMR δ 62.28 ($\text{Hf}^{13}\text{CH}_3$), 30.20 ($\text{Ph}_3^{13}\text{CH}_3$).

[[NON]HfCH₃(2,5-lutidine)][B(C₆F₅)₄] (5b). **5b** was prepared in a manner similar to that for **5a** from **3a** (15 mg, 0.028 mmol), $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (26 mg, 0.028 mmol), and 2,5-lutidine (3 mg, 0.028 mmol): ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 8.35 (br, 1), 7.28 - 6.8 (m), 2.22 (br, 3, Me_{ortho}), 2.04 (s, 3, Ph_3CCH_3), 2.00 (s, 3, Me_{meta}), 1.15 (s, 6, ^tBu), 0.64 (s, 3, HfCH_3); $^{13}\text{C}\{\text{H}\}$ NMR δ 62.08 ($\text{Hf}^{13}\text{CH}_3$), 30.20 ($\text{Ph}_3^{13}\text{CH}_3$).

[[NON]HfCH₃(2,6-lutidine)][B(C₆F₅)₄] (5c). **5c** was prepared in a manner similar to that for **5a** from **3a** (15 mg, 0.028 mmol), $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (26 mg, 0.028 mmol), and 2,6-lutidine (3 mg, 0.028 mmol): ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 7.15 - 6.5 (m, Ar), 2.39 (s, 6, 2,6-lut), 1.23 (s, 6, ^tBu), 0.73 (s, 3, HfMe); $^{13}\text{C}\{\text{H}\}$ NMR δ 65.96 ($\text{Hf}^{13}\text{CH}_3$), 30.20 ($\text{Ph}_3^{13}\text{CH}_3$).

[[NON]Hf^{*i*}Bu(2,6-lutidine)][B(C₆F₅)₄] (6). Solid **3c** (15 mg, 0.025 mmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (23 mg, 0.025 mmol) were dissolved in 0.7 mL $\text{C}_6\text{D}_5\text{Br}$ at 25°C followed by treatment with 2,4-lutidine (3 mg, 0.025 mmol) whereupon the orange solution turned yellow: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 8.50 (br, 1, 2,4-lut), 7.18 - 6.82 (m, Ar), 5.44 (s, 1, Ph_3CH), 4.68 (m, $\text{CH}_2\text{C}(\text{CH}_3)_2$), 2.42 (br, 4, $\text{CH}_2\text{CH}(\text{CH}_3)_2$ and Me_{ortho}), 2.03 (s, 3, Me_{para}), 1.61 (m, $\text{CH}_2\text{C}(\text{CH}_3)_2$), 1.02 (br, 6, ^tBu), 0.94 (d, 2, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 0.73 (d, 6, $\text{CH}_2\text{CH}(\text{CH}_3)_2$).

[[NON]HfCH₃]₂(μ -CH₃)[B(C₆F₅)₄] (7). Solid **3a** (30 mg, 0.056 mmol) and $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ (26 mg, 0.028 mmol) were dissolved in 0.8 mL $\text{C}_6\text{D}_5\text{Br}$ at 25°C to give a pale yellow solution: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 7.68 - 6.75 (m, Ar), 2.03 (s, 3, Ph_3CMe), 1.19 (s, 6, ^tBu), 0.68 (v br, 9, HfCH_3).

$\{[\text{NON}]\text{Hf}^{13}\text{CH}_3\}_2(\mu\text{-}^{13}\text{CH}_3)[\text{B}(\text{C}_6\text{F}_5)_4]$ (^{13}C -7) was prepared in an analogous manner from ^{13}C -3a (40 mg, 0.075 mmol) and $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ (35 mg, 0.038 mmol) in 0.8 mL $\text{C}_6\text{D}_5\text{Br}$: $^{13}\text{C}\{\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$, -35°C) δ 62.66 (br, $[\text{NON}]\text{HfCH}_3^+$), 55.47 (br, terminal CH_3), 48.07 (br, bridging CH_3), 30.02 ($\text{Ph}_3\text{C}^{13}\text{CH}_3$).

$\{[\text{NON}]\text{HfMe}(\text{THF})_2\}\text{BPh}_4$ (8a). A light blue mixture of 3a (700 mg, 1.318 mmol), $[\text{Cp}'_2\text{Fe}]\text{BPh}_4$ (703 mg, 1.318 mmol), and THF (209 mg, 2.900 mmol) in 15 mL toluene was stirred for 16 hours. A pale green solid was collected on a fine frit and was washed with 2 x 3 mL toluene followed by 2 x 1 mL pentane. The crude product was dissolved in THF and a small amount of white solid was filtered off. The product was crystallized from THF/pentane at -40°C as an off-white microcrystalline solid which was washed with pentane and dried *in vacuo*; yield 805 mg, 62%: ^1H NMR (CD_2Cl_2) δ 7.40 - 6.70 (m, 8), 7.31 (br, 8, *o*-H), 7.02 (m, 8, *m*-H), 6.89 (m, 4, *p*-H), 4.14/3.80 (bs, 8, THF), 1.76 (m, 8, THF), 1.61 (m, $^t\text{Bu}_{\text{mer}}$), 1.40 (m, $^t\text{Bu}_{\text{fac}}$), 0.72 (s, Me_{mer}), 0.55 (s, Me_{fac}); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 164.46 (q, C_{ipso} , $J_{\text{CB}} = 49$ Hz), 147.51 (b), 143.61, 142.72, 136.36 (C_{meta}), 127.59 (b), 126.33, 126.07 (C_{ortho}), 122.18 (C_{para}), 121.68 (b), 120.89, 120.12, 117.97, 113.85, 76.67 (THF), 62.14 (Me_{fac}), 60.57 (Me_{mer}), 57.43 (br, $\text{C}(\text{CD}_3)_2\text{CH}_3$, *fac*), 56.45 (br, $\text{C}(\text{CD}_3)_2\text{CH}_3$, *mer*), 30.77 (m, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 25.99/25.81 (THF). Anal. Calcd for $\text{C}_{53}\text{H}_{53}\text{N}_2\text{BD}_{12}\text{HfO}_3$: C, 64.86; H, 6.68; N, 2.86. Found: C, 64.88/64.91; H, 6.80/6.91; N, 2.82/2.81.

$\{[\text{NON}]\text{HfMe}(\text{DME})\}\text{BPh}_4$ (8b). A light blue mixture of 3a (1.500 g, 2.824 mmol), $[\text{Cp}'_2\text{Fe}]\text{BPh}_4$ (1.506 g, 2.824 mmol), and DME (305 mg, 3.389 mmol) in 50 mL toluene was stirred for 18 hours. An off-white solid was collected on a fine frit and was washed with 3 x 5 mL toluene followed by 3 x 2 mL pentane. The crude product was dissolved in 15 mL CH_2Cl_2 and a small amount of white solid was filtered off. The product was crystallized from CH_2Cl_2 at -40°C as a white microcrystalline solid which was washed with pentane and dried *in vacuo*; yield 1.658 g (63%): ^1H NMR (CD_2Cl_2) δ 7.35 (br, 8, *o*-H), 7.24 - 6.80 (m, 20), 3.57 (s, 6), 3.04 (m, 2), 2.70 (m, 2), 1.34 (s, 6), 0.51 (s, 3, Me); $^{13}\text{C}\{\text{H}\}$ NMR (CD_2Cl_2) δ 164.45 (q, C_{ipso} , $J_{\text{CB}} = 49$ Hz), 146.53, 140.70, 136.35 (C_{meta}), 127.83, 126.32 (C_{ortho}), 122.74, 122.45, 121.87 (C_{para}),

119.66, 73.47 (OMe), 67.84 (HfCH₃), 58.54 (CH₂O), 57.67 (m, C(CD₃)₂CH₃), 30.65 (C(CD₃)₂CH₃), 30.02 (m, C(CD₃)₂CH₃). Anal. Calcd for C₄₉H₄₇N₂BD₁₂HfO₃: C, 63.60; H, 6.43; N, 3.02. Found: C, 63.06; H, 6.54; N, 3.00.

[[NON]HfEt(THF)₂]BPh₄ (9a). A blue mixture of [Cp'₂Fe]BPh₄ (954 mg, 1.789 mmol) and **3b** (1.000 g, 1.789 mmol) was stirred in 10 mL toluene/3 mL THF whereupon the color changed rapidly to golden yellow. After 15 minutes, the volatile components were removed *in vacuo* and the resulting oil dissolved in minimum THF and added pentane to give a white precipitate which was filtered and washed with 3 x 5 mL pentane to remove Cp'₂Fe. The light tan solid was dissolved in 1 mL CH₂Cl₂/7 mL THF and crystallized at -40°C as colorless crystals which were washed with pentane and dried *in vacuo*; yield 878 mg (49%): ¹H NMR (CD₂Cl₂) δ 7.31 (br, 8, C_{ortho}), 7.2 - 6.7 (m, 20, Ar), 4.14 and 3.82 (br s, 8, THF), 1.75 (m, 14, THF and ^tBu), 1.66 and 1.38 (m, 2, CH₂CH₃), 1.01 (br, 2, CH₂CH₃). Elemental analyses gave consistently low values for %C and acceptable values for %H and %N.

[[NON]HfEt(DME)]BPh₄ (9b). A blue mixture of [Cp'₂Fe]BPh₄ (1.908 mg, 3.577 mmol), **3b** (2.000 g, 3.577 mmol), and DME (645 mg, 7.154 mmol) was stirred in 50 mL toluene for 16 hours. The crude white solid product was filtered off, washed with 3 x 3 mL toluene followed by 2 x 3 mL pentane, and crystallized from concentrated CH₂Cl₂/DME at -40°C to give an off-white microcrystalline solid; yield 772 mg (23%): ¹H NMR (CD₂Cl₂) δ 7.36 (br, 8, *o*-H), 7.22 (t, 2), 7.03 (m, 10), 6.90 (m, 8), 3.51 (br, 6, MeO), 3.00 (br, 2, CH₂O), 2.66 (br, 2, CH₂O), 1.48 (t, 3), 1.35 (s, 6, ^tBu), 0.92 (q, 2); ¹³C{¹H} NMR (CD₂Cl₂) δ 164.48 (q, C_{ipso}, J_{CB} = 49 Hz), 146.56, 141.29, 136.35 (C_{meta}), 127.54, 126.35 (C_{ortho}), 122.48 (C_{para}), 121.36, 119.45 (b), 73.74 (OMe), 71.88 (HfCH₂CH₃), 67.71 (CH₂O), 57.46 (br, C(CD₃)₂CH₃), 30.47 (m, C(CD₃)₂CH₃), 12.72 (br, HfCH₂CH₃).

[[NON]HfNp][MeB(C₆F₅)₃] (10a). Solid **3f** (20 mg, 0.034 mmol) and B(C₆F₅)₃ (17 mg, 0.034 mmol) were dissolved in 0.8 mL C₆D₅Br to give a pale yellow solution: ¹H NMR (C₆D₅Br) δ 7.07 (m, 2), 6.91 (m, 4), 6.77 (m, 2), 2.81 (br, 3, CH₃B(C₆F₅)₃⁻), 1.22 (s, 2,

$\text{CH}_2\text{C}(\text{CH}_3)_3$), 1.03 (s, 6, ^tBu), 0.70 (s, 9, $\text{CH}_2\text{C}(\text{CH}_3)_3$); ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$) δ -132.66 (m, 6, F_{ortho}), -159.67 (m, 3, F_{para}), -164.39 (m, 6, F_{meta}).

$\{[\text{NON}]\text{Hf}(\text{Np}')\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (10b). Separate suspensions of **3g** (195 mg, 0.301 mmol) and $\text{B}(\text{C}_6\text{F}_5)_3$ (154 mg, 0.301 mmol) in 0.5 mL $\text{C}_6\text{D}_5\text{Br}$ each were combined at -40°C and mixed thoroughly. The resulting bright yellow solution was transferred to an NMR tube which was flame-sealed and kept at -196°C until placed into the NMR probe: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 7.64 (br, 2, H_{ortho}), 7.57 (br, 2, H_{meta}), 7.34 (br, 1, H_{para}), 7.10 (t, 4), 6.84 (d, 2), 6.75 (t, 2), 1.21 (s, 2, $\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 1.15 (br, 3, $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$), 1.07 (br, 6, ^tBu), 1.03 (br, 6, $\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$); ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$) δ -132.06 (d, 6, F_{ortho}), -163.82 (t, 3, F_{para}), -166.43 (m, 6, F_{meta}); partial $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{C}_6\text{D}_5\text{Br}$, -30°C) δ 157.19 (C_{ipso}), 148.66 (d, $o\text{-C}_6\text{F}_5$, $^1\text{J}_{\text{CF}} = 240$ Hz), 146.22, 139.03, 138.12, 137.63 (d, $p\text{-C}_6\text{F}_5$, $^1\text{J}_{\text{CF}} = 245$ Hz), 136.52 (dm, $m\text{-C}_6\text{F}_5$, $^1\text{J}_{\text{CF}} = 226$ Hz), 128.12, 120.62, 119.74 ($\text{ipso-C}_6\text{F}_5$), 117.25, 84.33 (br, $\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 54.95 ($\text{C}(\text{CD}_3)_2\text{CH}_3$), 39.31 ($\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 31.95 ($\text{CH}_2\text{C}(\text{CH}_3)_2\text{Ph}$), 27.92 ($\text{C}(\text{CD}_3)_2\text{CH}_3$), 27.36 (br, $\text{C}(\text{CD}_3)_2\text{CH}_3$), 11.94 (br, CH_3B).

$\{[\text{NON}]\text{HfNp}(\text{MeCN})\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (11a). Solid **3f** (20 mg, 0.034 mmol) and $\text{B}(\text{C}_6\text{F}_5)_4$ (17 mg, 0.034 mmol) were dissolved in 0.8 mL $\text{C}_6\text{D}_5\text{Br}$ and stirred for 30 seconds to give a pale yellow solution. MeCN (1.40 mg, 0.034 mmol) was added *via* syringe and the color changed to deep yellow: ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 7.2 - 6.6 (m, 8, Ar), 1.90 (br, 3, CH_3CN), 1.27 (m, 6, ^tBu), 1.07 (br, 5, $\text{CH}_2\text{C}(\text{CH}_3)_3$ and $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$), 0.79 (s, 9, $\text{CH}_2\text{C}(\text{CH}_3)_3$); ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$) δ -132.17 (d, 6, F_{ortho}), -163.84 (m, 3, F_{para}), -166.52 (m, 6, F_{meta}).

$\{[\text{NON}]\text{HfNp}(\text{PhCN})\}[\text{MeB}(\text{C}_6\text{F}_5)_3]$ (11b) was generated in a manner similar to that for **11a** from **3f** (20 mg, 0.034 mmol), $\text{B}(\text{C}_6\text{F}_5)_4$ (17 mg, 0.034 mmol), and PhCN (3.5 mg, 0.034 mmol): ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$) δ 7.59 (d, 2), 7.37 (t, 1), 7.13 (m, 4), 7.06 (d, 2), 6.95 (d, 2), 6.78 (t, 2), 1.31 (m, 6, ^tBu), 1.21 (br, 2, $\text{CH}_2\text{C}(\text{CH}_3)_3$), 1.10 (br, 3, $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$), 0.83 (s, 9, $\text{CH}_2\text{C}(\text{CH}_3)_3$); ^{19}F NMR ($\text{C}_6\text{D}_5\text{Br}$) δ -132.05 (d, 6, F_{ortho}), -164.14 (m, 3, F_{para}), -166.60 (m, 6, F_{meta}).

{[NON]HfNp'(MeCN)[MeB(C₆F₅)₃] (12a)} was generated in a manner similar to that for **11a** from **3g** (20 mg, 0.031 mmol), B(C₆F₅)₄ (16 mg, 0.031 mmol), and MeCN (1.3 mg, 0.031 mmol): ¹H NMR (C₆D₅Br) δ 7.2 - 7.1 (m, 5), 7.0 - 6.9 (m, 6), 6.77 (m, 2), 1.72 (br, 3, CH₃CN), 1.44 (s, 2, CH₂C(CH₃)₂Ph), 1.11 (s, 6, ^tBu), 1.08 (br, 3, CH₃B(C₆F₅)₃⁻), 1.02 (br, 6, CH₂C(CH₃)₂Ph); ¹⁹F NMR (C₆D₅Br) δ -132.16 (d, 6, F_{ortho}), -163.89 (t, 3, F_{para}), -166.53 (m, 6, F_{meta}).

{[NON]HfNp'(PhCN)[MeB(C₆F₅)₃] (12b)} was generated in a manner similar to that for **11a** from **3g** (20 mg, 0.031 mmol), B(C₆F₅)₄ (16 mg, 0.031 mmol), and PhCN (3.2 mg, 0.031 mmol): ¹H NMR (C₆D₅Br) δ 7.50 (d, 2), 7.42 (t, 1), 7.17 (m, 6), 7.05 (m, 4), 6.99 (d, 2), 6.93 (t, 1), 6.81 (t, 2), 1.54 (s, 2, CH₂C(CH₃)₂Ph), 1.17 (s, 6, ^tBu), 1.11 (br, 3, CH₃B(C₆F₅)₃⁻), 1.08 (s, 6, CH₂C(CH₃)₂Ph); ¹⁹F NMR (C₆D₅Br) δ -132.06 (d, 6, F_{ortho}), -164.18 (t, 3, F_{para}), -166.63 (m, 6, F_{meta}).

[PhNMe₂(D)][B(C₆F₅)₄]. A mixture of LiB(C₆F₅)₄ (1.500 g, 1.882 mmol) and [PhNMe₂(D)]Cl (249 mg, 1.568 mmol; prepared from Me₂NPh and DCl in Et₂O) was stirred in 15 mL CH₂Cl₂ for 3 hours. LiCl was removed by filtration and solvent was removed *in vacuo* from the filtrate to leave a white solid which was partially dissolved in 15 mL toluene and stored at -40°C. The product was isolated as fluffy white needles, washed with 2 x 4 mL pentane, and dried at 65°C/60 millitorr overnight; yield 1.150 g (91%): ¹H NMR (CD₂Cl₂) δ 8.70 (br, 1, N-H), 7.64 (m, 3), 7.40 (m, 2), 3.35 (s, 6, Me₂N); ²H NMR (CH₂Cl₂) δ 8.58 (N-D), 7.69 (br, *ortho*-D), 7.43 (br, *para*-D); ¹⁹F NMR (CH₂Cl₂) δ -133.54 (br), -163.70 (t), -167.73 (m). The product contains 50% deuterium incorporation into the aromatic ring and therefore consists of a 1:1 mixture of NH/ND containing species.

{[(^tBuN-*d*₆-*o*-C₆H₄)(*d*₆-^tBuNH-*o*-C₆H₄)O]HfMe₂}[B(C₆F₅)₄] (13a). A solution of **3a** (20 mg, 0.038 mmol) in 0.5 mL C₆D₅Br at -40°C was combined with a suspension of [PhNMe₂(H)][B(C₆F₅)₄] (30 mg, 0.038 mmol) in 0.5 mL C₆D₅Br at 22°C whereupon the solids dissolved and the color rapidly turned pale green. The solution was kept at -40°C for 20 minutes, then quickly transferred to an NMR tube which was flame-sealed and kept at -196°C until

placed into an NMR probe pre-cooled to -35°C : ^1H NMR ($\text{C}_6\text{D}_5\text{Br}$, -35°C) δ 7.2 6.0 (m, 13), 4.33 (s, 1, NH), 2.53 (s, 6, Me_2NPh), 1.06 (s, 3, ^tBu), 1.03 (s, 3, ^tBu), 0.55 (s, 3, HfMe), 0.53 (s, 3, HfMe). The mixture also contained resonances for **4** and CH_4 (δ 0.16).

$\{[(^t\text{BuN-}d_6\text{-}o\text{-}\text{C}_6\text{H}_4)(d_6\text{-}^t\text{BuNH-}o\text{-}\text{C}_6\text{H}_4)\text{O}]\text{HfEt}_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**13b**). **3b** (15 mg, 0.027 mmol) and $[\text{PhNMe}_2(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ (21 mg, 0.027 mmol) were rapidly dissolved in 0.8 mL CD_2Cl_2 . The solution was transferred rapidly to an NMR tube which was flame-sealed and then kept at 0°C until placed into an NMR probe at 22°C : ^1H NMR (CD_2Cl_2) δ 7.60 - 6.60 (m, 14), 4.64 (s, 1, NH), 2.93 (s, 6, Me_2NPh), 1.78 (t, 3, CH_2CH_3), 1.61 (s, 3, ^tBu), 1.20 (m, 2, CH_2CH_3), 1.19 (t, 3, CH_2CH_3) 1.08 (s, 3, ^tBu), 0.87 (m, 2, CH_2CH_3). The solution also contained C_2H_6 (δ 0.85) and resonances for $[\text{NON}]\text{HfCl}(\text{Et})(\text{Me}_2\text{NPh})$: δ 7.65 (m, 3), 7.51 (m, 2), 7.17 (m, 6), 6.80 (m, 2), 3.66 (s, 6, Me_2NPh), 1.38 (s, 6, ^tBu), 1.28 (t, 3, CH_2CH_3), 0.69 (q, 2, CH_2CH_3).

$\{[(^t\text{BuN-}d_6\text{-}o\text{-}\text{C}_6\text{H}_4)(d_6\text{-}^t\text{BuNH-}o\text{-}\text{C}_6\text{H}_4)\text{O}]\text{Hf}^i\text{Bu}_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (**13c**). **3c** (20 mg, 0.033 mmol) and $[\text{PhNMe}_2(\text{H})][\text{B}(\text{C}_6\text{F}_5)_4]$ (26 mg, 0.033 mmol) were rapidly dissolved in 0.8 mL CD_2Cl_2 . The solution was transferred rapidly to an NMR tube which was flame-sealed and then kept at 0°C until placed into an NMR probe at 22°C : ^1H NMR (CD_2Cl_2) δ 7.60 - 7.07 (m, 10, Ar), 6.80 (m, 3, Ar), 4.49(s, 1, NH), 2.93 (s, 6, Me_2NPh), 2.41 (m, 1, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.62 (s, 3, ^tBu), 1.52 (m, 1, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.22 (m, 2, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.21 (s, 3, ^tBu), 1.10 (m, 2, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 1.02 (d, 3), 0.97 (d, 3), 0.81 (d, 3), 0.66 (d, 3). The solution also contained isobutane (δ 0.70 (d, 9), the methyne proton was not located) and a small amount of isobutylene (δ 4.61 (m) and 1.72 (m)). Resonances for $[\text{NON}]\text{HfCl}(^i\text{Bu})(\text{Me}_2\text{NPh})$: δ 7.65 (m, 3), 7.51 (m, 2), 7.17 (m, 6), 6.80 (m, 2), 3.66 (s, 6, Me_2NPh), 1.75 (m, $\text{CH}_2\text{CHC}(\text{CH}_3)_2$), 1.38 (s, 6, ^tBu), 0.89 (d, 6, $\text{CH}_2\text{CHC}(\text{CH}_3)_2$), 0.80 (d, 2, $\text{CH}_2\text{CHC}(\text{CH}_3)_2$).

Polymerization of 1-Hexene using $\{[\text{NON}]\text{HfMe}(\text{PhNMe}_2)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (4**).**

In a typical experiment varying amounts of 1-hexene (0.3-3.0 mL) were added to a solution of **4** (prepared from ca. 75 μmol of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ and ca. 1 equiv of $[\text{NON}]\text{HfMe}_2$ (**3a**) in chlorobenzene at 22°C). The reaction mixture was stirred for 1-6 hours and quenched by addition

of HCl in diethylether (3 mL, 1.0 M). Most solvent was removed at 15 Torr (water aspirator) at 60°C. The viscous oil was dried at 60 mTorr at 80°C for 20 hours. The yields were essentially quantitative (97-100%). The molecular weights and polydispersities were measured by light scattering.

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APPENDIX

Synthesis of Ti Complexes That Contain
the $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}]^{3-}$ Ligand

Most of the material in this appendix has appeared in the literature:

Schrock, R. R.; Cummins, C. C.; Wilhelm, T.; Lin, S.; Reid, S. M.; Kol, M.; Davis, W. M.
Organometallics **1996**, *15*, 1470.

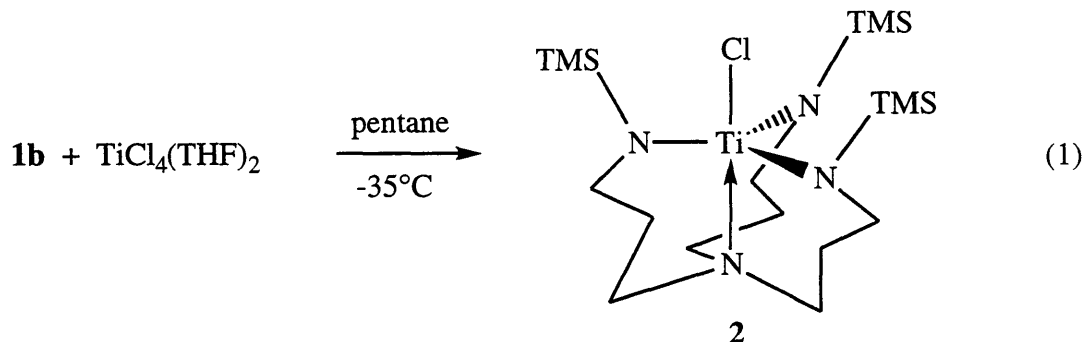
INTRODUCTION

A transition metal that is useful in initial studies involving multidentate amido ligands is titanium since the resulting complexes are, in general, readily prepared and diamagnetic. For example, Cummins *et al.* reported the synthesis of $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{TiCl}$ and some of its alkyl derivatives,¹ as well as trigonal monopyramidal $[(\text{Me}_2(\text{tBu})\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{Ti}$,² while others have reported ethyl- and isopropyl-substituted titanium derivatives.³ A potentially useful variation of ligands of the type $[(\text{RNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ($\text{R} = \text{alkyl, trialkylsilyl, C}_6\text{F}_5$)⁴ would be a trisubstituted tris(3-aminopropyl)amine ligand.^{5,6} A ligand that contains one more methylene unit per backbone arm might allow transition metals (especially larger second or third row metals, actinides, or early lanthanides) to reside deeper inside the steric “pocket”, quite possibly in the plane defined by the three equatorial nitrogens, although the apical nitrogen donor might also be more prone to dissociation than in analogous $[(\text{RNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ derivatives. For example, the X-ray crystal structures of several uranium complexes of $[(\text{Me}_2(\text{tBu})\text{SiNCH}_2\text{CH}_2)_3\text{N}]^{3-}$ show that the uranium atoms are displaced about 0.8 Å above this plane.⁷⁻⁹ This appendix therefore describes the synthesis of a new triamidoamine ligand and several titanium derivatives.

RESULTS AND DISCUSSION

Deprotonation of tris(3-aminopropyl)amine with 3.3 equivalents BuLi in THF at -70°C followed by quenching with 3.3 equivalents TMSCl gave $(\text{Me}_3\text{SiNHCH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ (**1a**) which was deprotonated once more with 3.3 equivalents BuLi in pentane at -70°C to give microcrystalline $\text{Li}_3[(\text{Me}_3\text{SiNCH}_2\text{CH}_2\text{CH}_2)_3\text{N}]$ (**1b**; $\text{Li}_3[\text{N}_3\text{N}']$) in 75% yield. Addition of $\text{Li}_3[\text{N}_3\text{N}']$ to a suspension of $\text{TiCl}_4(\text{THF})_2$ in pentane at -35°C gave amber $[\text{N}_3\text{N}']\text{TiCl}$ (**2**) in high yield (equation 1). Isolated yields were limited to ~50% as a consequence of the high solubility of **2** in hydrocarbon solvents. The ^1H NMR spectrum of **2** in C_6D_6 shows the expected TMS resonance at 0.52 ppm, but *six* complex $[\text{N}_3\text{N}']^{3-}$ methylene resonances in the 1.25 - 4.30 ppm range. Heating a sample of **2** in toluene- d_8 to 90°C did not induce any change in line shapes. Carbon NMR spectra, however, confirmed the presence of three unique methylene carbons, each of which

has two diastereotopic protons bonded to it. These data suggest that the ligand framework is unexpectedly "rigid" on the NMR time scale in **2**; that is, the methylene protons on a given carbon



atom cannot interconvert by "flipping" of a rigid six-member TiN_2C_3 ring. For comparison, the ligand methylene protons in $[\text{N}_3\text{N}_\text{F}]\text{Re}(\text{propylene})$ are equivalent at room temperature but are rendered diastereotopic at -90°C (see Figure 1.3 in Chapter I).

The structure of **2** was determined by X-ray crystallography. Two ORTEP views of the structure are shown in Figure 1. Selected bond distances and angles are presented in Table 1 while experimental details are listed in Table 2. The Ti atom is nearly coplanar with the equatorial nitrogens (average $\text{Ti-N}_{\text{eq}} = 1.90 \text{ \AA}$) and the Ti-N_{ax} distance ($\text{Ti-N}_{\text{ax}} = 2.360(6) \text{ \AA}$) is somewhat longer compared to the V-N_{ax} bond distance in $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{VCl}$ ($\text{V-N}_{\text{ax}} = 2.238 \text{ \AA}$).² The Ti-Cl bond distance ($2.353(2) \text{ \AA}$) is longer than that reported for $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{TiCl}$ ($2.259(6) \text{ \AA}$).¹⁰ An important structural feature that must be a consequence of the longer "arms" in **2** is the considerable puckering and locking of each six-membered TiN_2C_3 ring. The resulting "propeller" orientation of the trimethylsilyl groups can be measured by the dihedral angle $\text{N}_{\text{ax}}\text{-Ti-N}_{\text{eq}}\text{-Si}$. In **2** the average dihedral angle is 138° , a value that should be compared to analogous dihedral angles in $[(\text{Me}_2(\text{tBu})\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{V}$ (avg. 42°), $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{V=NH}$ (avg. 3°), and $[(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}]\text{VCl}$ (avg. 33°).¹¹ The silyl groups could be "tilted" to a greater degree in **2** as a consequence of the chair form of the TiN_2C_3 ring. The $\text{Ti-N}_{\text{eq}}\text{-Si}$ angle in **2** (120°) is slightly less than those in the vanadium complexes mentioned above (ca. 126°). The "pocket angle," (θ_{p}), defined by the angle between the axial ligand, metal, and methylsilyl

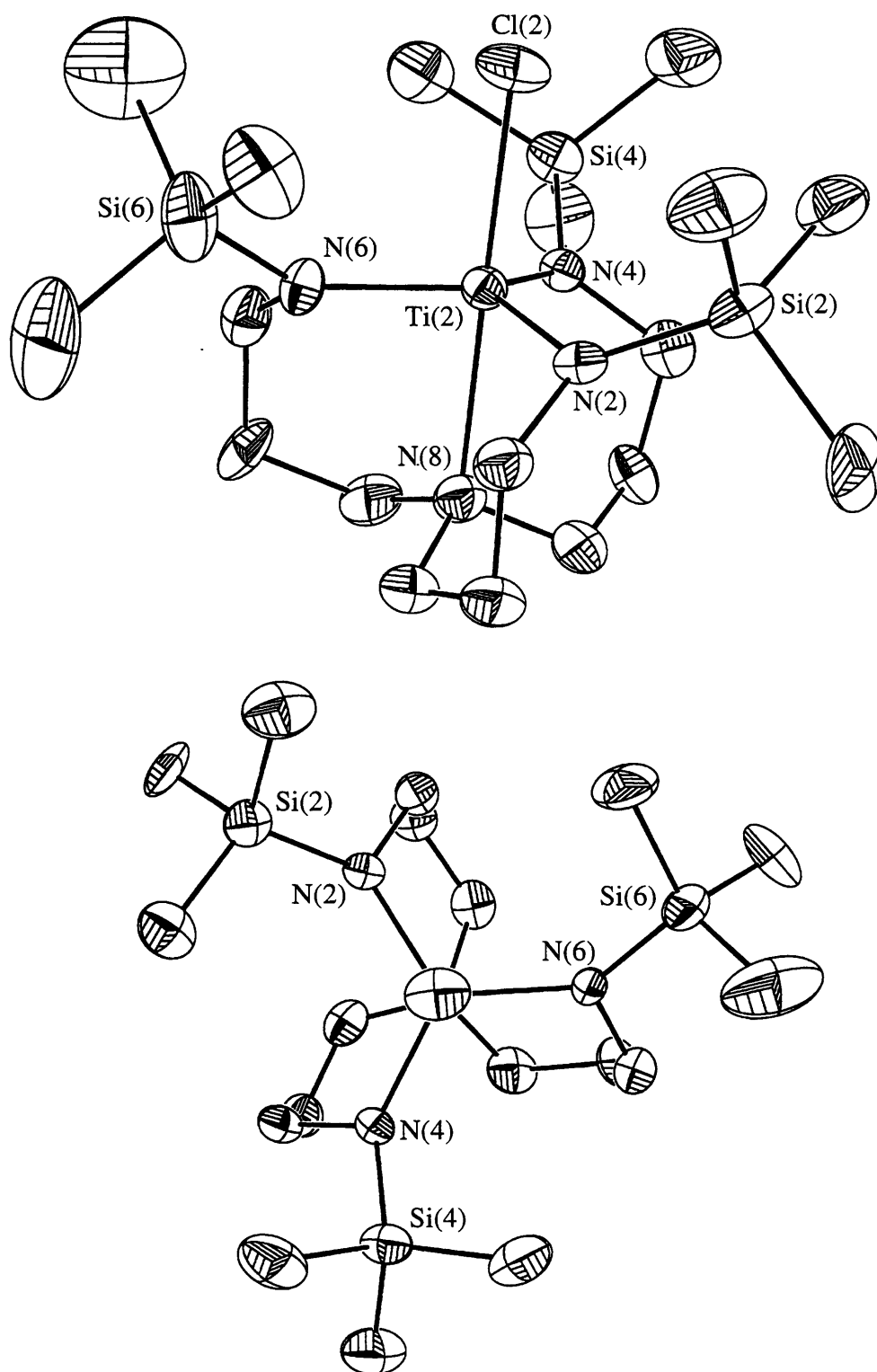


Figure 1. Side and Top Views of the Structure of $[\text{N}_3\text{N}']\text{TiCl}$ (2; 25% thermal ellipsoids).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms in [N₃N']TiCl (**2**).

Bond Lengths			
Ti(2)-N(2)	1.910 (5)	Ti(2)-Cl(2)	2.352 (2)
Ti(2)-N(4)	1.905 (6)	Ti(2)-N(8)	2.360 (6)
Ti(2)-N(6)	1.897 (5)		
Bond Angles			
Ti(2)-N(2)-Si(2)	129.7 (3)	N(2)-Ti(2)-N(6)	117.2 (2)
Ti(2)-N(4)-Si(4)	130.0 (3)	N(4)-Ti(2)-N(6)	119.6 (4)
Ti(2)-N(6)-Si(6)	129.7 (4)	N(8)-Ti(2)-N(2)-Si(2)	136.8 (4)
N(8)-Ti(2)-Cl(2)	179.0 (2)	N(8)-Ti(2)-N(4)-Si(4)	142.4 (4)
N(2)-Ti(2)-N(4)	120.6 (4)	N(8)-Ti(2)-N(6)-Si(6)	137.5 (4)

Table 2. Crystallographic data, collection parameters, and refinement parameters for [N₃N']TiCl (**2**).

Empirical Formula	C ₁₈ H ₄₅ N ₄ ClSi ₃ Ti
Formula Weight	485.19
Diffractometer	Enraf-Nonius CAD-4
Crystal Dimensions (mm)	0.28 x 0.32 x 0.18
Crystal System	monoclinic
a (Å)	17.900 (2)
b (Å)	17.134 (2)
c (Å)	20.116 (3)
α (deg)	90.00
β (deg)	113.60 (2)
γ (deg)	90.00
V (Å ³)	5653 (3)
Space Group	P2 ₁ /n
Z	8
D _{calc} (Mg/m ³)	1.140
F ₀₀₀	2096
λ, radiation	0.71069, MoK _α
Scan Type	ω – 2θ
Temperature (K)	25
2θ _{max} (deg)	44.9
Independent Reflections	7685
Absorption Correction	Transmission factors: 0.74 - 1.11
Refinement Method	Full-matrix least squares
Data/Restraints/Parameters	3619/0/488
Final R Indices [I>2σ(I)]	R1 = 0.052, wR2 = 0.051
GoF	1.40
Extinction Coefficient	Secondary: 0.53392 x 10 ⁻⁷
Largest Diff. Peak and Hole (eÅ ⁻³)	0.22 and -0.23

carbon atom at the point of closest approach to the axial ligand, is another convenient parameter by which to assess the steric encumbrance about the axial coordination site (Figure 2).¹² Values of θ_P

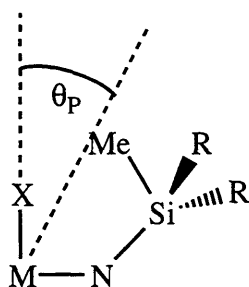


Figure 2. Pocket Angle (θ_P) for a Triamidoamine Complex
Fragment (M = transition metal, X = axial ligand).

and other metrical parameters for **2** noted previously are summarized in Table 3 along with analogous data collected for similar complexes. As predicted at the beginning of this study, the $[N_3N']^{3-}$ ligand accommodates the titanium ion deep within the steric pocket, indicated by the relatively small displacement of Ti from the equatorial NNN plane ($D_{NNN} = 0.203 \text{ \AA}$) which is less than that for $[(Me_2(tBu)SiCH_2CH_2)_3N]VCl$ ($D_{NNN} = 0.310 \text{ \AA}$). The small pocket angle for **2** ($\theta_P = 39^\circ$), however, is substantially less than that for the other complexes which contain axial ligands, a finding which probably reflects the ease with which the $[N_3N']^{3-}$ ligand effectively ensconces a metal.

Table 3. Metrical Parameters for **2** and Related Complexes.

Complex	$N_{ax}-M-N_{eq}-Si$ (deg) ^a	θ_P (deg) ^b	$M-N_{eq}-Si$ (deg) ^c	D_{NNN} (Å)
2	42	39	120	0.203
$[(Me_2(tBu)SiCH_2CH_2)_3N]V^2$	12	40	127	0.160
$[(Me_3SiCH_2CH_2)_3N]VCl^{11}$	33	65	126	0.310
$[(Me_3SiCH_2CH_2)_3N]V=NH^{11}$	3	57	123	0.330
$[(Me_3Si)_2N]_3TiCl^{10}$	-	-	118	0.274

^a Dihedral angles (averaged) are defined by the angles between the $N_{ax}-M$ and $N_{eq}-Si$ vectors;

^b Pocket angles (see text); ^c $M-N_{eq}-Si$ angles are averaged.

first, second, and third row transition metals.⁴ It is therefore interesting to note that triamidoamine transition metal complexes which contain a vacant axial coordination site can only be isolated for first row metals.

CONCLUSION

The new trianionic tetradentate ligand $[N_3N']^{3-}$ has been prepared in high yield and initial investigations showed that several titanium complexes could be readily prepared. From a practical synthetic standpoint, their extreme hydrocarbon solubilities might render future studies involving this ligand prohibitive, a difficulty which could be circumvented by substituting aryl rings for the trimethylsilyl groups. Nevertheless, the X-ray crystal structure of **2** indicated that modest gains in steric encumbrance about a transition metal (at least for one in the first row) could be expected for complexes of $[N_3N']^{3-}$ compared to that observed for complexes that contain $[(RNCH_2CH_2)_3N]^{3-}$ ligands. For example, this feature could prevent triamidoamine complexes of molybdenum from forming bimetallic bridging dinitrogen species as discussed in Chapter II and elsewhere.¹³⁻¹⁵ It is not known for certain at this stage why trigonal monopyramidal complexes for heavier transition metals related to **4** have not been isolated, but fresh approaches to the design of tetra-amine ligands¹⁶ and the potential for derivatives of $[N_3N']^{3-}$ to better ensconce a transition metal suggest that such complexes might still be in the offing.

EXPERIMENTAL

General Procedures. All air sensitive manipulations were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or under argon when using Schlenk techniques. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under N_2 . Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium. Deuterated solvents were purified in a manner similar to that for protio solvents, degassed by three freeze-pump-thaw cycles, and vacuum transferred to solvent storage flasks until use. $TiCl_4(THF)_2$ was prepared by a

literature procedure.¹⁷ $(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2)_3\text{N}$ was purchased from Strem Chemicals; other commercially available reagents were used as received.

NMR operating frequencies and reference standards for heteronuclei on the scale of ^1H (300 MHz, $\text{SiMe}_4 = 0$ ppm) are as follows: ^{13}C (75.4 Hz, $\text{SiMe}_4 = 0$ ppm). Proton and carbon spectra were referenced using the partially deuterated solvent as an internal reference. Chemical shifts are reported in ppm and coupling constants are in hertz. All spectra were acquired at $\sim 22^\circ\text{C}$ unless otherwise noted.

Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratory or by Schwarzkopf Micoranalytical Laboratory (Woodside, NY).

$\text{H}_3[\text{N}_3\text{N}']$ (1a). A 1 L Schlenk flask was charged with $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$ (18.00 g, 0.096 mol) in 350 mL THF. The solution was stirred magnetically and cooled to -65°C . Butyllithium (0.296 mol, 2.5M in hexane) was syringed in; a white precipitate formed immediately. The mixture was allowed to warm to room temperature over 7 h, cooled again to -65°C , and treated with TMSCl (32.16 g, 0.296 mol). The white mixture was allowed to warm to room temperature overnight. Solvents were removed *in vacuo* and the residue was extracted three times with 150 mL of pentane and filtered through a bed of Celite. The solvents were removed from an aliquot of the filtrate to give a pale yellow oil: ^1H NMR (CDCl_3) δ 2.68 (q, 6, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 2.37 (t, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.49 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 0.01 (s, 27H, SiMe_3).

$\text{Li}_3[\text{N}_3\text{N}']$ (1b). The pentane extracts from above were combined, cooled to -65°C , and treated with butyllithium (0.301 mmol, 2.5M in hexane). The mixture containing a thick white precipitate was allowed to warm to room temperature overnight, and then was chilled to -35°C overnight. The white microcrystalline powder was filtered off, washed quickly with cold pentane, and dried *in vacuo* to give pure product; yield 30.520 g (75%).

$[\text{N}_3\text{N}']\text{TiCl}$ (2). **1** (2.300 g, 5.44 mmol) was added in one portion to a stirred suspension of $\text{TiCl}_4(\text{THF})_2$ (2.00 g, 5.99 mmol) in 50 mL pentane at -35°C . The canary yellow

mixture darkened slightly and was allowed to stir at room temperature overnight. LiCl and excess $\text{TiCl}_4(\text{THF})_2$ were removed via filtration through Celite. The yellow filtrate was concentrated and chilled to -35°C to give amber plates of $[\text{N}_3\text{N}']\text{TiCl}$; yield 1.19g (45%): ^1H NMR (C_6D_6) δ 4.24 (td, 3), 3.36 (td, 3), 3.24 (m, 3), 1.64 (m, 6), 1.25 (m, 3), 0.52 (s, 27, SiMe₃); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ 59.24, 51.18, 27.66, 1.38. Anal. Calcd for $\text{C}_{18}\text{H}_{45}\text{N}_4\text{ClSi}_3\text{Ti}$; C, 44.56; H, 9.35; N, 11.55. Found: C, 44.44; H, 9.21; N, 11.38.

$[\text{N}_3\text{N}']\text{TiCH}_3$ (3). MeLi (0.79 mmol, 1.4M in ether) was added dropwise to a stirred solution of **2** (350 mg, 0.72 mmol) in 25 mL of ether at -35°C . The yellow mixture was stirred overnight and ether was removed *in vacuo*. The yellow residue was taken up in pentane and the solution was filtered through a bed of Celite. The filtrate was concentrated in vacuo and chilled to -35°C to give yellow crystals of the product; yield 67 mg (20%): ^1H NMR (C_6D_6) δ 4.26 (m, 3), 3.20 (m, 6), 1.60 (m, 6), 1.18 (m, 3), 0.89 (s, 3, TiCH₃), 0.35 (s, 27, SiMe₃); $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6) δ 58.01, 50.12, 44.18, 28.72 (TiCH₃), 1.44. Anal. Calcd for $\text{C}_{19}\text{H}_{48}\text{N}_4\text{Si}_3\text{Ti}$; C, 49.10; H, 10.41; N, 12.05. Found: C, 49.23; H, 10.02; N, 11.94.

$[\text{N}_3\text{N}']\text{Ti}$ (4). A vigorously stirred solution of **2** (400 mg, 0.82 mmol) in 30 mL pentane was treated with Na/Hg amalgam (1.06 g, 2.30 mmol, 5% amalgam). The yellow mixture rapidly turned green and was stirred for 16 hours. The dark mixture was then filtered through Celite and the filtrate was concentrated to 2 mL. Small green crystals of the product were deposited at -35°C which were dried *in vacuo*; yield 177 mg (48%): ^1H NMR (C_6D_6) δ 2.96 (b, 27, SiMe₃). Anal. Calcd for $\text{C}_{18}\text{H}_{45}\text{N}_4\text{Si}_3\text{Ti}$; C, 48.07; H, 10.08; N, 12.46; Cl, 0.00. Found: C, 47.30; H, 10.12; N, 12.73; Cl, 0.30.

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ACKNOWLEDGMENTS

No man is an Iland, intire of it selfe.

—Donne

On many occasions when I have revealed my profession to a lay audience, I was greeted with grimaces (or worse, blank stares) as the mere mention of chemistry conjures unpleasant memories of high school chemistry class or, for those with more persistence, college organic chemistry, a Waterloo for many in their undergraduate careers. Although I gave great sympathy for these troubled individuals, my experience with chemistry was markedly positive, in large part because of several influential people with whom I have overlapped to varying degrees. This section is devoted to them.

It would be most appropriate to begin by paying special tribute to a few of my academic mentors. My thirst for knowledge of the physical universe, considerably whetted by the time I reached high school, was greatly increased by my high school chemistry teacher, Mrs. Esther Wallace. I am indebted to her and, unfortunately, I believe that she is only remotely aware of how her zeal for chemistry ignited the same within me. While in my sophomore year at UC Davis, Prof. Alan Balch took me under his wing with the sole intent for me to assist a graduate student who broke his elbow. Of course, the elbow healed and I stayed. Alan took a gamble on an inexperienced undergraduate who had not taken any inorganic chemistry at that time. I benefited greatly from my research experience in his laboratory. A man who I did not consider to be particularly verbose, Alan offered three words of advice about my choice of graduate schools: Go to M.I.T. I am reluctant to admit that my background in organometallic chemistry was sorely wanting when I arrived here, evidenced in no small part by my dismal performance on a "cume" and final exam, both written by Dick Schrock. By that time I had joined his group and wondered how he might cope with someone like me. Former students have commented on the latitude offered to them in the course of their research by Dick; I am no exception and I believe that this quality, in addition to his superb guidance, has caused me to learn an immense amount of chemistry. I am indebted to him for his patience and vision to help me become a polished graduate student. Working in Dick's group was a tremendous experience. I would make the same decision again.

A special group of people deserve particular thanks. They are my labmates. I was very fortunate to have begun my graduate career with two postdocs, Drs. Karen Totland and Dan Dobbs. Both taught me a great deal about chemistry, especially air-sensitive manipulations. Thanks to them for punctuating our lab with hilarity and their good humor (future residents of 6-425 will notice the X-rated drawer labels). Dan quickly endeared himself to me as an honest friend and mentor, and although we rarely agreed on matters outside of chemistry, his influence on me and my graduate experience is immeasurably positive. He handed the "torch" to George Greco, my current labmate, who has become a good friend and confidante. A native New Yorker who is no stranger to stress, George deserves my special thanks for being patient with my sporadic demands for drybox use while I wrote this thesis and for proof-reading some of it. Good luck with dinitrogen chemistry, George!

Several people in the chemistry department, both past and present, have made M.I.T. a more palatable and enjoyable place for me. Early contributors include Anne LaPointe, who finally convinced me to work for Dick, and Joel Freundlich, an animated and sincere friend whose enthusiasm for chemistry was contagious. Tim Warren and Florian "Flo" Schattenmann were the former inhabitants of 6-427, a place I affectionately dubbed "The Black Hole." A trip to their lab was always fruitful, whether that included a discussion about chemistry or philosophy. The unquestionable and most emotional highlight of our experiences together was our undefeated march to glory when we claimed the 1996 Chemistry Summer Volleyball Championship with other team mates Jesse Lee, Shane Krska, Carlos Navas, and Sean Daughtry. I enjoyed many intense bike rides with Scott "Scotty" Seidel and Mike Fickes. Our tours through the countryside to Walden Pond at sunset were memorable. They still chide me for bailing from a ride to N.H. with them at the last second (I broke my shifter cable). In return, I thank them for giving me several opportunities to demonstrate to them how flat those hills to Walden Pond really are. Thanks to Dr. Bill Davis for teaching me all I know about X-ray crystallography. His colorful presence has certainly made M.I.T. a more interesting place to be. Thanks also to Dr. Jeff Simpson for undertaking a hefty responsibility with the new Spec Lab (I'll never call it the DCIF!) and for

contending fairly with my impatience while I was writing this dissertation. Former graduate students Matt Reding and Joel Houmes, my roommates for several years, became good friends who also understood what a bad day in lab was like. I extend special thanks to Shane "Shano" Krska, an early friend at M.I.T. who is now like a brother to me. While a competent chemist, he taught me that a graduate education consists of more than time spent in the lab. An incredibly diverse group of current Schrock group members warrant attention. Myra O'Donoghue has been a particularly boisterous and cheerful presence; I thank her for her friendship and for fostering levity in the lab. I am thankful to Alexander "Sasha" Kolchinski for numerous discussions about chemistry and Russian culture. Sasha rapidly established himself as a fount of anecdotal chemistry lore; to wit, he convinced me that the explosive mixture of KNO_2 and red P would not damage my fingers when snapped between them. Michael Aizenberg and Robert "Bob" Baumann, my longest standing companions in Group IV during my last project, deserve thanks for some great discussions about chemistry. Special thanks go to Robert for cooking up the $[\text{NON}]\text{H}_2$ ligand and proof-reading my Hf work. Yann Schrodi, one of few Francophones I have met, has become a trustworthy friend on both sides of the lab door. Plus he is a lot of fun to be around.

I would not have made it this far but for the support, love, and encouragement of my family. Both of my parents, teachers in their own right, have always nurtured in me a healthy desire to learn. I thank them deeply for believing in me while I pursued various interests. My sister Amy is one of the closest and dearest friends I have; I thank her for unwavering support and love through all these years. Finally, I have heard it quipped that behind every great man there is a woman. Regardless of my personal attributes, I would otherwise agree wholeheartedly for I know that my journey at MIT and through dark personal valleys have been more endurable and successful because of Lisa, my bride-to-be. Her immeasurable love, gentleness, and peace have left indelible marks upon my life that I shall carry forever. I thank Lisa for her unbelievable patience and sacrifice while I finished this dissertation. It is devoted to her.

AFTERWORD

For since the creation of the world His invisible attributes, His eternal power and divine nature, have been clearly seen, being understood through what has been made, so that they are without excuse.

—Romans 1:20

Perhaps more than a few people who have read the line by Young at the beginning of this thesis will wonder why I included it in a scientific work. His question, stated non-poetically, might be rendered: Do the things we apprehend in scientific study say anything about something beyond Nature? The numerous volumes devoted to science and theology indicate that many people are sharply divided on this issue and still others do not know what to think. I fall rather squarely in the camp that maintains the existence of a personal Creator, but I also am part of the scientific community, a quarter which many believe to be unfriendly to any claim of the supernatural. During one instance, I saw why this might be. While an undergraduate, I learned that a student in my research lab took astrology very seriously, a belief which struck me as unscientific (apparently others think so, too: *Nature* **1985**, 318, 419). Ironically, I often encounter educated people, especially those with some scientific training, who feel that my Christian beliefs are also unscientific. That is, about two millennia ago a Jewish carpenter in Galilee claimed to be God incarnate. He said He came to forgive our sins; He healed the sick and lame; and He walked on water. He reportedly died and rose from the dead to sit at the right hand of God. These sorts of things, scoff some skeptics, simply do not happen because (and let us be honest) science says they cannot. Therefore how can I, without giving a nod to hypocrisy, place faith in God without betraying the scientific principles I also embrace? Religion, in the broad and popular sense, may indeed find little sympathy from science. You can find all sorts of strange tales and lore that offends the modern mind. My concern here, however, is what science may have to say (if anything) about a particular "brand" of religion. This afterword is not meant to be a comprehensive treatise on the subject, but rather an acknowledgment to God and to offer some personal thoughts on why I think the claims of science and a belief in God are harmonious.

I would encourage the skeptic who wishes to expose Christianity as a hoax in the most expedient fashion to not bother with debates about morals or political agendas, but rather show that the miracles recorded in the Bible can be explained by something other than what is miraculous. I adopt the popular definition of "miracle": an interference with Nature by a supernatural power.

Strip miracles from almost every other religion and they remain intact, but take them from Christianity and you have removed everything which is distinctly Christian. The very center of the story is indeed a miracle (the Resurrection). One approach which seems to find widespread appeal is to disprove or explain away accounts of specific miracles. (By the way, this is a matter of historic and not scientific inquiry). The only way to show for certain that an account of a miracle is false is to show that the miracle did not happen in the first place. And that is what we are trying to find out. In my opinion, it would be better to find out if Nature is all there is--the "whole show"--or if there might be anything in her which would suggest that something exists outside of her. For example, it was long thought that Newtonian physics satisfactorily explained the movement of bodies until quantum theory told us that this movement is explained by a law of averages of much smaller bodies which, to us at least, seem to move on their own accord or in an indeterminate fashion. C. S. Lewis, for example, regards this as subnature: the backdoor through which quantum events are fed into Nature. But then we have no confidence that Nature has no doors and surely none that she might not also have a front door through which supernatural events are fed. One of these doors has an unexpected address.

We expend a great deal of effort in thinking about problems, but seldom do we consider the fact that we are thinking at all. The type of thinking we call rational thinking or inference must, the evolutionists would say, have evolved by natural selection (i.e. by an historical process). It follows that our thoughts once were not rational; that is, they were not an apprehension of objective truth. Natural selection eliminates the biologically hurtful responses and multiplies the helpful, but this process cannot turn irrational thought into an act of insight. An opposable thumb may render a hand more dexterous and useful than one which does not have an opposable thumb, but this is not the same as a knowledge of anatomy. Millennia of teaching and conditioning have also been proposed as means to rational thought. A difficulty with this mechanism is that it would sometimes produce wrong inferences. For example, one of my cats who learned to enter my house by jumping through a hole in a closed screen door was sometimes surprised, often to my amusement, to find the glass portion of the door also closed. Thus the imagined rational thinking

which we put into Nature really depends upon the thinking we are actually doing, not vice versa. Reason must stand outside of Nature and is used to control her. Chemists use their knowledge of matter to construct molecules and engineers use math to erect buildings. What happens when a person relaxes his vigilance against a nagging toothache, a mosquito bite, or intoxicated brain should convince him that Nature is powerless to produce rational thoughts. We possess more information about humans than for any other thing in the Universe, and when we look inside ourselves, we find that the flow of traffic at the frontier of Nature and rational thought, namely our minds, is one-way traffic.

A popular objection to miracles is that they are known to contradict the laws of Nature. Ancient people (like those who wrote the Bible) did not know the laws of Nature, but we now know that miracles are a scientific impossibility. This is a confusion of the mind, for experience (and especially the artificial kind we call experiments) tells us what regularly happens in Nature but cannot tell us whether or not a thing is possible. For example, Joseph was as surprised as any groom would be today when he discovered that his virgin bride-to-be, Mary, was pregnant. But he knew just as well as any modern gynecologist that women do not get pregnant unless they lay with men. A modern gynecologist may know a great deal more than Joseph, but on this point they would agree. Joseph certainly knew that a virgin birth is contrary to the course of nature and would be impossible unless the regular processes of Nature were being supplanted with something else. Belief in miracles does not depend upon an ignorance of the laws of Nature, but depends upon the extent to which those laws are known. In other words, unless you perceive that Nature works according to regular laws, you will not notice when those laws are being suspended. An increasing knowledge of Nature can never make a unique invasion of Nature by something outside of her either more or less credible. The march of science and progress of civilization should render it easier for us to accept miracles.

Every law of Nature, when reduced to its simplest form, says, "Given A, then B." A physicist knows that when a ball is tossed across a field, it usually travels in a parabolic path according to physical laws. This is provided, of course, that an unfortunate bird does not mistake

the ball for prey and carry it off mid-flight. As unlikely this event may be, the law of motion was nevertheless not broken but illustrated in a way the physicist had not expected. The bird has spoiled his experiment, yet even its interference has left the law of motion perfectly true. The physicist does not know beforehand how likely it is that a bird may interfere; he had better ask an ornithologist. If the events in Nature are tampered with by any agent (natural or supernatural), then our predictions of their outcome must differ from what we expected, not because the laws of Nature are false, but because they are true. We do not know, as scientists, whether or not God might be one of these agents. But we do know, as scientists, whether or not a set of conditions does not yield the expected result according to the laws of Nature. Notice how easily we smuggle into our everyday talk the idea that the laws of Nature cause events to happen. But they have never caused anything to happen. They merely state the pattern to which every event must conform. In one sense, the laws of Nature have something to say about everything in space and time. But in another sense, they leave out the whole universe-- the raw materials of reality. To think that laws can produce anything is like thinking that molecules are synthesized by balancing chemical equations. If A, then B; but first get your A. If God does tamper with Nature, then the initial conditions will not be A but AC, and the results not B but BC. Nature is an accomplished hostess. She is not in the least incommoded by events fed into her by a psychological nature any more than those which are fed into her by God.

One often finds that a beginner who has just mastered strict rules tends to be rather pedantic about them. The first few times that I saw a chemistry professor (of organic chemistry, I think) write unbalanced equations, I thought, "Surely he just made a mistake," until I realized that the long scheme of reactions he was presenting would have been encumbered by undue attention to stoichiometry. He was, in fact, taking license to convey greater meaning to his students. There are rules behind the rules. The extent to which one may discern an "allowable" license from a mistake or failure depends upon the extent to which one understands the real significance of the work as a whole. Who thinks that a sculptor takes as his starting point the quality of marble which we can determine scientifically, or the writer who creates his poetry from rules of meter and

rhyme? We cannot determine by studying the complexity of Nature by science whether or not God's external act, viewed from within, is of the same complexity. Suppose that one takes a very close look at a photo mosaic-- a picture composed of hundreds or even thousands of tiny photographs arranged in a grid. Through a magnifying glass, he may discover increasingly complex relations between each tiny photograph, and sort these relations out, with great toil, into certain regularities. These regularities, or laws, will hold for most of the little pictures. But if he was to conclude that any departure from the laws was unworthy of the artist and an arbitrary violation of his own rules, he would be far astray. In the same way, to think that a disturbance of the regular patterns of Nature we have discovered would constitute a breach of the living rule whereby God, from His own point of view, works, is a mistake.

Up to this point, it seems that Nature is not safe from miracles. But even if God could intervene in Nature, it does not follow that He necessarily would. Interestingly, some feel that if there is a God, then He should tamper with Nature (presumably by a miracle) and this sentiment is usually expressed this way: "If there is a God out there, then why doesn't He show Himself?" I have great sympathy for this point of view, not only on intellectual grounds, but also because it sometimes reflects deeply emotional appeals. We might expect God to emblazon His name across the sky in flaming letters, speak to us from a burning bush, or shake the Earth with a booming voice. Why, after all these years of studying science (a wide window into His supposed Creation) is His existence not more obvious to us? I suggest that His fingerprint upon Nature is *so* obvious that we often fail to recognize it. You will hardly notice for a long time the safety glasses you wear in the laboratory. Only when you bump them or, in my case, experience an explosion does it become obvious that they are perched upon your nose. When speaking English, I am following rules of grammar, though I do not know it. When I was trying to learn Spanish, I was painfully aware of it. These examples show that the fact which is the most basic and obvious fact, and through which alone we have access to all other facts, may be the one which is most easily forgotten not because it is so remote and intangible, but because it is so close and obvious.

Science offers a powerful means by which to examine the close and obvious. Chemistry (the "central science") offers rich opportunities in which to apprehend the complexity and organization of matter on a molecular level. In *Darwin's Black Box*, Professor Michael Behe furnishes several examples of how biochemical systems pose insurmountable obstacles to Darwinian evolution (in the undirected and purposeless sense) since the chemistry involved in each example is *irreducibly complex* : "well-matched, interacting parts that contribute to the basic function, wherein the removal of any one of the parts causes the system to effectively cease functioning." The chemistry of blood coagulation, for example, involves many compounds in specific concentrations which are related by a cascading (i.e., interdependent) set of reaction mechanisms. No one knows how this system came to be. Behe concludes that no natural mechanism could ever form chemical systems of this complexity. Astronomer Dr. Hugh Ross explains in *Creation and Time* that there are at least 25 specific requirements for the universe which must be satisfied in order for life to be merely *possible* on a planet such as Earth. For example, the size and age of the sun, the existence and mass of the moon, and density of galaxies in the universe must all fall within a narrow range of values. Like Behe, he argues that natural mechanisms and chance are inadequate to produce this level of fine-tuning and complexity. Both of these scientists join the ranks of many others in asserting the theory of intelligent design. One will learn something about an architect (such as his existence) from studying his buildings. In the same way, we may learn something about the Creator by a study of His creation.

Several prominent scientists are reluctant, however, to embrace the theory of intelligent design. There are a few reasons why this might be. First, the purpose of science is to explain the physical world. It can tell us how often we observe solar eclipses or what the melting point of water is under various conditions. The purpose of theology is also to explain parts of the world. Theology can tell us something about getting to Heaven or what the origin of morality is. Unfortunately, members from both camps sometimes attempt to address questions in one discipline with an explanation from the other and this often leads to a perceived conflict of disciplines. It is not difficult to see why one might harbor a distaste for the "opposing" discipline. The Huxley-

Wilberforce debate from last century and the Scopes Trial earlier this century have all but stamped into the minds of many the perception that science is at odds with a belief in God. More recently, some creationist groups who espouse the theory of a young earth (an untenable theory, in my opinion) have unwittingly nurtured this perception. Second, many hold the belief that science, sooner or later, can explain everything by using the scientific method (e.g., hypothesis, testability, repeatability). This obviously leaves no room for someone who maintains a belief in miracles and intelligent design. Unfortunately, neither the scientist nor theologian gains anything with this credo since God cannot be tested any more than can an historical process (such as Darwinian evolution). However, the *effects* that God has had (or may have had) on Nature may be tested. Finally, many individuals simply do not want there to be anything beyond Nature. Earlier this century, astronomers' announcement of the Big Bang caused many to be uneasy. What begins to exist has a cause, and since the universe was shown to have a beginning, it follows that the universe had a cause. The cause must have been *timeless* (outside of time) since the universe began a finite time ago, suggesting that the cause is personal (e.g., it chose to create). The conclusion from this line of reasoning is admittedly distasteful to many, but they may breathe easily: no scientific theory on its own can forcibly compel belief in God by sheer logic.

Although I and other scientists have reached the conclusion that a belief in God is quite friendly with the claims of science, a large number of people (including many scientists) conclude the opposite. How are we to decide? Does it matter? Science provides us with a wealth of information about the universe, but it does not necessarily tell us how (or if) we can use this information to answer these questions. For that, one would have to turn to other disciplines. We know on a primal level that there is such a thing as water because we thirst, bread because we hunger. Would it not be a hoax of cosmic proportions if our appetite for knowledge was never completely satisfied, the yearning to learn what hides 'round each corner never fulfilled, and our unquenchable determination to know the underpinnings of the universe thwarted? In science, we find the margin notes to a poem. In Christianity, we find the poem itself.