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Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Alkylidene Complexes That Contain a 2,6-Dimesitylphenylimido Ligand

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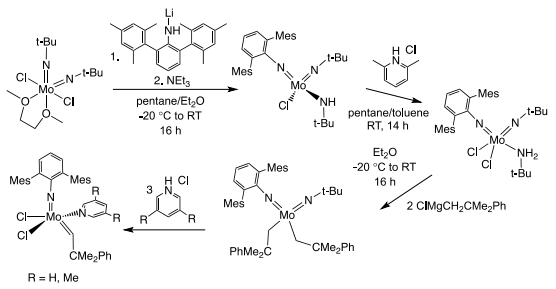
ABSTRACT: Molybdenum and tungsten bispyrrolide alkylidene complexes that contain a 2,6-dimesitylphenylimido (NAr*) ligand have been prepared in which the pyrrolide is the parent pyrrolide or 2,5-dimethylpyrrolide. Monoalkoxide pyrrolide (MAP) complexes were prepared through addition of one equivalent of an alcohol to the bispyrrolide complexes. MAP compounds that contain the parent pyrrolide ($NC_4H_4^-$) are pyridine adducts, while those that contain 2,5-dimethylpyrrolide are pyridine-free. Molybdenum and tungsten MAP 2,5-dimethylpyrrolide complexes that contain O-t-Bu, $OCMe(CF_3)_2$, or O-2,6-$Me_2C_6H_3$ ligands were found to have approximately equal amounts of *syn* and *anti* alkylidene isomers, which allowed a study of the interconversion of the two employing ^1H-^1H EXSY methods. The K_{eq} values ([*syn*]/[*anti*]) are all 2-3 orders of magnitude smaller than those observed for a large number of Mo bisalkoxide imido alkylidene complexes as a consequence of a destabilization of the *syn* isomer by the sterically demanding NAr* ligand. The rates of interconversion of *syn* and *anti* isomers were found to be 1-2 orders of magnitude faster for W MAP complexes than for Mo MAP complexes.

INTRODUCTION

Bulky alkoxides and imido ligands in Mo- and W-based olefin metathesis catalysts of the type $M(NR)(CHR')(OR'')_2$ slow or prevent intermolecular decomposition and/or ligand scrambling reactions, which allows the monomeric nature of these four-coordinate imido alkylidene complexes to be maintained.[1] Chiral versions that contain biphenolates or binaphtholates have been employed for enantioselective metathesis reactions (when the biphenolate or binaphtholate is enantiomerically pure)[2] or in order to control the structure of polymers prepared in ROMP reactions[3] (usually when the biphenolate or binaphtholate is racemic). The most recent development has been the synthesis of monoalkoxide (or monoaryloxide) pyrrolide (MAP) complexes of the type M(NR)(CHR')(OR'')(Pyr), where Pyr is usually the parent pyrrolide or a 2,5-dimethylpyrrolide (Me_2Pyr).[1c] MAP complexes have proven to be more efficient in many olefin metathesis reactions in terms of higher turnover numbers, but more interestingly, they can provide high *Z* selectivities. *Z*-selective MAP catalysts have now been developed for ring-opening metathesis polymerization (ROMP),[4] homocoupling,[5] ring-opening/cross-metathesis,[6] ethenolysis,[7] and formation of natural products through ring-closing reactions.[8] *Z*-selective reactions have been possible when one large OR" ligand is present, e.g., a terphenoxide such as 2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3O$ (HIPTO),[9] 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3O$ (HMTO),[10] or 2,6-$(C_6F_5)_2C_6H_3O$ (DFTO),[11] especially in combination with a relatively small imido ligand. The theory of metathesis by MAP complexes, which are members of the large class of four-coordinate stereogenic-at-metal (SAM) complexes, M(NR)(CHR')(X)(Y), continues to be explored through theoretical calculations.[12] A large N-heterocyclic carbene and a stereogenic metal center also are found in *Z*-selective ruthenium catalysts.[13]

Although it has been established that the electronic and steric nature of the imido ligand play a significant role in determining the reactivity and selectivity of metathesis catalysts, no catalysts have been prepared in which the imido ligand is an analog of a 2,6-terphenoxide. Anilines analogous to the large 2,6-terphenonols that we have employed have been prepared, namely 2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3NH_2$ (2,6-$Trip_2C_6H_3NH_2$) and 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3NH_2$ (2,6-$Mes_2C_5H_3NH_2$ = Ar*NH_2), as have several transition metal complexes that contain amido or imido derivatives of these large anilines.[14] In anticipation of the less sterically demanding nature of an NAr* ligand than the 2,6-$Trip_2C_5H_3N$ ligand, we targeted NAr* imido alkylidene catalysts of Mo and W. The NAr* ligand is the approximate steric equivalent of the OHMT ligand. A shorter M=N bond as opposed to a M-O bond (M=N is expected to be ~0.12 Å shorter) would suggest that the steric demand of a NAr* ligand may be greater than that of an OHMT ligand. However, this effect may be counteracted by an essentially linear M-N-C_{ipso} angle in most circumstances.

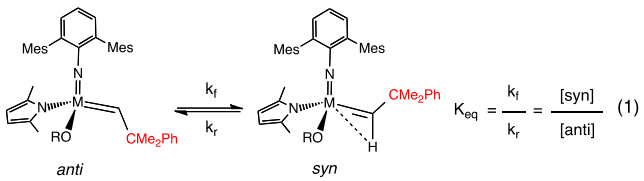
In our initial communication[15] we reported the synthesis of MoNAr* alkylidene complexes. A synthetic route had to be devised (Scheme 1) that did not require formation of $Mo(NAr^*)_2(CH_2R)_2$ precursors (R = t-Bu or CMe_2Ph) analogous to those employed for synthesizing virtually all imido alkylidene complexes of Mo and W to date. The synthetic route shown in Scheme 1 was inspired by observations published by Gibson.[16] $Mo(N\text{-}t\text{-}Bu)_2Cl_2(dme)$ was treated with LiNHAr* to give $Mo(N\text{-}t\text{-}Bu)_2(NHAr^*)Cl$,



Scheme 1. Synthesis of Mo alkylidenes that contain the NAr* ligand.

which was then transformed into Mo(N-t-Bu)(NAr*)(NH-t-Bu)Cl upon treatment with NEt_3. Addition of 2,6-lutidinium chloride to Mo(N-t-Bu)(NAr*)(NH-t-Bu)Cl yielded Mo(N-t-Bu)(NAr*)(NH_2-t-Bu)Cl_2, which was then alkylated to give Mo(N-t-Bu)(NAr*)($CH_2CMe_2Ph)_2$. Upon addition of pyridinium chloride or 3,5-dimethylpyridinium chloride to Mo(N-t-Bu)(NAr*)($CH_2CMe_2Ph)_2$ the t-butylimido group was protonated selectively and Mo(NAr*)($CHCMe_2Ph)Cl_2$(L) complexes (L = pyridine or 3,5-dimethylpyridine) were isolated in high yield. This was the first time we were able to use a form of HCl instead of triflic acid to generate the alkylidene complex. Addition of triflic acid to Mo(N-t-Bu)(NAr*)($CH_2CMe_2Ph)_2$ in the presence of 1,2-dimethoxyethane led only to decomposition instead of formation of Mo(NAr*)($CHCMe_2Ph)(OTf)_2$(dme).

The only Mo(NAr*) MAP compound that was reported[15] is Mo(NAr*)($CHCMe_2Ph)(Me_2pyr)$(O-t-Bu). It was synthesized either by treating Mo(NAr*)($CHCMe_2Ph)(Me_2pyr)_2$ (**2_{Mo}**) with t-butanol or by treating Mo(NAr*)($CHCMe_2Ph$)Cl(O-t-Bu)(py) with $LiMe_2pyr$. Mo(NAr*)($CHCMe_2Ph)(Me_2pyr)$(O-t-Bu) was found to have two alkylidene resonances in the proton NMR spectrum (at 11.861 ppm and 11.695 ppm in C_6D_6) in approximately a 1:1 ratio. The $^1J_{CH}$ value for the downfield resonance (118 Hz) is consistent with it being a *syn* alkylidene and for the upfield proton resonance (152 Hz) an *anti* alkylidene; the substituent on a *syn* alkylidene points toward the imido ligand and the substituent on an *anti*



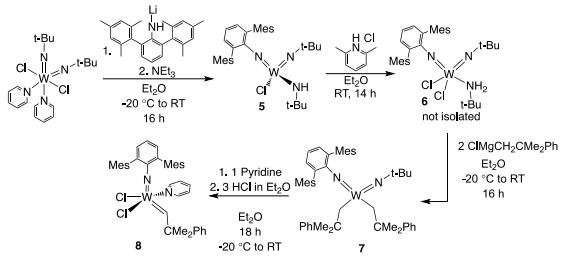
$$K_{eq} = \frac{k_f}{k_r} = \frac{[syn]}{[anti]} \quad (1)$$

alkylidene points away from the imido ligand (equation 1). The *syn* isomer is the only one observed in all other MAP complexes prepared to date, although *anti* isomers have been observed upon irradiation of *syn* isomers at low temperatures.[4b] Preliminary 2D ^{1}H-^{1}H EXSY experiments[15] suggested that the *syn* and *anti* forms of Mo(NAr*)($CHCMe_2Ph)(Me_2pyr)$(O-t-Bu) interconvert at a rate of ~0.05 s^{-1} at 22 °C. Since the rate of interconversion of *syn* and *anti* isomers and the equilibrium between them is a crucial feature of many metathesis reactions with imido alkylidene complexes,[17] and since little is known about *syn* and *anti* isomers in MAP species,[4b] we set out to expand the chemistry of MoNAr* MAP species, and to prepare WNAr* MAP complexes.

RESULTS AND DISCUSSION

Synthesis of W(NAr*) compounds

We chose W(N-t-Bu)$_2Cl_2(py)_2$[18] as the starting point for expanding NAr* chemistry to tungsten. The approach (Scheme 2) is the same as that employed to prepare the Mo(NAr*) species (Scheme 1). Upon addition of LiNHAr* to W(N-t-Bu)$_2Cl_2(py)_2$, W(N-t-Bu)$_2$Cl(NHAr*) is formed, which without isolation is treated with NEt_3 to give W(NAr*)(N-t-Bu)Cl(NH-t-Bu) (**5**) in 74 % yield. W(N-t-Bu)$_2Cl_2(py)_2$ did not react with Ar*NH_2 after 16 h at 80 °C. Attempts to use $[(t\text{-BuN})_2WCl_2(NH_2\text{-t-Bu})]_2$[19] instead of W(N-t-Bu)$_2Cl_2(py)_2$ as a starting material were also unsuccessful.



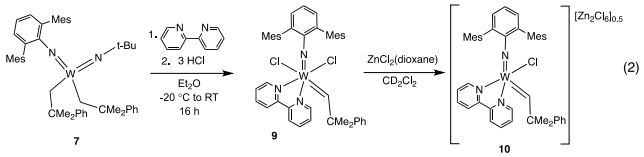
Scheme 2. Synthesis of W complexes that contain the NAr* ligand.

W(NAr*)(N-t-Bu)$Cl_2(NH_2$-t-Bu) (**6**) was synthesized through addition of 2,6-lutidineHCl to **5** (Scheme 2). Rather than reduce the yield of **6** as a consequence of a lengthy purification, W(NAr*)(N-t-Bu)($CH_2CMe_2Ph)_2$ (**7**) was synthesized through the addition of two equivalents of $MgClCH_2CMe_2Ph$ to crude **6**. W(NAr*)(N-t-Bu)($CH_2CMe_2Ph)_2$ was isolated in 68 % yield.

Addition of one equivalent of pyridine to **7** followed by three equivalents of HCl in diethyl ether gave W(NAr*)($CHCMe_2Ph)Cl_2$(py) (**8**) in 63 % yield. Only the *anti* alkylidene isomer is visible in the ^{1}H NMR spectrum of **8** ($^1J_{CH}$ = 144 Hz). Compound **8** could *not* be prepared employing three equivalents of pyridineHCl. Employing HCl in diethyl ether or triflic acid also resulted in decomposition with little or no identifiable alkylidene species being observed in ^{1}H NMR spectra of the crude reaction product.

An alkylidene species, W(NAr*)($CHCMe_2Ph)Cl_2$(bipy) (**9**), was also was synthesized through a reaction between

$W(NAr^*)(N\text{-}t\text{-}Bu)(CH_2CMe_2Ph)_2$ and 2,2'-bipyridine (bipy) followed by three equivalents of HCl (equation 2). Compound **9** is insoluble in pentane, diethyl ether, benzene, and toluene. Its low solubility in CH_2Cl_2 allows $W(NAr^*)(CHCMe_2Ph)Cl_2(bipy)$ to be extracted and thereby separated from $t\text{-}BuNH_3Cl$. Bipy adducts have been employed



(2)

as synthetic intermediates previously,[19,20] in part because their low solubility allows them to be obtained readily in pure form.

$ZnCl_2$ or $ZnCl_2$(1,4-dioxane) can be employed to remove 2,2′-bipyridine or 1,10-phenanthroline from Mo imido alkylidene complexes.[19,20,21] When $ZnCl_2$(dioxane) is added to $W(NAr^*)(CHCMe_2Ph)Cl_2(bipy)$ suspended in CD_2Cl_2, a new product and free dioxane are observed by ^1H NMR spectroscopy, but bipyridine resonances are still visible. An X-ray structure showed that the product is $[W(NAr^*)(CHCMe_2Ph)Cl(bipy)][Zn_2Cl_6]_{0.5}$ (**10**), i.e., $ZnCl_2$ abstracts a chloride ligand to form a cationic W bipyridine complex in which $[Zn_2Cl_6]^{2-}$ is the (di)anion (equation 2).

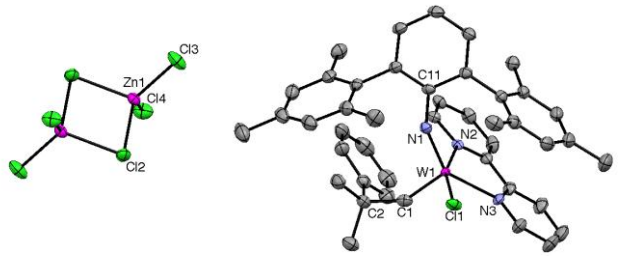


Figure 1. Crystal structure of $[W(NAr^*)(CHCMe_2Ph)Cl(bipy)][Zn_2Cl_6]_{0.5}$ in thermal ellipsoid representation at the 50% probability level. Only one half of the $Zn_2Cl_6^{2-}$ anion is present in the asymmetric unit, but the whole unit is pictured. Hydrogen atoms, toluene solvent molecule and minor component of disorder are omitted for clarity. Selected bond angles: C11-N1-W1 = 153.03(15), C2-C1-W1 = 148.42(17).

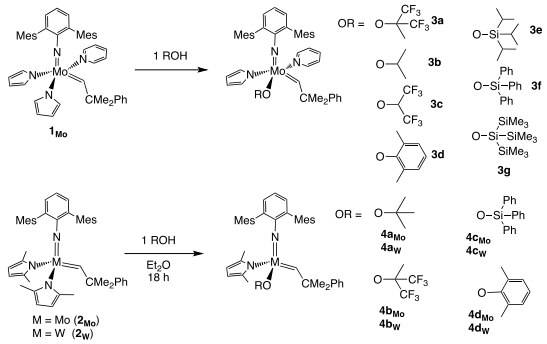
$[W(NAr^*)(CHCMe_2Ph)Cl(bipy)][Zn_2Cl_6]_{0.5}$ crystallizes in the space group $P\bar{1}$ with one $[W(NAr^*)(CHCMe_2Ph)Cl(bipy)][Zn_2Cl_6]_{0.5}$ unit and one toluene molecule per asymmetric unit (Figure 1). The alkylidene ligand is in the *syn* orientation. The bipyridine ligand is disordered over two positions. The geometry about W is best described as a distorted square pyramid (τ = 0.34, where τ = 0 for a perfect square pyramid[22]) with the alkylidene ligand at the apical site. The W1-N1-C11 angle (153.03(15)°) is relatively small compared to the 175-180° found in many other imido alkylidene complexes, possibly as a consequence of some attractive π interaction between one of the mesityl rings and the bipy ring system, but otherwise the bond lengths and angles (see SI) are those expected for W imido alkylidene complexes. The coordination geometry around each zinc is a slightly distorted tetrahedron, as expected.

Since bipyridine could not be removed easily from $W(NAr^*)(CHCMe_2Ph)Cl_2(bipy)$, possibly in part because of the π interaction noted above, further syntheses focused on $W(NAr^*)(CHCMe_2Ph)Cl_2(py)$ as a starting material. $W(NAr^*)(CHCMe_2Ph)(Pyr)_2(py)$ (**1_W**) can be synthesized through addition of excess LiC_4H_4 to a solution of **8** in diethyl ether. Addition of $LiMe_2C_4H_2$ to **8** gives $W(NAr^*)(CHCMe_2Ph)(Me_2pyr)_2$ (**2_W**). Proton NMR spectra of **2_W** show free pyridine unless the product is left under a good vacuum for several hours. The resonances in the ^1H NMR spectrum of **2_W** are broad at room temperature. A proton NMR spectrum at –40 ºC reveals that all pyrrolide protons and methyl groups are inequivalent. A $^1J_{CH}$ of 126 Hz, which can be observed at –40 ºC, suggests that the alkylidene is in the *syn* orientation. (The $^1J_{CH}$ value for $Mo(NAr^*)(CHCMe_2Ph)(Me_2pyr)_2$ (**2_{Mo}**) is 130 Hz.[15]) We do not know whether one pyrrolide ligand is bound in an η^1 fashion and the other in an η^5 fashion in both **2_W** and **2_{Mo}**, or both pyrrolides are bound in an η^1 fashion. In either case, restricted rotations of ligands at –40 ºC could result in the observed lack of symmetry for **2_W** at that temperature.

Synthesis of M(NAr*) MAP compounds

Addition of two equivalents of LiPyr to $Mo(NAr^*)(CHCMe_2Ph)Cl_2(py)$ led to formation of $Mo(NAr^*)(CHCMe_2Ph)(Pyr)_2(py)$ (**1_{Mo}**) in good yield. Pyridine is retained in the coordination sphere in **1_{Mo}** simply for steric reasons. Synthesis of **1_{Mo}** completes the syntheses of $M(NAr^*)(CHCMe_2Ph)(Pyr)_2(py)$ (M = Mo or W; **1_{Mo}** and **1_W**, respectively) and $M(NAr^*)(CHCMe_2Ph)(Me_2Pyr)_2$ (**2_{Mo}**[15] and **2_W**, respectively), and sets the stage for the synthesis of MAP complexes.

Complexes **3a–g** are formed upon addition of one equivalent of alcohol to **1_{Mo}** (Scheme 3). The pyridine ligand remains bound to the metal in **3a–g**. In all cases in solution, according to ^1H NMR spectroscopy, the alkylidene is in the *anti* form. This is unusual for Mo or W imido alkylidene complexes in general if they are four-coordinate, but less so when the complex is five-coordinate. Several five-coordinate NAr* monochloride monoalkoxide species reported previously were also *anti* alkylidenes in solution.[15] Other *anti* group 6 imido alkylidenes that are base-stabilized species have been known for some time.[23]



Scheme 3. Synthesis of Mo and W MAP complexes from bispyrrolides.

Since pyridine essentially blocks a coordination site and thereby reaction of the alkylidene complex with olefins, Lewis acids were employed with the goal of removing pyridine and isolating base-free alkylidene complexes. It was found that upon addition of one equivalent of $B(C_6F_5)_3$ to **3a–g**, $B(C_6F_5)_3(NC_5H_5)$ formed immediately, according to ^1H and ^{19}F NMR spectra. Unfortunately, the similar solubilities of any base-free species and $B(C_6F_5)_3(NC_5H_5)$ prevented isolation of the base-free alkylidene complexes in pure form. Also, clean conversion to one base-free alkylidene species, which we expected to have two alkylidene resonances, was not observed when $B(C_6F_5)_3$ was added to **3a** – **3e**, so further characterization of the target MAP species *in situ* did not seem feasible. However, only two alkylidene resonances are observed in ^1H NMR spectra of base-free **3f** and **3g** (**3f'** and **3g'**, respectively). In each case the two resonances were confirmed as being those of *syn* and *anti* alkylidenes on the basis of the $^1J_{CH}$ values. For **3f'** K_{eq} = 2.0 and for **3g'** K_{eq} = 2.3 (where K_{eq} = [*syn*]/[*anti*]).

In order to isolate pyridine-free MAP compounds, attention shifted toward pyridine-free $\mathbf{2_{Mo}}$ as a precursor. Four representative alcohols were chosen in order to prepare MAP species. The MAP complexes Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu) (**4a$_{Mo}$**), Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$] (**4b$_{Mo}$**), Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OSiPh$_3$) (**4c$_{Mo}$**), and Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OAr') (**4d$_{Mo}$**, Ar' = 2,6-Me$_2$C$_6$H$_3$) could all be synthesized through addition of one equivalent of the appropriate alcohol to $\mathbf{2_{Mo}}$ (Scheme 3). Like many MAP complexes, **4a$_{Mo}$-4d$_{Mo}$** were all found to be extremely soluble in solvents that have previously been employed for recrystallization (e.g., pentane or diethyl ether), and therefore not isolable in crystalline form from such solvents. However, **4a$_{Mo}$-4d$_{Mo}$** could be isolated in pure crystalline form from acetonitrile and isolated as acetonitrile-free species; there was no evidence for any reaction between the MAP species and acetonitrile at room temperature. Compounds **4a$_{Mo}$-4d$_{Mo}$** are all mixtures of *syn* and *anti* alkylidene isomers, according to ^1H NMR studies.

Addition of one equivalent of an alcohol to W(NAr*)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (**2$_W$**) led to W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu) (**4a$_W$**), W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$] (**4b$_W$**), W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OSiPh$_3$) (**4c$_W$**), and W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OAr') (**4d$_W$**) (Scheme 3). All could be isolated in pure form through crystallization from acetonitrile.

An X-ray study of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu) (**4a$_W$**) revealed a whole molecule disorder, with the major component representing approximately 90 % of the electron density (Figure 2). The alkylidene ligand in the major component is in the *syn* orientation and is slightly twisted with an N1-W1-C1-C2 dihedral angle of 12.25 °. The W1-C1 bond length is 1.875(2) Å, the W1-N1-C21 angle is 173.4(3) °, and the C2-C1-W1 angle is 147.33(19) °, all typical of Group 6 MAP complexes. When the molecule is viewed along the C21-N1-W1 axis, one mesityl group of the NAr* ligand is seen to be located over the alkoxide while the other mesityl group falls between the pyrrolide and alkylidene ligands.

A study of alkylidene rotation

Compounds **4a-4d** for Mo and W (Table 1), are a mixture of *syn* and *anti* alkylidene isomers (equation 1) in C_6D_6 solution, according to ^1H NMR studies. The *syn* isomer is often the major isomer in imido alkylidene complexes of Mo and W due to an agostic interaction that stabilizes it relative to the *anti* isomer. Significant additional factors include the counteracting steric demands of the alkylidene, imido, and other ligands. Compounds similar to those reported here, but with a relatively smaller 2,6-diisopropylphenyl imido ligand, such as Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(OCMe$_3$) and Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$], only show the *syn* isomer in solution.[24]

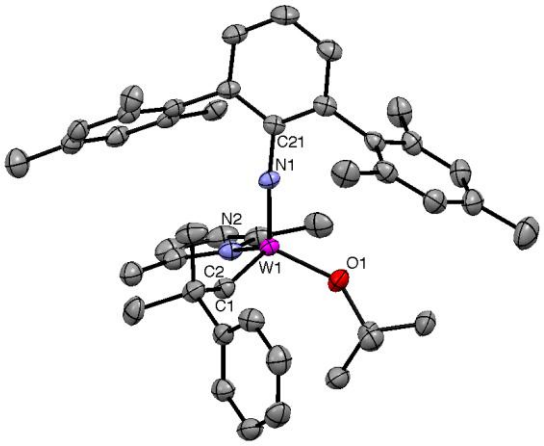


Figure 2. Crystal structure of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu), **4a$_w$**, in thermal ellipsoid representation at the 50% probability level. Hydrogen atoms and minor disorder component are omitted for clarity. Selected bond lengths (Å): C1-W1 = 1.875(2), W1-N1 = 1.750(2), W1-O1 = 1.8682(19), W1-N2 = 2.033(2). Selected bond angles (°): C2-C1-W1 = 147.33(19), N1-W1-O1 = 115.59(14), N1-W1-C1 = 106.04(16), O1-W1-C1 = 109.35(10), N1-W1-N2 = 111.05(13), O1-W1-N2 = 110.03(10), C1-W1-N2 = 104.07(11), C21-N1-W1 = 173.4(3).

Table 1. Rate and equilibrium constants for MAP species at 21 ºC for Mo and W M(NAr*)(CHCMe$_2$Ph)(Me$_2$Pyr)(OR) ("M(OR)") compounds.

Compound	K_{eq}	k_f (s^{-1})	k_r (s^{-1})
Mo(O-t-Bu) (**4a$_{Mo}$**)	0.9	0.05(0.01)	0.06(0.01)
Mo[OCMe(CF$_3$)$_2$] (**4b$_{Mo}$**)	2.7	0.029(0.006)	0.011(0.004)
Mo(OSiPh$_3$) (**4c$_{Mo}$**)	26	~ 0.5	~ 0.02
Mo(O-2,6-C$_6$H$_3$) (**4d$_{Mo}$**)	2.2	0.10(0.02)	0.05(0.01)
W(O-t-Bu) (**4a$_W$**)	1.8	1.4(0.6)	0.8(0.4)
W[OCMe(CF$_3$)$_2$] (**4b$_W$**)	12	1.8(1.1)	0.15(0.2)
W(OSiPh$_3$) (**4c$_W$**)	100	~ 50	~ 0.5
W(O-2,6-C$_6$H$_3$) (**4d$_W$**)	5.6	2(2)	0.4(0.4)

The K_{eq} values in Table 1 are all 2-3 orders of magnitude smaller than those observed for a large number of Mo bisalkoxide imido alkylidene complexes in benzene or toluene.[17] K_{eq} values in Mo bisalkoxide complexes[17] are approximately the same order of magnitude as those listed in Table 1 when data are obtained in THF-d_8 as a consequence of THF binding more strongly to the *anti* form and therefore shifting the equilibrium in that direction. We propose that the "low" K_{eq} values in Table 1 are simply a consequence of the demanding steric bulk of the NAr* ligand and therefore destabilization of the *syn* isomer relative to the *anti* isomer.

The values for K_{eq} for $Mo(OSiPh_3)$ (**4c$_{Mo}$**) and $W(OSiPh_3)$ (**4c$_{W}$**) (26 and 100, respectively) are consistent with the larger steric demand of the $OSiPh_3$ ligand compared with the three other OR ligands.

^{1}H-^{1}H EXSY studies were conducted to obtain the rate constants for alkylidene rotation for **4a**, **4b**, and **4d** for Mo and W (Table 1).[25] The relatively large values for K_{eq} for $Mo(OSiPh_3)$ (**4c$_{Mo}$**) and $W(OSiPh_3)$ (**4c$_{W}$**) (26 and 100, respectively) did not allow us to obtain rate constants for interconversion of *syn* and *anti* isomers using the ^{1}H-^{1}H EXSY method. Therefore, **4c$_{Mo}$** and **4c$_{W}$** were photolyzed[17] at 350 nm at −78 °C to generate a larger proportion of the *anti* isomer. Rate constants were obtained over a 20 °C range (−20 °C to −40 °C for **4c$_{Mo}$** and −40 °C to −60 °C for **4c$_{W}$**) for the rotation of the *anti* alkylidene to the *syn* form, and the data were extrapolated to give k_f at 21 °C. Because rate constants can only be obtained over a small temperature range, k_f at 21 °C is not highly accurate and is therefore listed with only one significant figure in Table 1.

The values for k_f for the four Mo complexes (**4a$_{Mo}$**, **4b$_{Mo}$**, **4c$_{Mo}$**, and **4d$_{Mo}$**) vary from 0.029 to 0.10 while the values for k_r vary from 0.011 to 0.06. For comparison, k_f for $Mo(NAr)(CHCMe_2Ph)(OTPP)(Pyr)$ (OTPP = 2,3,5,6-tetraphenylphenoxide) at 21 °C has been found to be 0.67 s^{-1},[4b] roughly an order of magnitude larger. Another example is k_f for $Mo(NAd)(CHCMe_2Ph)(OHIPT)(Pyr)$ (Ad = 1-adamantyl) at 298 K, which is 0.96 s^{-1}.[4d] For $Mo(NAd)(CHCMe_2Ph)(OHIPT)(Pyr)$ the equilibrium constant is estimated to be on the order of 4000 or more and the value for k_r therefore is 2.5 x 10^{-4} s^{-1} or less. Although few data are available, we can tentatively draw the conclusion that the NAr* ligand not only destabilizes the *syn* isomer, but restricts the rate of *anti* to *syn* alkylidene rotation. Both are consistent with the unusually large steric demand of the NAr* ligand.

The data in Table 1 can be compared to data for $Mo(NAr)(CHR)(OR')_2$ complexes.[17] For $Mo(NAr)(CHCMe_2Ph)(OR)_2$ complexes in toluene the k_f values at 298 K for OR = O-t-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and $OC(CF_3)_3$ are ~500 (estimated), 6.8, 0.10, and 0.0015 s^{-1}, respectively. This is a dramatic trend that spans approximately five orders of magnitude. Since the K_{eq} values for this series of bisalkoxides (in toluene at 298 K) are 1200, 1800, 1400, and 190, the k_r values are 2-3 orders of magnitude smaller than k_f. The most obvious reason why the rates of interconversion vary more dramatically in bisalkoxides than in the MAP species in Table 1 is that MAP species contain only one alkoxide, so the "alkoxide effect" is diluted in MAP species. Another possibility is that in a MAP species, in which the metal is a stereogenic center, the alkylidene might rotate in only one direction, one that is regulated largely by the pyrrolide ligand, which is the same in all the MAP species in Table 1. The "alkoxide effect" would again be diluted, perhaps dramatically. Finally, it should be noted that a "bending" of the NAr* ligand in bisalkoxide complexes[17] was proposed to stabilize the intermediate alkylidene that has rotated by 90°. One might expect that the NAr* ligand would not bend as readily as (e.g.) the 2,6-diisopropylphenyl ligand, which also could contribute to a less dramatic variation in the MAP species than in the bisalkoxide complexes. What is required are k_f data for $Mo(NR)(CHR')(Me_2Pyr)(OR")$ species in which OR" is varied widely and R is constant. Currently, we know k_f at 298 K only for $Mo(NAr)(CHCMe_2Ph)(OTPP)(Pyr)$ (0.67 s^{-1})[4b] and $Mo(NAd)(CHCMe_2Ph)(OHIPT)(Pyr)$ (0.96 s^{-1}).[4d]

Another important feature of the data in Table 1 is that the values for k_f are 1-2 orders of magnitude larger for W than for analogous Mo compounds. This result is consistent with reported data for k_f for $M(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ (M = Mo or W) complexes.[17] Values for k_f for $W(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ over a range of temperatures extrapolated to −27.4 °C gave k_f = 153 x 10^{-4} s^{-1}, while k_f for $Mo(NAr)(CHCMe_3)[OCMe(CF_3)_2]_2$ at −27.4 °C was found to be 2.26 x 10^{-4} s^{-1}. The value for W is 68 times that for Mo. For the complexes listed in Table 1, k_f values are larger for W by a factor of 28 (for O-t-Bu), 62 (for $OCMe(CF_3)_2$), ~100 (for $OSiPh_3$), and 20 (for O-2,6-$Me_2C_6H_3$) at 21 °C. A similar trend was observed for rotation of a methylidene ligand in W complexes versus one in Mo complexes.[26] The rate of methylidene rotation in $W(NAr)(CH_2)(OTPP)(Me_2Pyr)$ at 20 °C was 90 s^{-1}, while in $Mo(NAr)(CH_2)(OHIPT)(Me_2Pyr)$ the rate was <0.2 s^{-1}. Although the quantity of data is again relatively small and direct comparisons are few, the trend is clearly toward a more rapid interconversion of alkylidenes for W versus Mo.

CONCLUSIONS

Molybdenum and tungsten alkylidene compounds that contain the 2,6-dimesitylphenylimido (NAr*) ligand have been synthesized and several MAP species for both Mo and W prepared. The demanding steric bulk of the NAr* ligand is reflected in the relatively low K_{eq} values ([*syn*]/[*anti*]) along with a slower rate of conversion of the *anti* to the *syn* alkylidene isomers in NAr* complexes relative to complexes that contain a smaller imido ligand, even NAr. Alkylidene rotation in four-coordinate MAP species was found to be at least an order of magnitude larger in W(NAr*) complexes than in Mo(NAr*) complexes. It remains to be seen how the steric bulk of the NAr* ligand will effect the reactivity of M(NAr*) MAP species, the stability of metallacyclobutanes, and the performance of M(NAr*) MAP species in a variety of olefin metathesis reactions.

ASSOCIATED CONTENT

Supporting Information. Experimental details for the synthesis of all compounds along with Tables and CIF files that provide crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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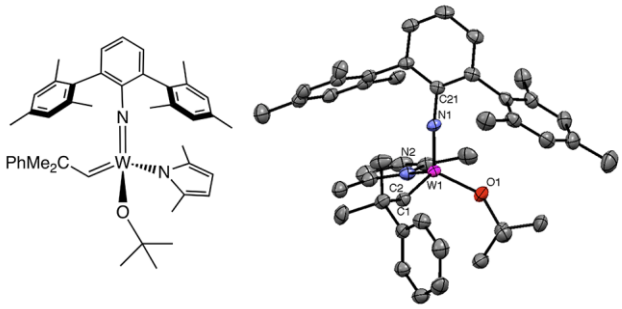
Table of Contents



Synthesis of Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Alkylidene Complexes That Contain a 2,6-Dimesitylphenyl Imido Ligand

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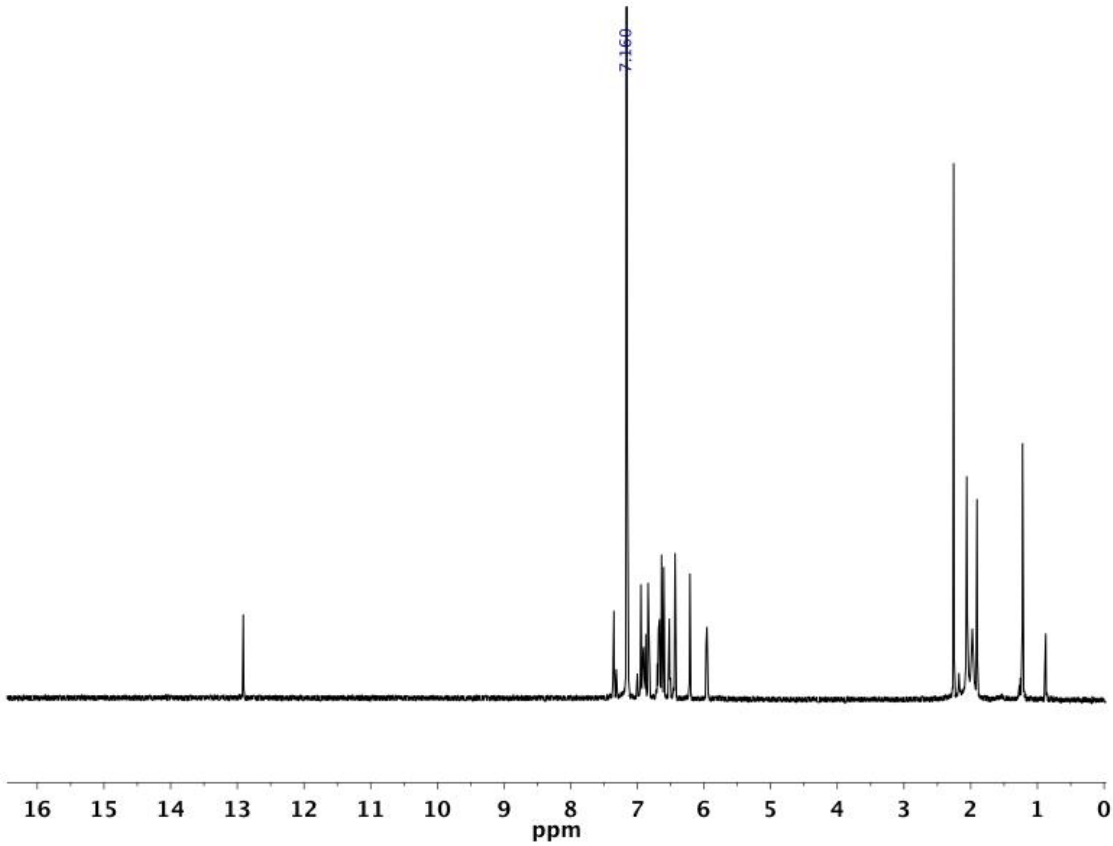
EXPERIMENTAL

General Considerations. All air-sensitive manipulations were performed under nitrogen atmosphere in a glovebox or an air-free dual-manifold Schlenk line. All glassware was oven-dried and allowed to cool under vacuum before use. NMR spectra were obtained on Varian 300 MHz, Varian 500 MHz, Bruker 400 MHz, or Bruker 600 MHz spectrometers. ^{1}H and ^{13}C NMR spectra are reported in δ (parts per million) relative to tetramethylsilane, and referenced to residual ^{1}H/^{13}C signals of the deuterated solvent (^{1}H (δ) benzene 7.16, chloroform 7.27, methylene chloride 5.32, toluene 2.09; ^{13}C (δ) benzene 128.39, chloroform 77.23, methylene chloride 54.00, toluene 20.40). ^{19}F NMR spectra are reported in δ (parts per million) relative to trichlorofluoromethane and referenced using an external standard of fluorobenzene (δ -113.15). Diethyl ether, toluene, tetrahydrofuran, pentane, benzene, dichloromethane, and dimethoxyethane were sparged with nitrogen and passed through activated alumina. All solvents were stored over 4 Å molecular sieves. Liquid reagents were degassed, brought into the glovebox, and stored over 4 Å molecular sieves. HCl solution in Et_2O was prepared by bubbling gaseous HCl through Et_2O at atmospheric pressure. Lipyr and $LiMe_2Pyr$ were prepared by addition of one equivalent of nButyllithium to a cold pentane solution of pyrrole or 2,5-dimethylpyrrole, and the solids were collected on a frit, washed with pentane and dried *in vacuo*. $Mo(NAr^*)(CHCMe_2Ph)Cl_2(py)$,[1] $Mo(NAr^*)(CHCMe_2Ph)(Me_2pyr)_2$,[1] $W(NtBu)_2Cl_2(py)_2$[2] were prepared according to literature procedures. All other reagents were used as received.

$Mo(NAr^*)(CHCMe_2Ph)(Pyr)_2(py)$ ($\mathbf{1_{Mo}}$). Solid LiPyr (56 mg, 0.77 mmol) was added to a −25 °C stirred suspension of $Mo(NAr^*)(CHCMe_2Ph)Cl_2(py)$ (269 mg, 0.38 mmol) in 8 ml Et_2O. The solution became brown and a yellow precipitate formed. After 2 h, the volatiles were removed *in vacuo*. The yellow solid was extracted with benzene and the mixture was filtered through a pipette filter. The volatiles were removed from the filtrate to leave a brown oil. The oil was triturated by adding 3 mL pentane and stirring until a yellow powder formed. The mixture was chilled to −25 °C and then the yellow solid was collected on a frit and washed with 3 x 1 mL cold pentane and then dried in vacuo; yield 280 mg, 96%: ^{1}H NMR (C_6D_6) δ 12.910 (s, 1H, $^{1}J_{CH}$ = 145 Hz, Mo=C*H*), 7.355 (d, 1H, J_{HH} = 5 Hz, py*H*), 6.946 – 6.826 (overlapping signals, 7H, Ar*H*), 6.714 – 6.664 (overlapping signals, 3H, Ar*H*), 6.628 (s, 2H), 6.584 (s, 2H), 6.517 (d, 2H, J_{HH} = 7 Hz), 6.471 (t, 1H, J_{HH} = 7 Hz), 6.423 (s, 2H), 6.204 (s, 2H), 5.977 (t, 2H, J_{HH} = 7 Hz) 2.255 (s, 6H, MesCH_3), 2.058 (br s, 6H, MesCH_3), 1.971 (br s, 6H, MesCH_3), 1.903

(s, 3H, Mo=CHC*Me*$_2$Ph), 1.223 (s, 3H, Mo=CHC*Me*$_2$Ph); ^{13}C {^{1}H} NMR (C_6D_6) δ 319.1 (Mo=*C*), 155.5, 152.5, 146.5, 138.0, 137.7, 137.2, 135.5, 130.1,129.8, 129.6, 128.9, 128.7, 128.5, 128.3, 128.0, 127.5, 125.9, 125.8, 124.1, 108.6, 108.1, 52.0 (Mo=CH*C*Me$_2$Ph), 32.0 (Mo=CHC*Me*$_2$Ph), 26.8 (Mo=CHC*Me*$_2$Ph), 21.7 (Mes*Me*), 21.6 (Mes*Me*), 21.5 (Mes*Me*). Anal. Calcd for $C_{47}H_{50}MoN_4$: C, 73.61; H, 6.57; N, 7.31. Found: C, 73.46; H, 6.52; N, 7.30.

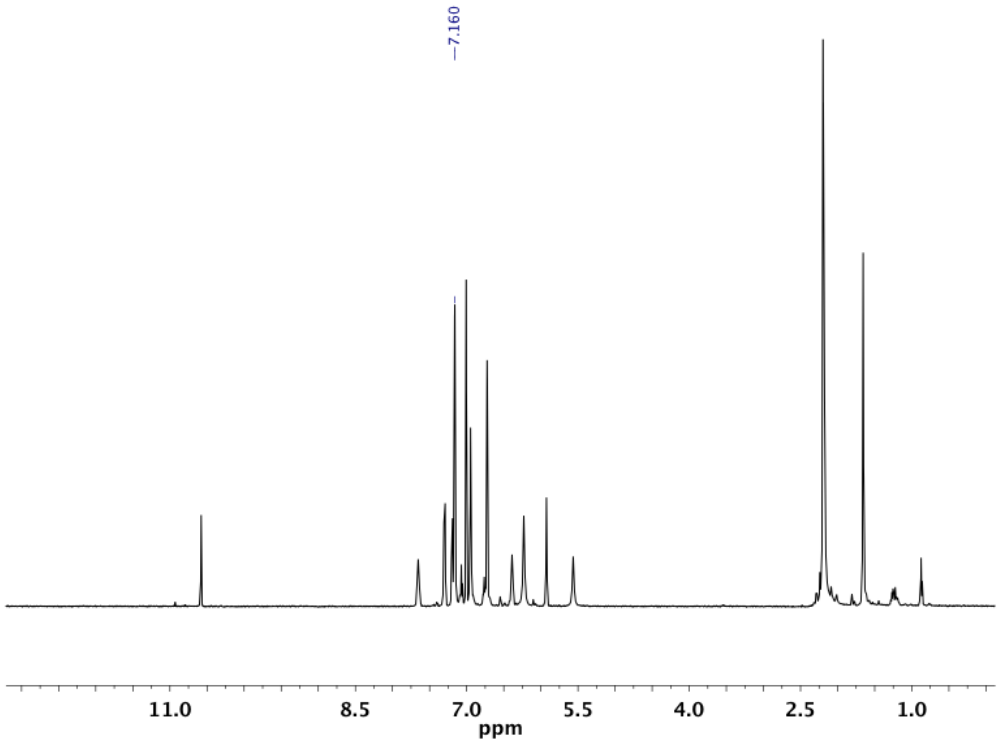
^{1}H NMR in C_6D_6:



W(NAr*)(CHCMe$_2$Ph)(Pyr)$_2$(py) (1$_W$). Solid Lipyr (49.3 mg, 0.675 mmol) was added to a solution of W(NAr*)(CHCMe$_2$Ph)Cl$_2$(py), **8**, (90.0 mg, 0.113 mmol) in Et$_2$O and stirred 8 h at ambient temperature. The volatiles were removed *in vacuo*. The brown oil was extracted with toluene and benzene and filtered through a pipette filter. The volatiles were removed *in vacuo* from the filtrate to leave a yellow oil, which was triturated with pentane (2 mL) by stirring for 16 h. The mixture was cooled to −25 °C, and the yellow power was collected on a fritted filter and

washed with cold pentane to give 75.3 mg, 78 %. ^{1}H NMR (C_6D_6) δ 10.579 (s, 1H, W=C*H*), 7.654 (s, 2H), 7.298 (d, 2H, J_{HH} = 8 Hz), 7.175 (t, 2H, J_{HH} = 8 Hz), 7.072 (t, 1H, J_{HH} = 8 Hz), 7.007 (s, 4H), 6.948 (s, 2H), 6.763 (t, 1H, J_{HH} = 8 Hz), 6.725 (s, 4H), 6.389 (t, 1H, J_{HH} = 6 Hz), 6.230 (s, 2H), 5.924 (s, 2H), 5.565 (s, 2H), 2.196 (18 H, C_6H_2*Me*$_3$), 1.656 (s, 6H, W=CHC*Me*$_2$Ph); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 284.6 (W=*C*H), 154.6, 152.4, 149.6, 139.1, 137.9, 137.7, 137.1, 133.1, 129.6, 129.1, 128.3, 127.1, 126.0, 125.7, 125.6, 124.8, 107.9, 49.0, 31.8, 21.4, 20.8. Anal. calcd for $C_{47}H_{50}N_4W$: C, 66.04; H, 5.90; N, 6.55. Found: C, 66.14; H, 5.88; N, 6.22.

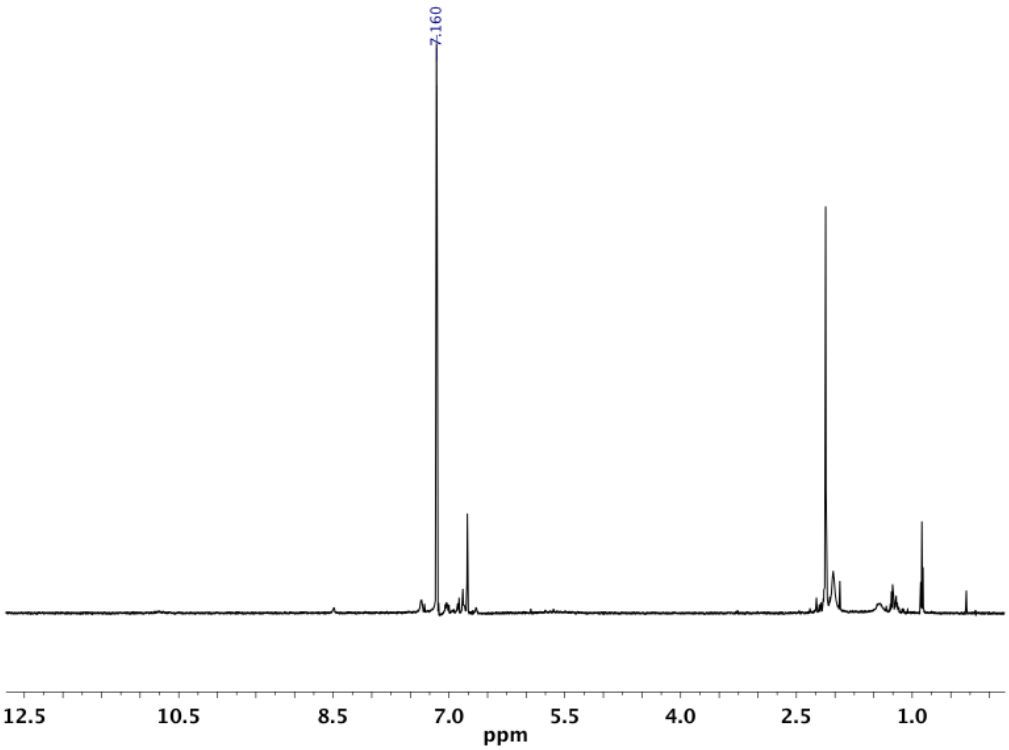
^{1}H NMR in C_6D_6:



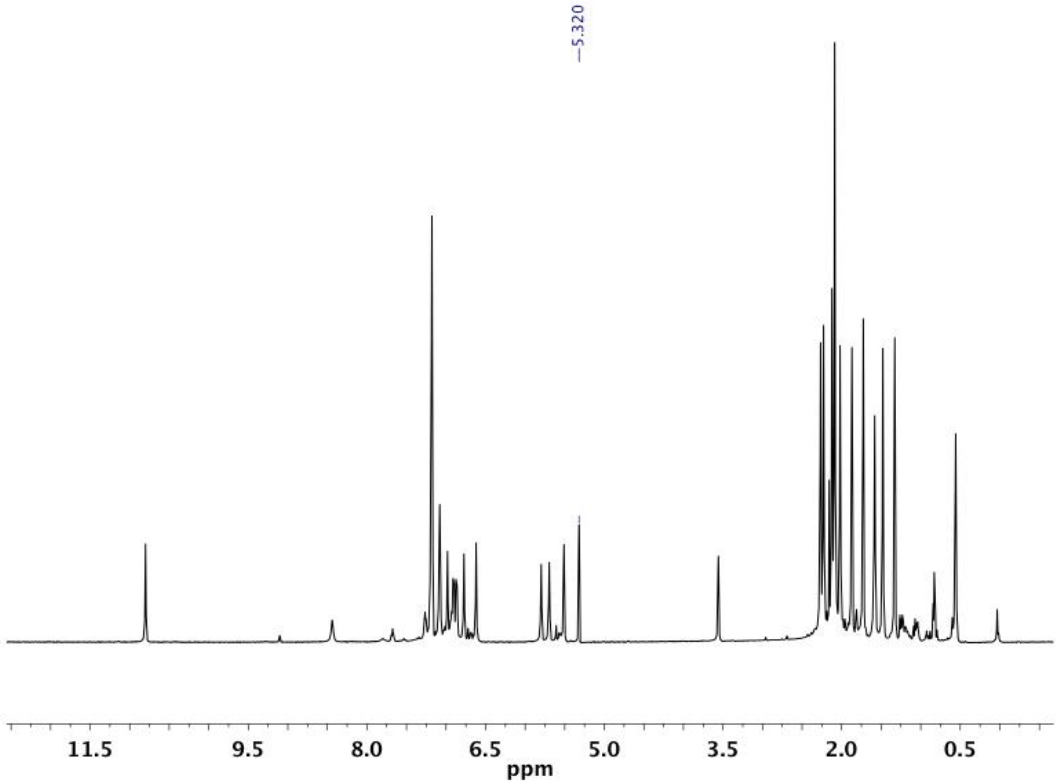
W(NAr*)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (2$_W$). Solid LiMe$_2$pyr (235 mg, 2.33 mmol) was added in one portion to a −25 °C, stirring solution of W(NAr*)(CHCMe$_2$Ph)Cl$_2$(py), **8** (922 mg, 1.16 mmol) in 25 mL Et$_2$O. The mixture was stirred 16 h at ambient temperature. The volatiles were removed *in vacuo*. The dark yellow oil was extracted with pentane and filtered through frit with a pad of Celite. The pentane volume was reduced *in vacuo*, and a yellow precipitate formed. The mixture was cooled to −25 °C for 2 h. The yellow solid was collected on a frit and washed with cold pentane (760 mg, 79 %). ^{1}H NMR (CD_2Cl_2, 20 °C) δ 10.528 (br s, 1H, W=C*H*), 7.222 – 7.189 (overlapping signals, Ar*H*, 5H), 7.104 (m, 1H, Ar*H*), 6.945 (d, J_{HH} = 8

Hz), 6.856 (br s, 4H, Ar*H*), 6.4 – 4.4 (br s, $NC_4H_2Me_2$), 2.227 (s, 6H, *p*-Mes CH_3), 2.008 (br s, 12H), 1.835 (br s, 12H), 1.5 – 0.9 (br s, 6H, CHCMe_2Ph); ^{1}H NMR (CD_2Cl_2, −40 °C) δ 10.799 (s, 1H, W=C*H*, $^1J_{CH}$ = 126 Hz), 7.179 (s, 5H, Ar*H*), 7.080 (s, 2H, Ar*H)*, 6.906 (d, 1H, $^1J_{HH}$ = 8 Hz, Ar*H*), 6.868 (d, 1H, $^1J_{HH}$ = 8 Hz, Ar*H*), 6.774 (s, 1H, Ar*H*), 6.620 (s, 1H, Ar*H*), 5.797 (s, 1H, Me_2pyr*H*), 5.696 (s, 1H, Me_2pyr*H*), 5.510 (s, 1H, Me_2pyr*H*), 3.558 (s, 1H, Me_2pyr*H*), 2.266 (s, 3H), 2.228 (s, 3H), 2.123 (s, 3H), 2.088 (s, 6H), 2.020 (s, 3H), 1.870 (s, 3H), 1.726 (s, 3H), 1.582 (s, 3H), 1.479 (s, 3H), 1.328 (s, 3H), 0.558 (s, 3H); ^{13}C{^{1}H} NMR (CD_2Cl_2, −40 °C) δ 285.3 (Mo=*C*H), 158.1, 153.6, 139.8, 138.3, 138.0, 137.9, 137.6, 137.6, 137.1, 136.8, 136.6, 136.5, 131.8, 130.3, 129.4, 128.4, 128.1, 128.0, 127.3, 125.7, 125.5, 125.4, 109.5, 108.6, 105.4, 99.4, 98.1 (Aromatic), 51.5 (W=CH*C*Me_2Ph), 33.9, 32.5, 22.2, 21.2, 21.0, 21.0, 20.8, 20.4, 20.1, 19.1, 19.0, 13.0 (*C*H_3). Anal calc'd for $C_{46}H_{53}N_3W$ C, 66.42; H, 6.42; N, 5.05; Found: C, 66.26; H, 6.47; N, 4.98.

^{1}H NMR in C_6D_6 at 20 ºC:

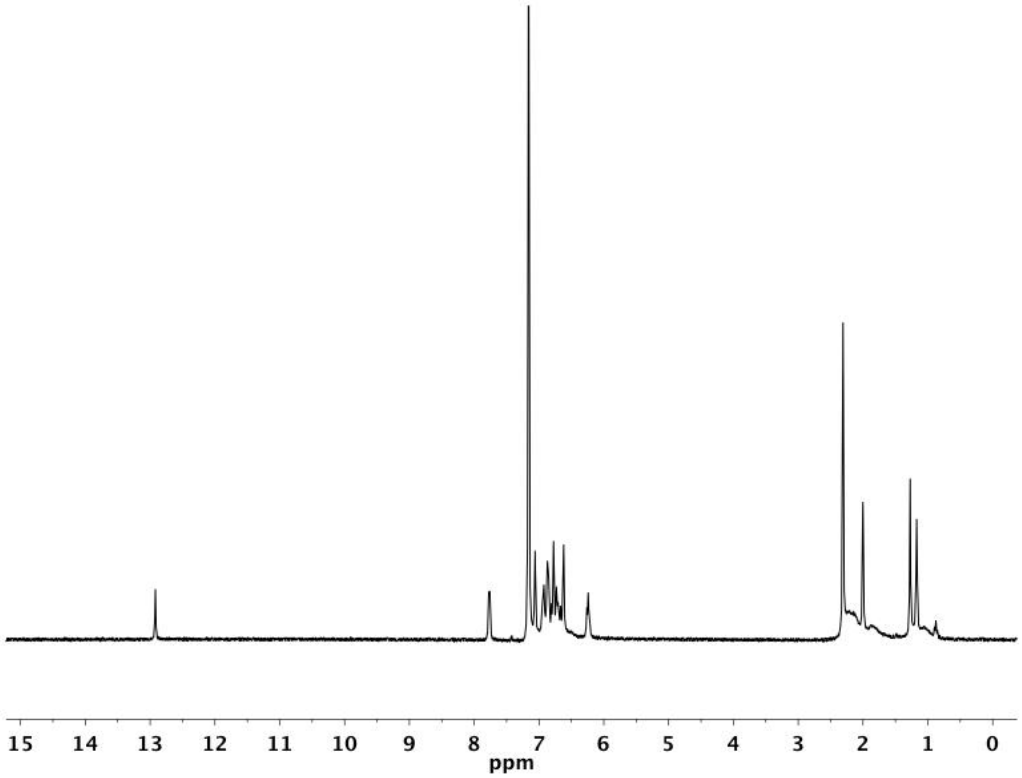


^{1}H NMR in CD_2Cl_2 at −40 °C:



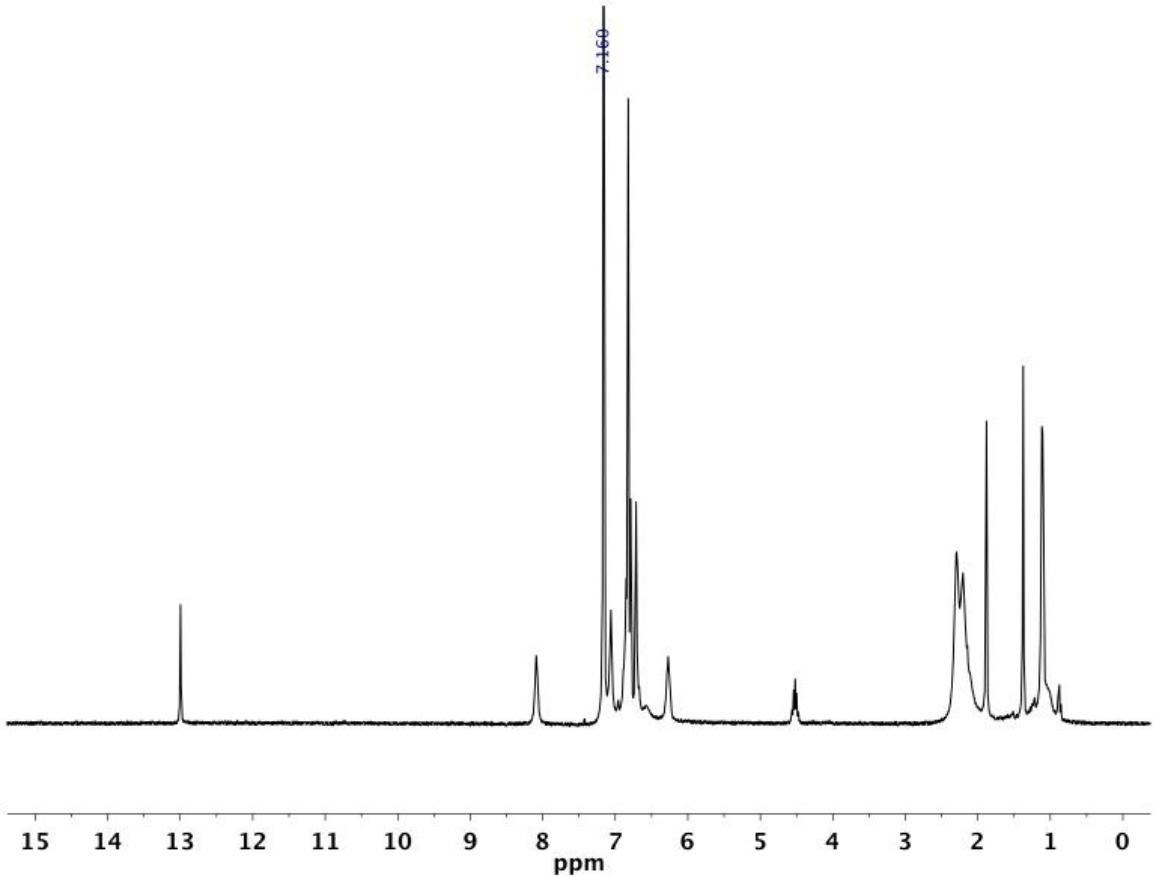
Mo(NAr*)(CHCMe$_2$Ph)(pyr)[OCMe(CF$_3$)$_2$](py) (3a). Hexafluoro-t-butanol (6.4 μL, 0.052 mmol) was added to Mo(NAr*)(CHCMe$_2$Ph)(pyr)$_2$(py), **1$_{Mo}$**, (40 mg, 52 μmol) in 2 mL C_6H_6. After 45 m, the reaction mixture was filtered through a pipette filter. The volatiles were removed from the filtrate. To the resulting brown oil, 2 mL pentane was added and a yellow solid formed. The mixture was cooled to −25 °C, after which the yellow solid was collected on a frit and washed with 2 x 0.5 mL cold pentane, and dried *in vacuo*; yield 31 mg, 68 %: ^{1}H NMR (C_6D_6) δ 12.919 (s, 1H, Mo=C*H*) 7.767 (d, J_{HH} = 6 Hz, 2H, Pyridine), 7.060 (s, 2H), 6.923 – 6.619 (overlapping signals, 15H), 6.241 (t, J_{HH} = 6 Hz, 2H), 2.309 (s), 2.207 (br s), 2.002 (s), 1.882 (br s, 18 H integrated over previous 4 signals), 1.273 (s), 1.172 (s), 1.049 (br s, 9 H integrated over previous 3 signals); ^{1}H NMR (CD_2Cl_2, alkylidene) δ 12.739 ($^1J_{CH}$ = 148 Hz); ^{13}C NMR (CD_2Cl_2) δ 326.8 (Mo=*C*H), 153.8, 152.4, 146.4, 138.5, 132.1, 129.9, 128.4, 127.5, 126.4, 126.3, 124.4, 106.5, 82.9 (m, only 3 lines visible above baseline, J_{CF} = 27 Hz), 52.5, 31.1, 27.8, 21.5 (br s), 19.9, 16.0; ^{19}F{^{1}H} NMR (C_6D_6) δ -76.12 (quartet, J_{FF} = 9 Hz), 77.06 (quartet, J_{FF} = 9 Hz). Anal. Calcd for $C_{47}H_{49}F_6MoN_3O$: C, 64.01; H, 5.60; N, 4.76. Found: C, 63.97; H, 5.63; N, 4.54.

^{1}H NMR in C_6D_6:



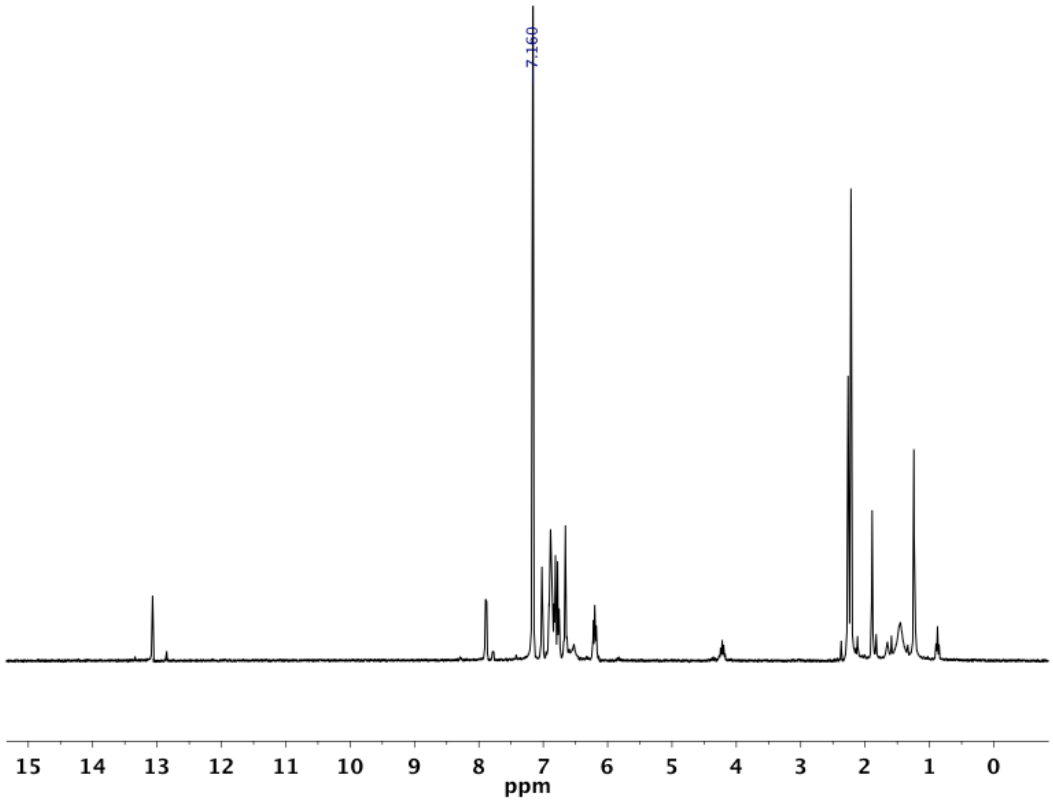
Mo(NAr*)(CHCMe$_2$Ph)(pyr)(O^{i}Pr)(py) (3b). HO^{i}Pr was added to a stirred solution of Mo(NAr*)(CHCMe$_2$Ph)(pyr)$_2$(py), **1$_{Mo}$** (45.4 mg, 59.2 μmol), in 2 mL benzene. After 1.5 h, the reaction mixture was filtered through a pipette filter and the volatiles removed *in vacuo* from the filtrate. Pentane (1 mL) was added and the mixture was stirred at ambient temperature for 1 h and then cooled to −25 °C. The resulting yellow solid was collected on a frit and dried *in vacuo*; yield 24.2 mg, 70 %: ^{1}H NMR (C_6D_6) δ 12.996 (s, 1H), 8.090 (br s, 2H, pyridine), 7.060 (s, 2H), 6.889 – 6.573 (overlapping signals, 15 H), 6.270 (br s, 2H), 4.520 (septet, J_{HH} = 6 Hz, 1H, OC*H*Me$_2$), 2.292, 2.205, 2.144 (overlapping br s, 18H, Mes*Me*), 1.881 (s, 3H, Mo=CHC*Me$_2$*Ph), 1.375 (s, 3H, Mo=CHC*Me$_2$*Ph), 1.116 (d, J_{HH} = 6 Hz), 1.107 (d, J_{HH} = 6 Hz, 6H integrated together with previous signal); ^{13}C{^{1}H} NMR (C_6D_6) δ 319.0 (Mo=*C*H), 153.9, 152.0, 147.8, 137.6, 132.1, 129.3, 128.9, 128.7, 128.1, 126.3, 126.3, 125.6, 123.8, 107.8, 74.3, 51.2, 31.3, 29.4,27.3, 21.7. Anal. Calcd for $C_{46}H_{53}MoN_3O$: C, 72.71; H, 7.03; N, 5.53. Found: C, 72.47; H, 6.91; N, 5.36.

^{1}H NMR in C_6D_6:



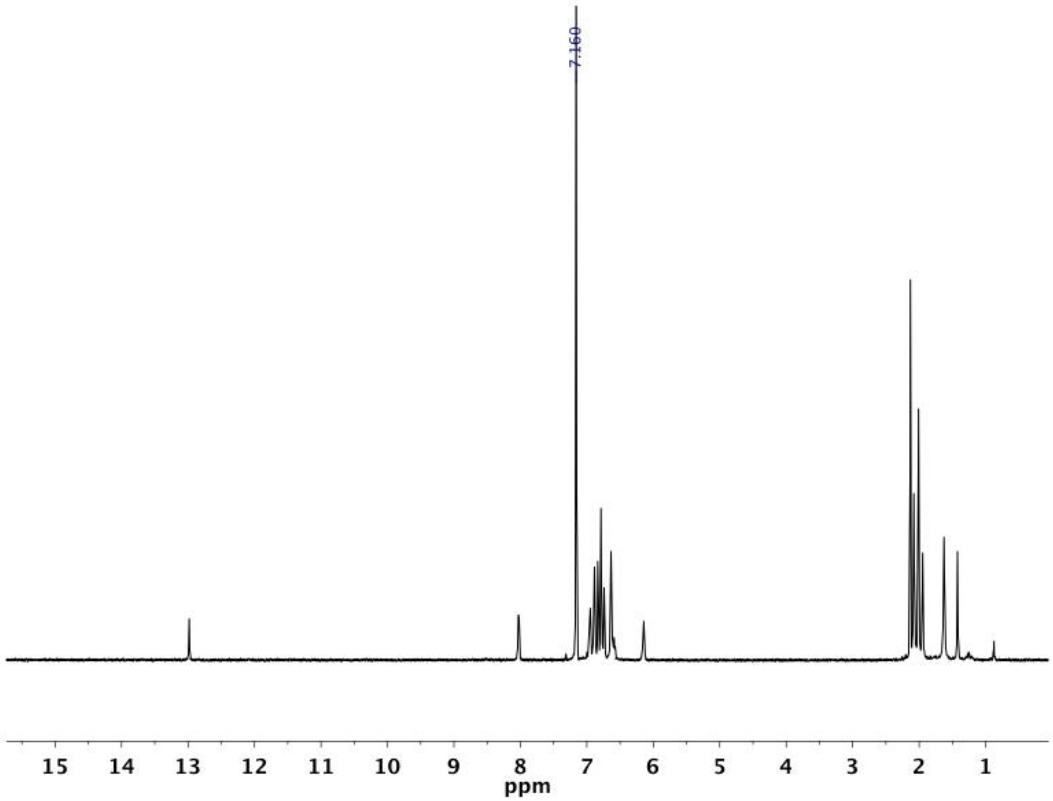
Mo(NAr*)(CHCMe$_2$Ph)(pyr)[OCH(CF$_3$)$_2$](py) (3c). Hexafluoroisopropanol (4.9 μL, 0.047 mmol) was added to a solution of Mo(NAr*)(CHCMe$_2$Ph)(pyr)$_2$(py), **1$_{Mo}$** (35.6 mg, 0.051 mmol), in 1.5 mL benzene. The reaction mixture was stirred for 1.5 h and filtered through a frit. The volatiles were removed *in vacuo* from the filtrate. Pentane (2 mL) was added to the remaining oil. The mixture was cooled to −25 °C, and the yellow solid was collected on a fritted filter and dried *in vacuo*; yield 27 mg, 76%: ^{1}H NMR (C_6D_6) δ 13.069 (s, 1H, Mo=C*H*), 7.888 (d, 2H, J_{HH} = 5 Hz), 7.021 (s, 2H, Mes $C_6H_2Me_3$), 6.897 – 6.754 (overlapping signals, 13 H), 6.655 (s, 2H, Mes $C_6H_2Me_3$), 6.200 (t, 2H, J_{HH} = 7 Hz), 4.220 (septet, J_{CF} = 7 Hz, 1H, OC*H*(CF$_3$)$_2$), 2.264 (s, 6H, MesC*H*$_3$), 2.219 (s, 6H, MesC*H*$_3$), 1.890 (s, 3H, Mo=CHC*Me*$_2$Ph), 1.455 (br s, 6H, MesC*H*$_3$), 1.242 (s, 3H, Mo=CHC*Me*$_2$Ph)); ^{1}H NMR (CD_2Cl_2, alkylidene) δ 12.887 ($^1J_{CH}$ = 148 Hz); ^{13}C NMR (CD_2Cl_2) δ 324.4 (Mo=*C*H), 153.8, 153.2, 152.3, 146.5, 139.0, 137.4, 136.3, 130.2, 129.9, 128.9, 127.9, 126.2, 124.8, 75.8 (m, 5 lines visible above baseline, J_{CF} = 30 Hz), 52.2, 30.8, 27.7, 21.4, 21.4, 20.0; ^{19}F{^{1}H} NMR (C_6D_6) δ -73.34 (apparent quintet, J = 9 Hz, 3F), -74.41 (apparent quintet, J = 9 Hz, 3F). Anal. Calcd for $C_{46}H_{47}F_6MoN_3O$: C, 63.66; H, 5.46; N, 4.84. Found: C, 63.46; H, 5.51; N, 4.72.

^{1}H NMR in C_6D_6:



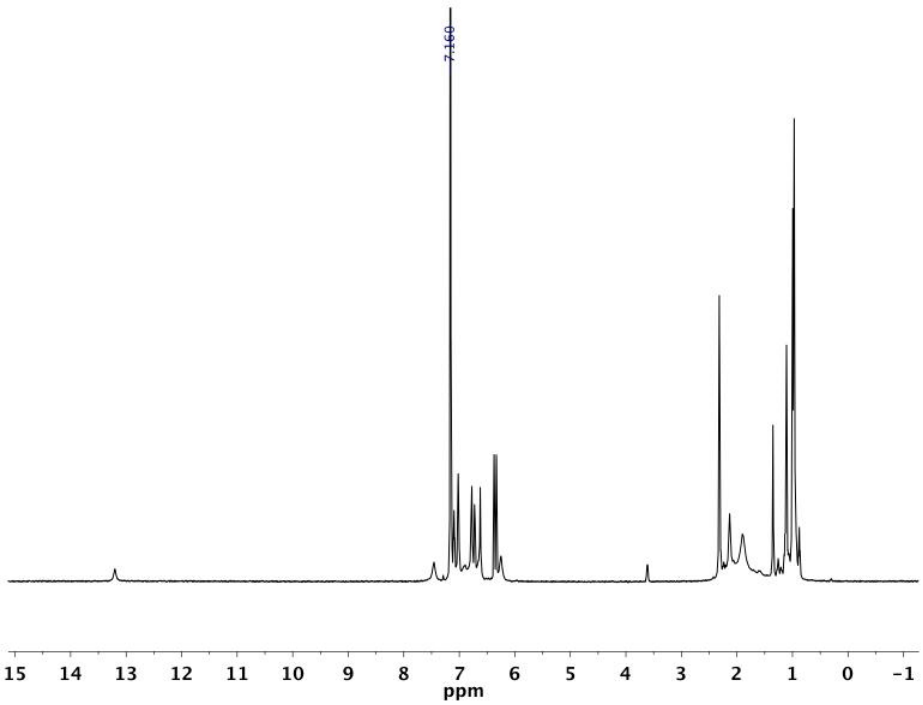
Mo(NAr*)(CHCMe$_2$Ph)(pyr)(O2,6-Me$_2$C$_6$H$_3$)(py) (3d). Solutions of Mo(NAr*)(CHCMe$_2$Ph)(Pyr)$_2$(py), **1$_{Mo}$**, (34 mg, 0.044 mmol) and 2,6-Me$_2$C$_6$H$_3$OH (5.4 mg, 0.044 mmol) each in 0.5 mL C_6D_6 were combined in a Teflon-stoppered NMR tube. After 2 h, the reaction mixture was filtered through a pipette filter with Celite. The volatiles were removed *in vacuo* from the filtrate. Two mL of pentane were added to the residue and the mixture was cooled to −25 °C. The yellow solid was collected on a frit and washed with cold pentane; yield 27 mg, 76 %: ^{1}H NMR (C_6D_6) δ 13.982 (s, 1H, Mo=C*H*), 8.026 (d, 2H, J_{HH} = 5 Hz), 6.955 (d, 2H, J_{HH} = 7 Hz), 6.901 – 6.873 (overlapping signals, 4H), 6.836 (s, 1H), 6.822 (s 1H), 6.787 – 6.763 (overlapping signals, 5H), 6.740 (s, 2H), 6.635 (s, 4H), 6.590 (t, J_{HH} = 8 Hz,1H), 6.143 (t, 2H, J_{HH} = 7 Hz), 2.133 (s, 6H, MesC*H*$_3$), 2.080 (s, 6H, MesC*H*$_3$), 2.010 (s, 6H, MesC*H*$_3$), 1.947 (s, 3H, Mo=CHC*Me*$_2$Ph), 1.627 (s, 6H, C$_6$H$_3$*Me*$_2$OH), 1.423 (s, 3H, Mo=CHC*Me*$_2$Ph); ^{1}H NMR (CD_2Cl_2, alkylidene) δ 12.768 ($^1J_{CH}$ = 148 Hz); ^{13}C NMR (CD_2Cl_2) δ 321.2 (Mo=*C*H), 161.0, 154.2, 151.9, 149.3, 140.5, 139.0, 137.4, 137.4, 137.0, 131.4, 130.5, 129.3, 129.2, 128.3, 128.2, 127.5, 127.3, 126.1, 126.0, 124.9, 119.4, 106.5, 52.2, 31.5, 29.3, 21.4, 21.3, 21.2, 19.0. Anal. Calcd for $C_{51}H_{55}MoN_3O$: C, 74.52; H, 6.74; N, 5.11. Found: C, 74.22; H, 6.56; N, 4.97.

^{1}H NMR in C_6D_6:



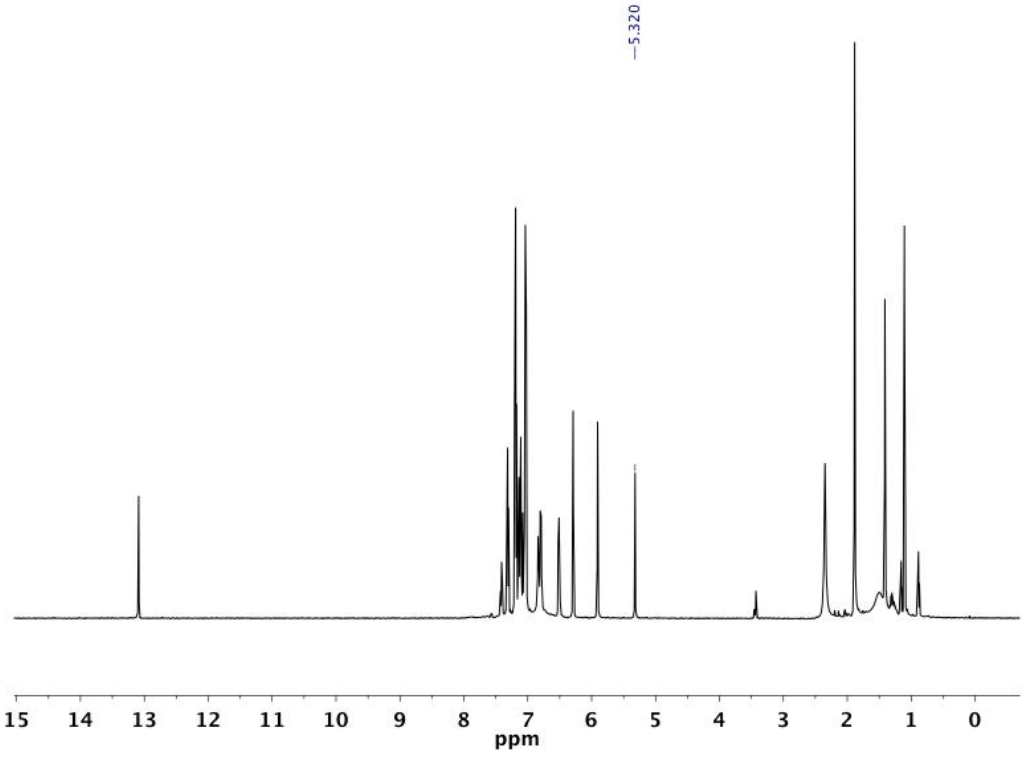
Mo(NAr*)(CHCMe$_2$Ph)(pyr)[OSi(i-Pr)$_3$](py) (3e). HOSi(i-Pr)$_3$ (8.8 μL, 44 μmol) was added to a suspension of Mo(NAr*)(CHCMe$_2$Ph)(pyr)$_2$(py), **1$_{Mo}$**, (34 mg, 44 μmol) in 0.7 mL C_6D_6 in a Telfon-stoppered NMR tube. A ^{1}H NMR spectrum obtained after 1 h shows complete consumption of starting materials. The reaction mixture was filtered through a pipette filter with Celite, and the volatiles removed *in vacuo* from the filtrate to leave a brown oil. Pentane (1 mL) was added to the residue and the mixture was cooled to −25 °C. The orange solid was collected on a frit filter and washed with cold pentane; yield 30 mg, 77 %: ^{1}H NMR (C_6D_6) δ 13.204 (br s, 1H, Mo=C*H*), 7.456 (br s, 2H), 7.094 (t, 2H, J_{HH} = 8 Hz), 7.019 (m, 4H), 6.774 (s, 3H), 6.727 (m, 2H), 6.623 (s, 2H), 6.373 (s, 2H), 6.332 (s, 2H), 6.253 (br s, 2H), 2.318 (s, 6H, MesC*H*$_3$), 2.131 (br s, MesC*H*$_3$), 1.900 (br s, MesC*H*$_3$, 12 H integrated with previous signal), 1.351 (s, 3H, Mo=CHC*Me*$_2$Ph), 1.298 – 1.137 (overlapping m, 3H, C*H*Me$_2$), 1.107 (s, 3H, Mo=CHC*Me*$_2$Ph), 0.995 (br m, CH*Me*$_2$), 0.969 (br m, CH*Me*$_2$, 18 H integrated together with previous signal); ^{13}C{^{1}H} NMR (CD_2Cl_2, –30 ºC) δ 321.5 (Mo=*C*H), 152.9, 151.6, 147.2, 139.4, 138.4, 138.3, 138.0, 137.8, 137.4, 136.7, 136.7, 136.2, 135.7, 135.1, 131.7, 129.7, 129.4, 129.2, 129.0, 128.5, 128.4, 128.1, 126.3, 126.1, 125.9, 124.1, 105.4, 51.1 (Mo=CH*C*Me$_2$Ph), 31.5, 28.3, 21.4, 21.4, 20.7, 20.6, 20.6, 20.4, 18.6, 18.6, 14.0. Anal. Calcd for $C_{52}H_{67}MoN_3OSi$: C, 71.45; H, 7.73; N, 4.81. Found: C, 71.19; H, 7.54; N, 4.86.

^{1}H NMR in C_6D_6:



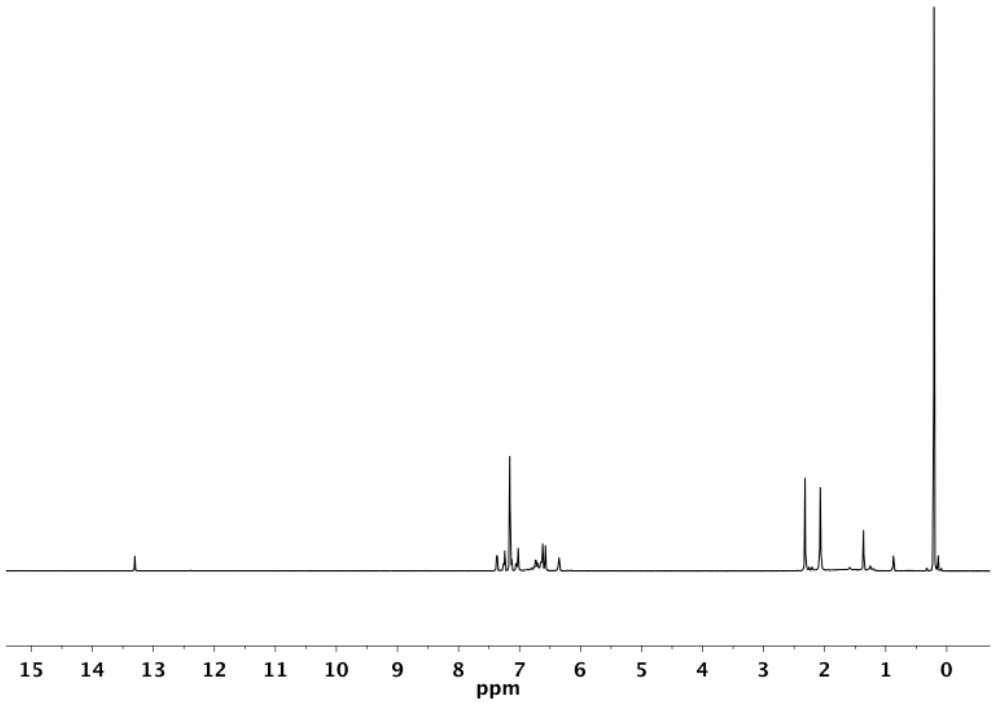
Mo(NAr*)(CHCMe$_2$Ph)(pyr)(OSiPh$_3$)(py) (3f). A solution of triphenylsilanol (14.8 mg, 0.054 mmol) in 1 mL toluene was added to a solution of Mo(NAr*)(CHCMe$_2$Ph)(pyr)$_2$(py), **1$_{Mo}$** (41 mg, 0.054 mmol), in 3 mL toluene and the reaction mixture was stirred for 5 h. The reaction mixture was filtered through a pipette filter with Celite, and the volatiles removed *in vacuo* from the filtrate. The residue was dissolved in 1:1 toluene:pentane mixture and the solution was cooled to −25 °C. The solid was collected on a frit, washed with cold pentane, and dried *in vacuo*. The filtrate was concentrated to collect a second crop in the same manner; total yield 26.1 mg, 50 %: ^{1}H NMR (C_6D_6) δ 13.320 (s, 1H, $^1J_{CH}$ = 148 Hz, Mo=C*H*), 7.375 (dd, 6H, J_{HH} = 8 Hz, J_{HH} = 2 Hz), 7.290 (d, 2H, J_{HH} = 5 Hz), 7.197 and 7.183 (overlapping s, 7 H), 7.049 – 6.931 (overlapping signals, 9 H), 6.796 – 6.703 (overlapping signals, 7 H), 6.584 – 6.548 (overlapping signals, 3H), 6.021 (t, 2H, J_{HH} = 7 Hz), 2.246 (s, 6H, Mes $C_6H_2Me_3$), 2.045 (s, 6H Mes $C_6H_2Me_3$), 1.756 (s, 3H, Mo=CHC*Me*$_2$Ph), 2.0 – 1.4 (very br s, 6H, Mes $C_6H_2Me_3$), 1.250 (s, 3H, Mo=CHC*Me*$_2$Ph). ^{1}H NMR (CD_2Cl_2, alkylidene) δ 13.089 ($^1J_{CH}$ = 147 Hz); ^{13}C NMR (CD_2Cl_2) δ 323.2, 152.6, 147.8, 138.8, 137.9, 137.0, 136.1, 132.2, 129.7, 129.3, 129.2, 128.8, 128.5, 127.8, 126.8, 126.7, 126.3, 124.3, 106.6, 52.5, 31.2, 28.8, 21.6, 21.1, 20.8. Analysis calc'd for $C_{52}H_{67}MoN_3OSi$: C,75.05; H, 6.30; N, 4.30. Experimental: C, 74.64; H, 6.04; N, 4.34.

^{1}H NMR in CD_2Cl_2:



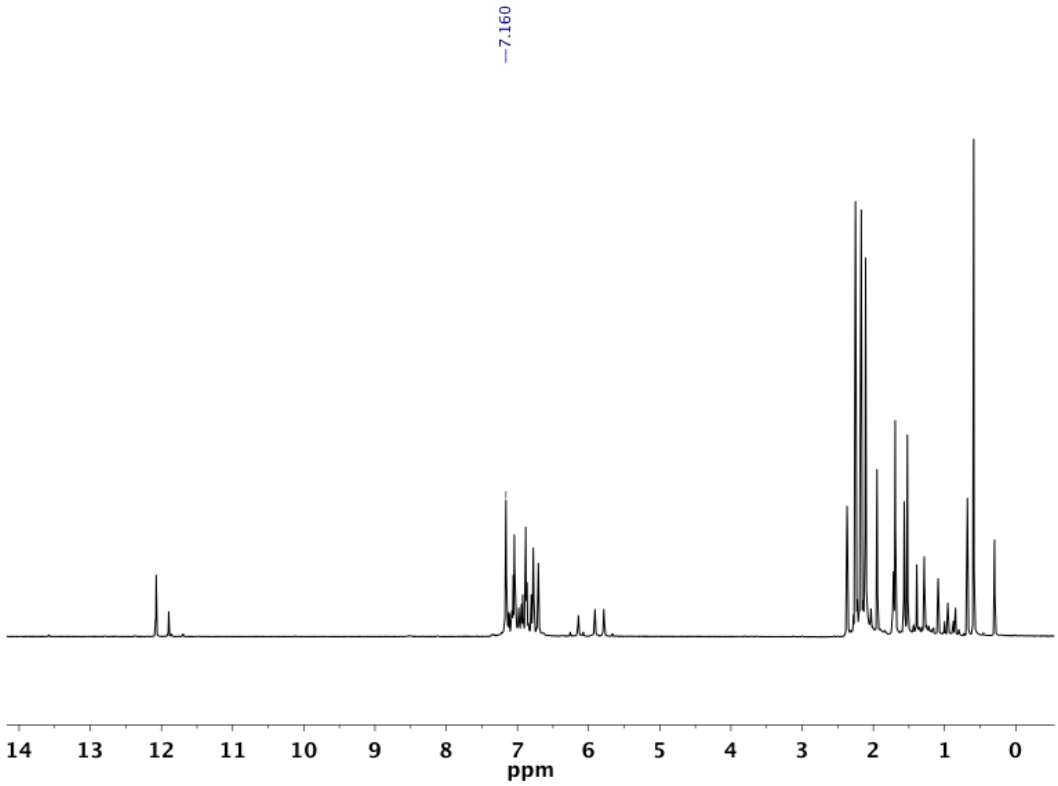
Mo(NAr*)(CHCMe$_2$Ph)(pyr)[OSi(SiMe$_3$)$_3$](py) (3g). A solution of HOSi(SiMe$_3$)$_3$ (14 mg, 0.053 mmol) in 0.3 mL C_6D_6 was added to a suspension of Mo(NAr*)(CHCMe$_2$Ph)(pyr)$_2$(py), **1$_{Mo}$** (40 mg, 0.052 mmol), in 0.3 mL C_6D_6 in a Teflon-stoppered NMR tube. A ^{1}H NMR spectrum obtained after 1 h shows that consumption of starting materials was complete. The reaction mixture was filtered through a pipette filter with Celite, and the volatiles were removed *in vacuo* from the filtrate. Pentane (1 mL) was added to the residue and the mixture was cooled to −25 °C. The dark yellow crystals were collected by decantation of the supernatant, and dried *in vacuo*; yield 31 mg, 61 %: ^{1}H NMR (C_6D_6) δ 13.303 (s, 1H, Mo=C*H*), 7.371 (d, 2H, J_{HH} = 5 Hz), 7.250 (d, 2H, J_{HH} = 8 Hz), 7.135 (d, 2H, J_{HH} = 8 Hz), 7.053 (d, 1H, J_{HH} = 7 Hz), 7.023 (s, 2H), 6.866 – 6.691 (overlapping signals, 4H), 6.653 – 6.621 (overlapping signals, 4H), 6.576 (s, 2H), 6.352 (t, 2H, J_{HH} = 7 Hz), 2.322 (s, 6H, Mes C_6H_2*Me*$_3$), 2.072 (s, 9H), 1.3 – 2.0 (br s, 6H, Mes C_6H_2*Me*$_3$), 1.364 (s, 3H, Mo=CHC*Me*$_2$Ph), 0.209 (s, 27 H, OSi(SiMe$_3$)$_3$). ^{1}H NMR (CD_2Cl_2, alkylidene) δ 13.096 ($^1J_{CH}$ = 147 Hz); ^{13}C NMR (CD_2Cl_2) δ 322.5 (Mo=*C*H), 153.6, 152.5, 148.3, 138.1, 136.8, 131.3, 130.0, 129.3, 128.6, 126.9, 126.4, 126.2, 125.0, 106.8, 52.3, 31.4, 30.8, 21.7, 21.0, 20.9, 1.5. Anal. Calcd for $C_{52}H_{73}MoN_3OSi_4$: C, 64.76; H, 7.63; N, 4.36; Experimental: C, 64.84; H, 7.75; N, 4.32.

^{1}H NMR in C_6D_6:



Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$] (4b$_{Mo}$) Hexafluoro-t-butanol (9.8 μL, 80 μmol) was added by microsyringe to a −25 °C, stirred solution of Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$, **2$_{Mo}$** (59.5 mg, 80.0 μmol), in 2 mL Et$_2$O. The solution was stirred at ambient temperature for 16 h. The volatiles were removed *in vacuo*. The oil was extracted with pentane and the mixture was filtered through a pipette filter. The volatiles were removed *in vacuo* from the filtrate. The dark yellow oil was dissolved in minimal acetonitrile and the solution was stored at −25 °C for 16 h. The mother liquor was removed from the crystals by pipette and the crystals were washed with cold acetonitrile and dried under vacuum; yield 45 mg, 68 %; ^{1}H NMR (C$_6$D$_6$, *syn* isomer, 70%, selected resonances) δ 12.073 (s, 1H, Mo=C*H*, $^1J_{CH}$ = 120 Hz), 5.910 (s, 1H, Me$_2$C$_4$*H*$_2$N), 5.786 (s, 1H, Me$_2$C$_4$*H*$_2$N), 2.251 (s, 6H, MesC*H*$_3$), 2.170 (s, 6H, MesC*H*$_3$), 1.948 (s, 3H, Methyl), 1.692 (s, 3H, Methyl), 1.566 (s, 3H, Methyl), 1.521 (s, 3H, Methyl), 0.678 (s, 3H, Methyl); ^{1}H NMR (C$_6$D$_6$, *anti* isomer, 30%, selected resonances) δ 11.896 (s, 1H, Mo=C*H*), 6.143 (s, 2H, Me$_2$C$_4$*H*$_2$N), 2.369 (s, 6H, MesC*H*$_3$), 2.185 (s, 6H, MesC*H*$_3$), 1.718 (s, 6H, *Me*$_2$C$_4$H$_2$N), 1.390 (s, 3H, Methyl), 1.284 (s, 3H, Methyl), 1.089 (s, 3H, Methyl); ^{1}H NMR (C$_6$D$_6$, remaining resonances reported together) δ 7.143 – 7.206 (overlapping signals, Ar*H*), 6.996 – 6.925 (overlapping signals, Ar*H*), 6.883 (s, Ar*H*), 6.868 (s, Ar*H*), 6.804 (s, Ar*H*), 6.776 (m, Ar*H*), 6.706 (s, Ar*H*), 2.108 (s, MesC*H*$_3$, coincident signal from both isomers; ^{13}C {^{1}H} NMR (CD$_2$Cl$_2$, both isomers reported together) δ 293.0, 155.3, 148.0, 140.6, 137.8, 137.2, 136.5, 136.0, 135.9, 135.8, 135.7, 132.4, 130.9, 130.2, 129.6, 129.1, 128.8, 128.7, 128.6, 128.5, 128.5, 128.3, 128.3, 128.2, 127.5, 126.8, 126.6, 126.5, 126.3, 108.9, 108.2, 54.8, 51.3, 31.7, 29.9, 29.2, 27.6, 21.7, 21.4, 21.3, 21.3, 20.1, 18.8, 18.3, 15.8; ^{19}F NMR (C$_6$D$_6$) δ -77.00 (quartet, J_{FF} = 9 Hz), -77.287 (quartet, J_{FF} = 9 Hz).

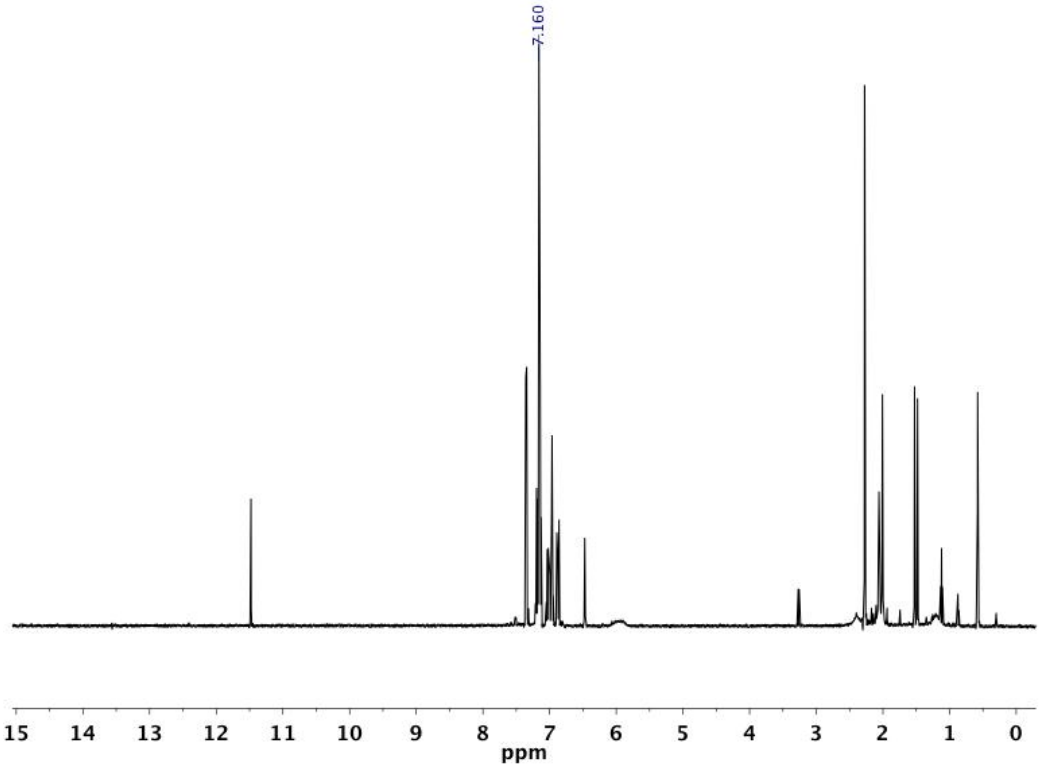
^{1}H NMR in C_6D_6:



Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OSiPh$_3$) (4c$_{Mo}$). Solid HOSiPh$_3$ (18.9 mg, 68.4 μmol) was added to a −25 °C, stirred solution of Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$, **2$_{Mo}$** (49.5 mg, 66.5 μmol), and the mixture was stirred at ambient temperature for 16 h. The volatiles were removed *in vacuo*. The brown oil was extracted with pentane, filtered through a pipette filter, and the volatiles removed *in vacuo* from the filtrate. The brown oil was dissolved in minimal acetonitrile and the soluton was stored at −25 °C for 16 h. The mother liquor was removed from the orange precipitate by pipette and the precipitate was washed with cold MeCN and dried under vacuum; yield 51 mg, 82 % yield: ^{1}H NMR (C_6D_6) δ 11.479 (s, 1H, Mo=C*H*), 7.357 (t, 3H, Ar*H*), 7.348 (d, 3H, Ar*H*), 7.212 – 7.17 (overlapping signals, 3H, Ar*H*), 7.158 (overlapping with solvent), 7.144 – 7.125 (overlapping signals, 4H), 7.049 – 6.945 (overlapping signals, 6H), 6.891 (m, 1H, Ar*H*), 6.877 (m, 1H), 6.858 (s, 2H, C$_6$*H*$_2$Me$_3$), 6.472 (s, 2H, C$_6$*H*$_2$Me$_3$) 5.990 and 5.905 (overlapping br s, 2H, Me$_2$*pyr*), 2.392 (br s, 3H, *Me*$_2$pyr), 2.274 (s, 6H, C$_6$H$_2$*Me*$_3$), 2.059 (s, 6H, C$_6$H$_2$*Me*$_3$), 2.007 (s, 6H, C$_6$H$_2$*Me*$_3$), 1.525 (s, Mo=CHC*Me*$_2$Ph), 1.481 (s, Mo=CHC*Me*$_2$Ph), 1.203 (br s, 3H, *Me*$_2$pyr); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 288.0 (Mo=*C*H), 154.9, 148.4, 139.9, 137.1,

136.6, 136.3, 136.1, 135.9, 135.7, 130.6, 130.3, 129.0, 128.7, 128.5, 128.2, 127.4, 126.3, 126.0, 108.4, 53.0, 32.0, 30.7, 21.8, 21.2, 20.7. Anal. Calcd for $C_{58}H_{60}MoN_2OSi$: C, 75.30; H, 6.54; N, 3.03. Found: C, 75.09; H, 6.49; N, 3.07.

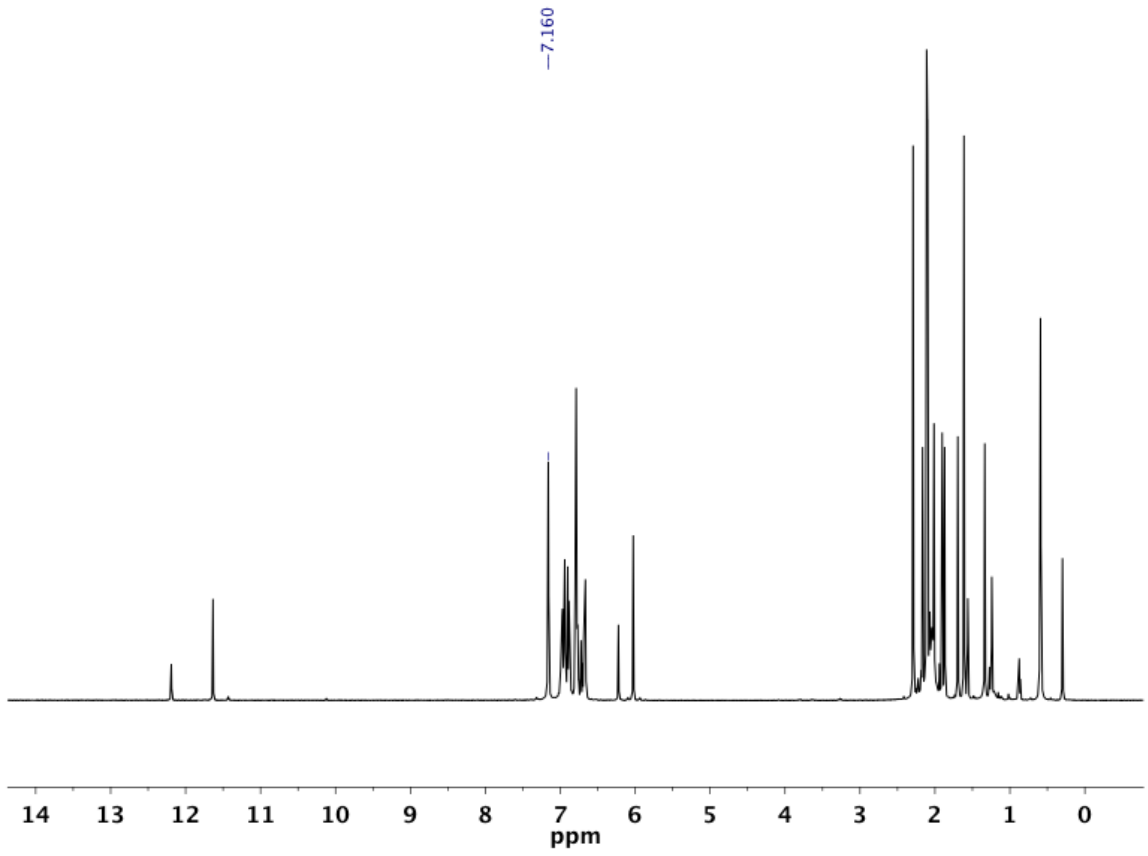
^{1}H NMR in C_6D_6:



Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-2,6-Me$_2$C$_6$H$_3$) (4d$_{Mo}$). Solid 2,6-$Me_2C_6H_3OH$ (6.9 mg, 56 μmol) was added to a −25 °C stirred solution of Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$, **2$_{Mo}$** (40.9 mg, 55.0 μmol), and the brown mixture was stirred 16 h at ambient temperature. The volatiles were removed *in vacuo* and the brown oil was extracted with pentane and the extract was filtered through a pipette filter with Celite. The volatiles were removed under reduced pressure from the filtrate. The remaining oil was dissolved in 1 mL MeCN/0.1 mL Et_2O and the mixture was cooled to −25 °C. The supernatant was removed from the organge precipitate by pipette and the orange solid was washed with cold MeCN and dried *in vacuo*; yield 21.5 mg, 51 %: ^{1}H NMR (C_6D_6, *syn* and *anti* reported together with the *anti* alkylidene proton integrated as 1H) δ 12.191 (s, 1H, $^1J_{CH}$ = 155 Hz, anti Mo=C*H*), 11.635 (s, 2H, $^1J_{CH}$ = 118 Hz, syn Mo=C*H*), 7.004 – 6.860

(overlapping signals, Ar*H*, 21H), 6.803 – 6.767 (overlapping signals, 16H, Ar*H*), 6.723 – 6.665 (overlapping signals, 8H, Ar*H*), 6.224 (s, 2H, anti $NC_4H_2Me_2$), 6.026 s, 4H, syn $NC_4H_2Me_2$), 2.291 (s, 12H, syn MesCH_3), 2.165 (s, 6H, anti MesCH_3), 2.110 (s, 18 H), 2.100 (s, 12H), 2.041 (br s, 12H), 2.013 (s, 6H), 1.903 (s, 6H), 1.871 (s, 6H), 1.695 (s, 6H), 1.613 (s, 12H), 1.561 (s, 3H, anti Mo=CHCMe_2Ph), 1.335 (s, 6H), 1.242 (s, 3H, anti Mo=CHCMe_2Ph); ^{13}C {^1H} NMR (C_6D_6, syn and anti isomers reported together) δ 310.4 (Mo=*C*H), 291.2 (Mo=*C*H), 165.4, 160.8, 155.6, 148.7, 148.6, 140.6, 137.6, 137.4, 137.1, 136.8, 136.6, 136.5, 135.9, 134.3, 131.0, 130.0, 129.9, 129.5, 129.2, 129.0, 129.0, 128.8, 128.7, 127.9, 126.8, 126.6, 126.5, 126.4, 126.4, 125.9, 121.9, 121.5, 109.9, 109.6, 54.0, 51.9, 32.8, 30.9, 29.4, 22.0, 21.5, 21.5, 21.4, 21.4, 20.9, 18.4, 18.2, 17.9, 17.8, 17.2. $C_{48}H_{54}MoN_2O$: C, 74.78; H, 7.06; N, 3.63. Found: C, 74.56; H, 6.78; N, 3.10.

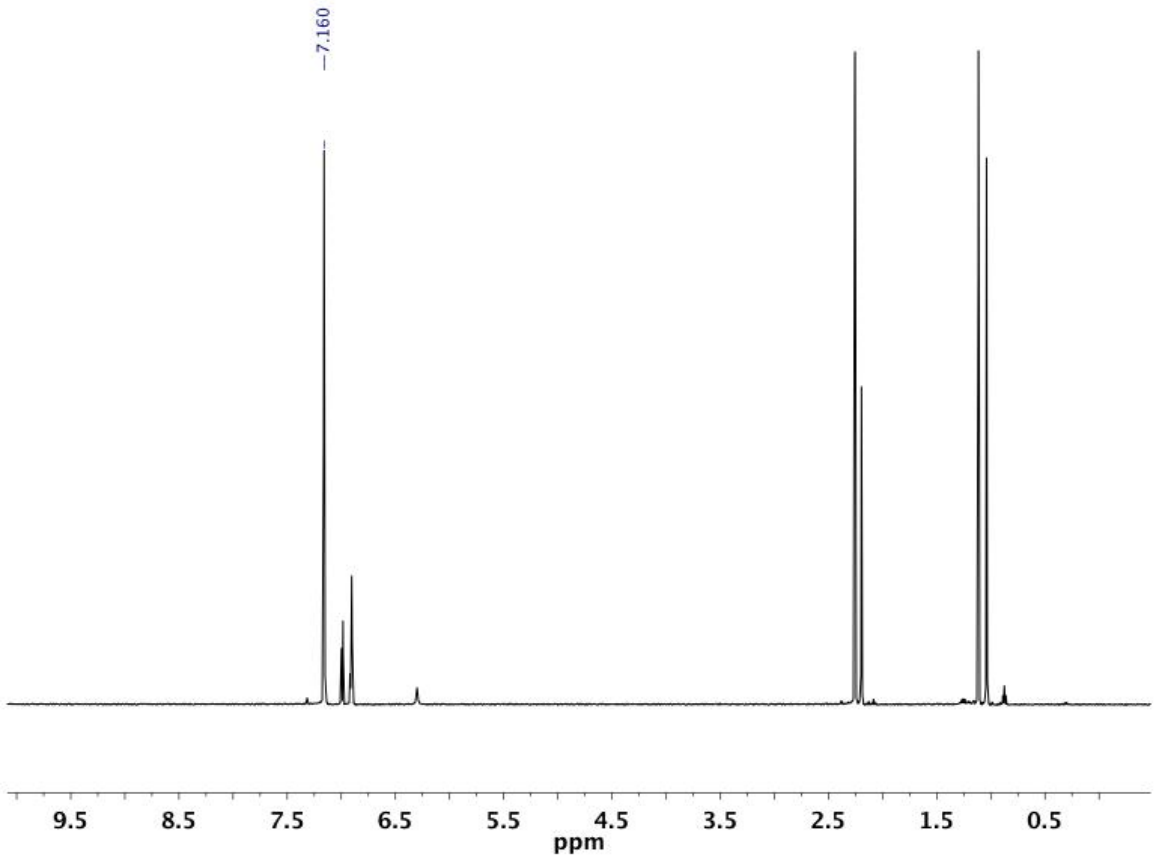
^1H NMR in C_6D_6:



W(NAr*)(N-t-Bu)Cl(NH-t-Bu) (5). A solution of n-butyllithium in hexane (2.8 M, 4.5 mL, 12.6 mmol) was added to a stirred solution of H_2NAr* (4.16 g, 12.6 mmol) in 15 mL Et_2O; the

resulting solution immediately became yellow. After 15 minutes, a solution of LiNHAr* was added to a stirred solution of $W(N\text{-}t\text{-}Bu)_2Cl_2(py)_2$ (7.01 g, 12.6 mmol) in 100 mL Et_2O at −25 °C. After 30 m, NEt_3 was added (10 mL, 140 mmol). After stirring the mixture for 16 h, the volatiles were removed *in vacuo*. The resulting solid was extracted with pentane and the mixture was filtered through a frit containing a layer of Celite. The volume of the filtrate was reduced *in vacuo* and a beige precipitate formed. The beige solid was collected on a frit and washed with 3 x 1 mL cold pentane. The filtrate was concentrated, cooled to −25 °C and a second crop of beige precipitate formed. Four crops of beige solid were collected for a total yield of 6.701 g, 77 %: ^{1}H NMR (C_6D_6) δ 6.992 (d, 2H, J_{HH} = 7.5 Hz, meta aniline), 6.919 – 6.890 (overlapping signals, 5H, para aniline and aromatic mesityl), 6.299 (s, 1H, N*H*^{t}Bu), 2.254 (s, 12H, Mes*Me*-ortho), 2.194 (s, 6H, Mes*Me*-para), 1.113 (s, 9H, N^{t}Bu), 1.038 (s, 9H, N^{t}Bu); ^{13}C {^{1}H} NMR (C_6D_6) δ 137.7, 137.5, 136.7, 136.6, 129.4, 129.3, 128.9, 125.1 (Aromatic), 68.3, 56.6 (tertiary), 33.0, 32.6 (tBu), 21.6, 21.2 (Mesityl Me). Anal. Calcd for $C_{32}H_{44}ClN_3W$: C, 55.70; H, 6.43; N, 6.09. Experimental: C, 55.78; H, 6.42; N, 6.08.

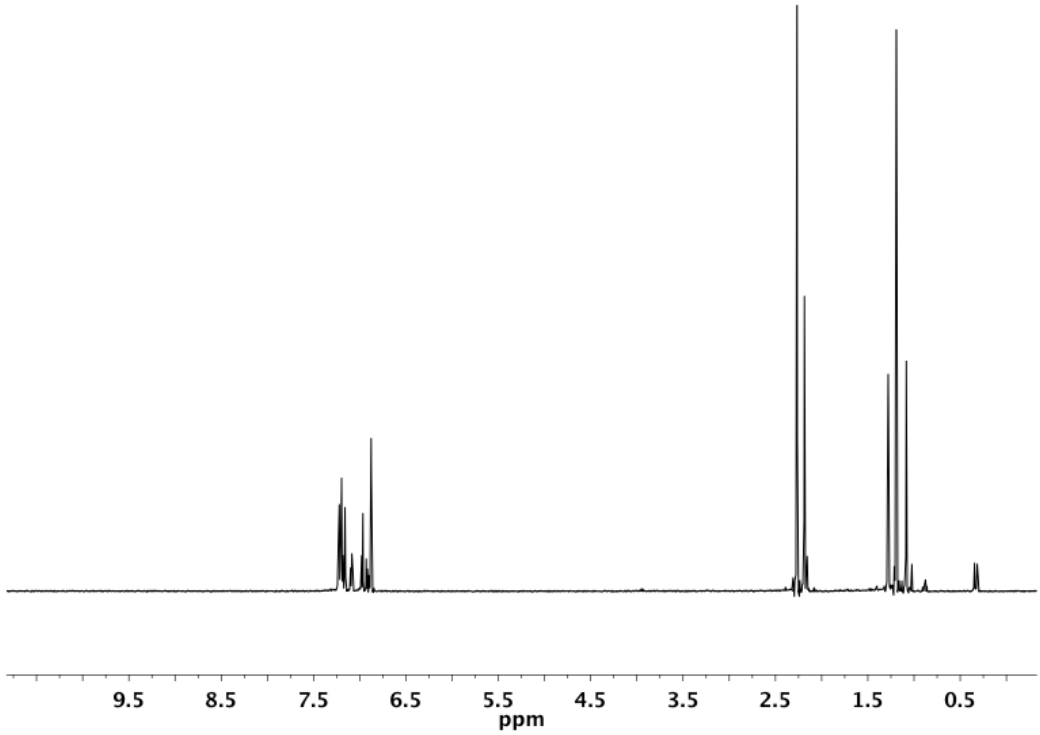
^{1}H NMR in C_6D_6:



W(NAr*)(N-t-Bu)Cl_2(NH_2-t-Bu) (6). 2,6-LutidineHCl (0.427 g, 2.97 mmol) was added in one portion to a −25 °C solution of W(NAr*)(N-t-Bu)Cl(NH-t-Bu), **5** (2.035 g, 2.95 mmol), in 50 mL Et_2O. The mixture was stirred 16 h, and the volatiles were removed *in vacuo*. The residue was extracted with benzene and filtered through a layer of Celite on a frit. The volatiles were removed from the filtrate. The remaining solid was used directly for the synthesis of W(NAr*)(N-t-Bu)($CH_2CMe_2Ph)_2$ without further purification (2.110 g): ^{1}H NMR (C_6D_6) δ 7.010 – 6.995 (overlapping signals, 3H), 2.652 (br s, 2H, NH_2^{t}Bu), 2.328 (s, 12H, mesityl ortho CH_3), 2.182 (s, 6H, mesityl para, CH_3), 1.146 (s, 9H, CMe_3), 1.018 (s, 9H, CMe_3).

W(NAr*)(N^{t}Bu)($CH_2CMe_2Ph)_2$ (7). A 0.5 M solution of $ClMgCH_2CMe_2Ph$ in hexane (11.6 mL, 5.80 mmol) was added to a stirring solution of W(NAr*)(N-t-Bu)Cl_2(NH_2-t-Bu), **6** (2.110 g, 2.90 mmol), in 100 mL Et_2O at −25 °C. The mixture was warmed to room temperature and stirred for 16 h. The volatiles were removed *in vacuo*. The remaining solids were extracted with pentane and filtered through Celite on a frit. The filtrate volume was reduce *in vacuo* and cooled to −25 °C. A yellow precipitate formed and was collected on a frit. The filtrate volume was reduced *in vacuo* to collect three crops in a similar manner; total yield 1.666 mg, 68 %: ^{1}H NMR (C_6D_6) δ 7.238 - 7.185 (overlapping signals, 8H), 7.103 – 7.069 (m, 2H), 6.983 – 6.966 (overlapping signals, 2H), 6.931 – 6.902 (overlapping signals, 1H), 6.877 (s, 4H, mesityl Ar*H*), 2.267 (s, 12H, mesityl ortho CH_3), 2.187 (s, mesityl para, CH_3) and 2.159 (one half a doublet visible, MoCH_2, 8H integrated together with previous signal), 1.281 (s, 6H, $MoCH_2C$$Me_2$Ph), 1.192 (s, 9H, NC$Me_3$), 1.085 (s, 6H, $MoCH_2C$$Me_2$Ph), 0.332 (d, 2H, MoC$H_2$); ^{13}C {^{1}H} NMR ($CD_2Cl_2$) δ 125.2, 138.2, 137.1, 136.6, 136.4, 129.9, 128.7, 128.4, 126.1, 125.7, 123.8, 89.5, 68.2, 40.4, 33.9, 33.2, 32.4, 21.4, 21.3. Anal. Calcd for $C_{48}H_{60}WN_2$: C, 67.92; H, 7.12; N, 3.30. Found: C, 68.22; H, 7.06; N, 3.21.

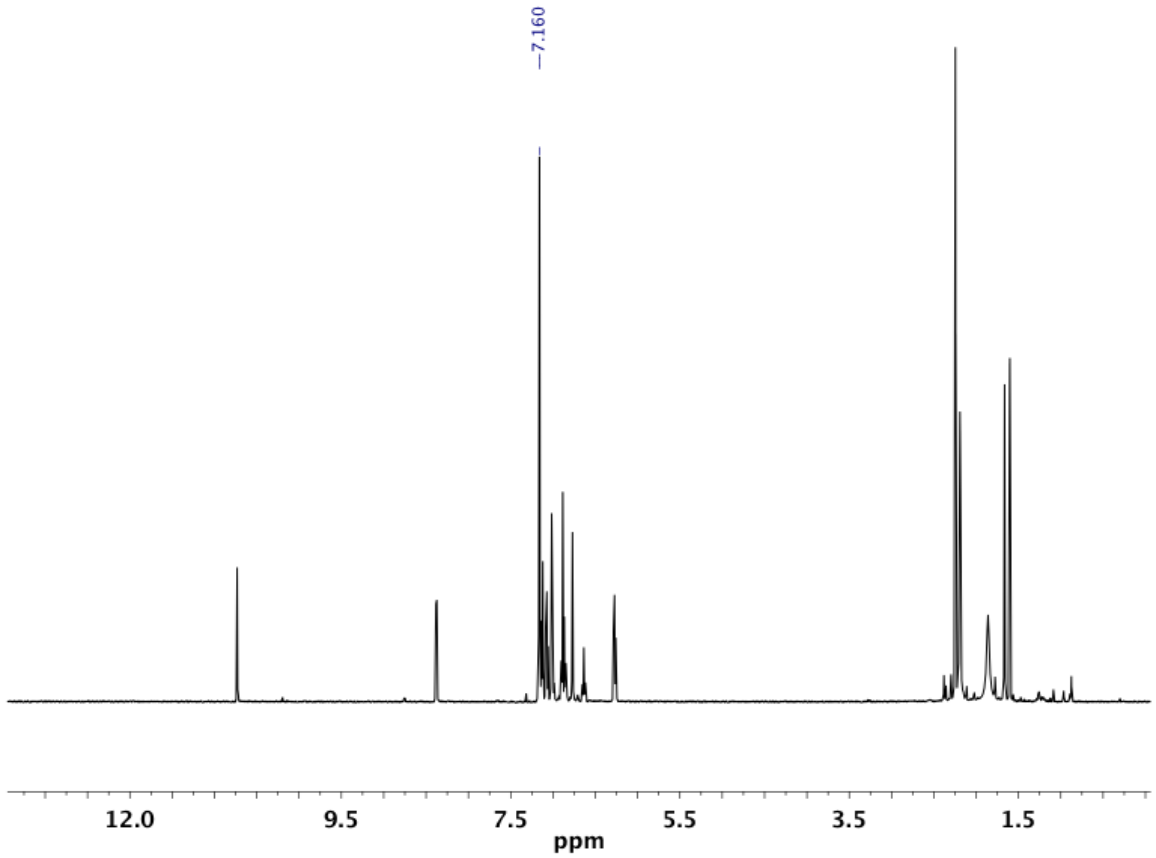
^{1}H NMR in C_6D_6:



W(NAr*)(CHCMe$_2$Ph)Cl$_2$(py) (8). A solution of pyridine (0.227 g, 2,87 mmol) in 2 mL Et_2O was added to a solution of W(NAr*)(N-t-Bu)($CH_2CMe_2Ph)_2$, **7** (2.418 g, 2.85 mmol), in 50 mL Et_2O and a pale yellow precipitate formed. The mixture was chilled to −25 °C and HCl (1.1 M in Et_2O, 7.8 mL) was added and the mixture was stirred for 16 h over which time it became orange. The volatiles were removed *in vacuo*. The residue was washed with pentane and then extracted with toluene and benzene and filtered through a pad of Celite on a frit. The volatiles were removed *in vacuo* to give a yellow powder. The pentane wash was concentrated and cooled to −25 °C. A yellow precipitate formed which was collected on a frit and washed with cold pentane to give a combined yield of 1.565 g (69 %): ^{1}H NMR (C_6D_6) δ 10.732 (s, 1H, $^1J_{CH}$ = 144 Hz, W=C*H*), 8.379 (d, 2H, J_{HH} = 5 Hz), 7.123 (d, 2H, J_{HH} = 8 Hz), 7.075 (t, 2H, J_{HH} = 8 Hz), 7.016 – 6.988 (overlapping signals, 3H), 6.770 (s, 2H), 6.649 (t, 1H, J_{HH} = 8 Hz), 6.282 (t, 2H, J_{HH} = 7 Hz), 2.245 (s, 6H, Mes CH_3), 2.191 (s, 6H, Mes CH_3), 1.861 (br s, 6H, Mes CH_3), 1.662 (s, 3H, Mo=CHCMe_2Ph), 1.603 (s, 3H, Mo=CHCMe_2Ph); ^{13}C NMR (C_6D_6) δ 298.0 (Mo=*C*H), 155.6, 154.4, 152.9, 139.9, 138.6, 137.8, 137.0, 136.9, 129.5, 129.2, 128.9, 128.7,

128.5, 127.7, 126.6, 126.2, 124.7, 47.7 (Mo=CH*C*Me$_2$Ph), 30.8, 29.5, 21.9, 21.6, 21.2. Anal. Calcd for $C_{39}H_{42}Cl_2N_2W$: C, 59.03; H, 5.33; N, 3.53. Found: C, 58.92; H, 5.38; N, 3.47.

^{1}H NMR in C_6D_6:

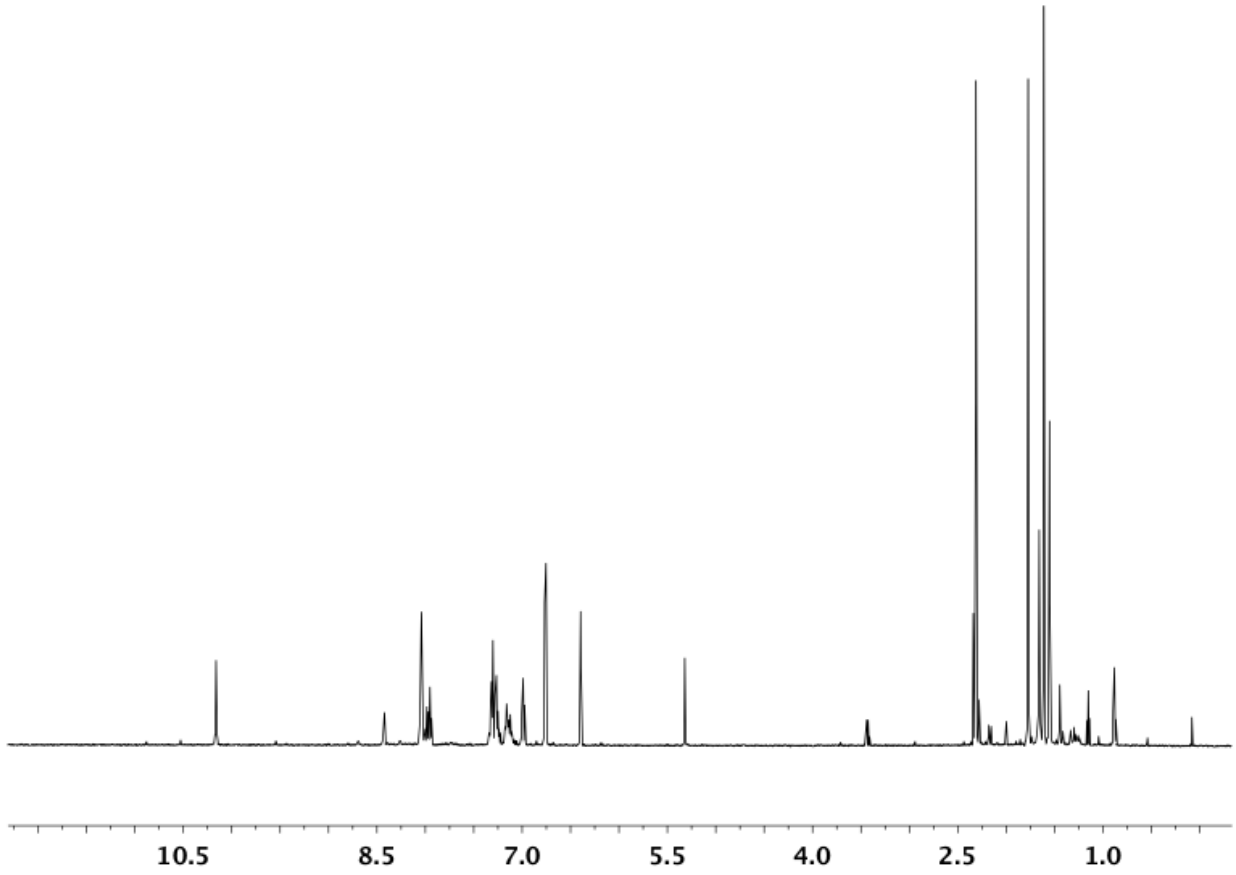


W(NAr*)(CHCMe$_2$Ph)Cl$_2$(bipy) (9). Method A: A 1.1 M solution of HCl in Et$_2$O (0.324 mL, 0.356 mmol) was added to a −25 °C solution of bipyridine (19.1 mg, 0.122 mmol) and W(NAr*)(N-t-Bu)(CH$_2$CMe$_2$Ph)$_2$, **7** (101 mg, 0.119 mmol), in 4 mL Et$_2$O. A precipitate formed immediately and the yellow mixture became orange. After stirring 16 h at room temperature, the volatiles were removed *in vacuo* and the orange solid was extracted with 30 mL CH$_2$Cl$_2$ and filtered through a pad of Celite on a frit. The volatiles were removed *in vacuo* from the filtrate to leave 85 mg (82 %) of orange solid.

Method B: Solid 4,4'-bipyridine (25.7 mg, 0.165 mmol) was added to a stirring solution of W(NAr*)(CHCMe$_2$Ph)Cl$_2$(py) (129.8 mg, 0.164 mmol) in 4 mL toluene. The yellow became orange and orange precipitate formed. After 1.5 h, the orange solid was collected on a frit,

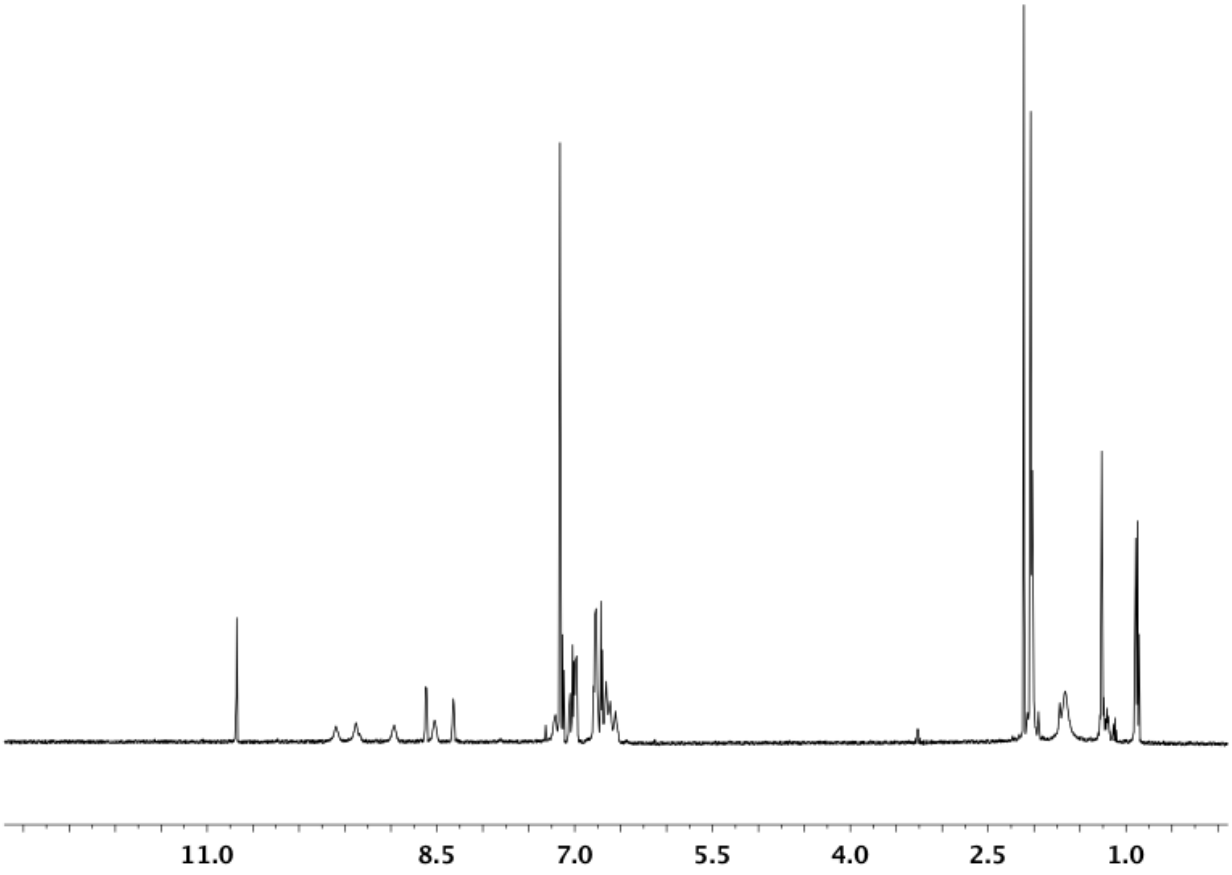
washed with 5 x 1 mL toluene, and dried *in vacuo* to give 110 mg (77 %). ^{1}H NMR (CD_2Cl_2) δ 10.164 (s, 1H, Mo=C*H*), 8.428 (d, 1H, J_{HH} = 4 Hz), 8.043 (s, 3H), 7.973 (m, 2H), 7.338 – 7.220 (overlapping signals, 5H), 7.162 and 7.121 (overlapping br s, 2H), 6.991 (t, 1H, J_{HH} = 7 Hz), 6.756 (s, 4H), 6.396 (s, 2H), 2.309 (s, 6H, mesitylCH_3), 1.774 (s, 6H, mesitylCH_3), 1.654 (s, 3H, Mo=CHCMe_2Ph), 1.609 (s, 6H, mesitylCH_3), 1.548 (s, 3H, Mo=CHCMe_2Ph). Anal. Calcd for $C_{44}H_{45}Cl_2N_3W$: C, 60.70; H, 5.21; N, 4.83. Found: C, 60.91; H, 5.24; N, 4.62.

^{1}H NMR in CD_2Cl_2:



[W(NAr*)(CHCMe$_2$Ph)Cl(bipy)][Zn$_2$Cl$_6$]$_{0.5}$ (10). Solid $ZnCl_2$(1,4-dioxane) (12.6 mg, 51.6 μmol) was added to a suspension of W(NAr*)(CHCMe$_2$Ph)Cl$_2$(bipy) (44.2 mg, 50.8 μmol) in 4 mL CH_2Cl_2 in a scintillation vial. The orange suspension became a clear orange solution. After stirring 1.5 h the volatiles were removed *in vacuo*, and orange solid was extracted with benzene and filtered through a pipette filter. The volatiles were removed *in vacuo*. The orange oil was dissolved in minimal toluene and cooled to −25 °C and orange crystals formed. The mother

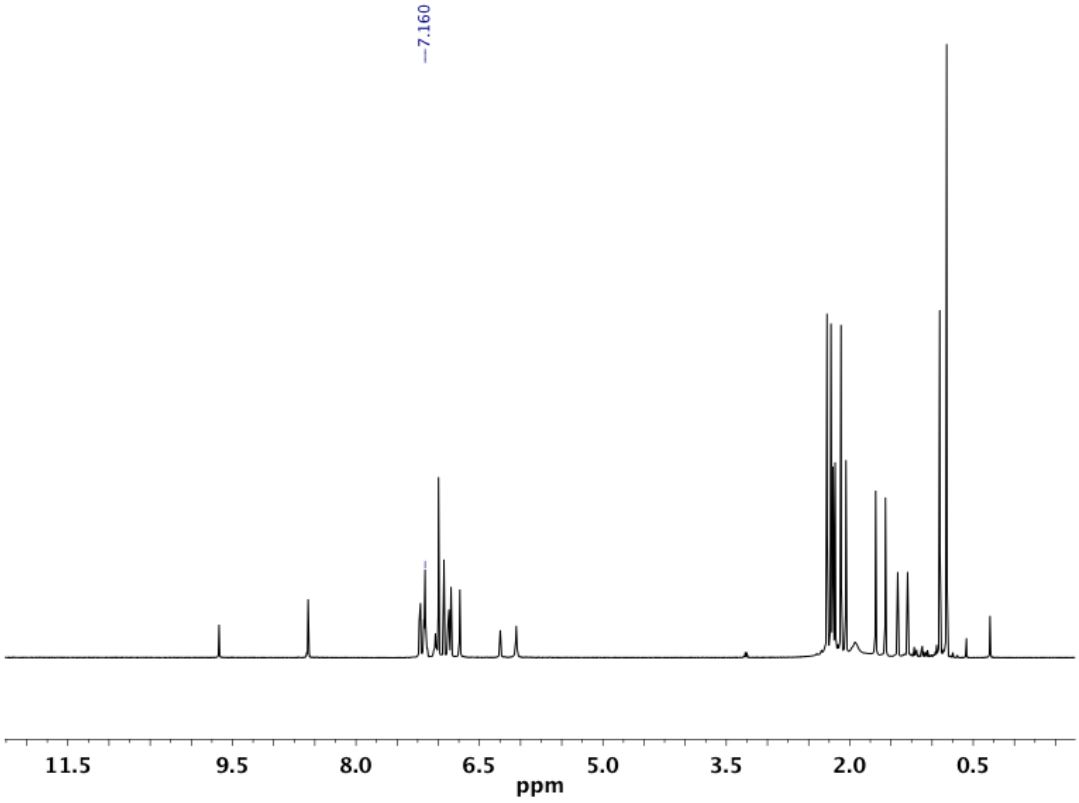
liquor was removed by pipette, the crystals were washed with cold toluene, and dried *in vacuo* to give 22.8 mg (45 % yield). ^{1}H NMR (CD_2Cl_2) δ 10.707 (s, 1H, Mo=C*H*), 8.890 – 8.852 (overlapping signals, 2H, bpy*H*), 8.699 (d, 1H, J_{HH} = 8 Hz, bpy*H*), 8.583 (t, 1H, J_{HH} = 8 Hz, bpy*H*), 8.479 – 8.434 (overlapping signals, 2H bpy*H*), 7.581 (q, 2H, J_{HH} = 8 Hz), 7.330 (t, 1H, J_{HH} = 8 Hz), 7.129 (d, 2H, J_{HH} = 8 Hz), 6.973 (d, 2H, J_{HH} = 8 Hz), 6.760 (s, 2H, mes*H*), 6.670 (t, 2H, J_{HH} = 8 Hz), 6.612 (s, 2H, mes*H*), 6.417 (t, 1H, J_{HH} = 8 Hz), 2.078 (s, 6H, mesitylCH_3), 2.031 (s, 6H, mesitylCH_3), 1.601 (s, 6H, mesitylCH_3), 1.296 (s, 3H, Mo=CHCMe_2Ph), 0.979 (s, 3H, Mo=CHCMe_2Ph); ^{13}C NMR (CD_2Cl_2) δ 297.1 (Mo=*C*H), 156.7, 154.3, 153.4, 151.5, 145.3, 144.9, 140.7, 140.4, 139.9, 137.8, 137.4, 137.2, 136.7, 136.7, 136.4, 136.2, 130.4, 129.7, 129.7, 129.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.1, 127.6, 127.5, 126.8, 126.6, 126.2, 125.0, 47.6, 30.4, 26.6, 21.7, 21.2, 20.4.



W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O^{t}Bu) (4a$_W$) HO^{t}Bu (6.4 μL, 66.9 μmol) was added to a −25 °C, stirring solution of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$, **2$_W$** (55.3 mg, 66.5 μmol), in 2 mL

Et_2O. The solution was stirred at ambient temperature for 16 h. The volatiles were removed *in vacuo*. The orange oil was extracted with pentane and filtered through a pipette filter. The volatiles were removed *in vacuo* from the filtrate. The orange oil was dissolved in minimal MeCN/Et_2O and stored at −25 °C for 16 h over which time crystals formed. The mother liquor was removed by pipette and the crystals were washed with cold MeCN and dried under vacuum to give 42.0 mg, 78 % yield. ^{1}H NMR (C_6D_6, *Anti* isomer, 38 %, selected resonances) δ 9.663 (s, $^1J_{CH}$ = 150 Hz, W=C*H*), 6.246 (s, 2H, pyr*H*), 2.203 (s, 6H, MesCH_3), 2.179 (s, 6H, MesCH_3), 2.046 (s, 6H, MesCH_3), 1.417 (s, 3H, W=CHCMe_2Ph), 1.297 (s, 3H, W=CHCMe_2Ph), 0.907 (s, 9H, OCMe_3); ^{1}H NMR (C_6D_6, *Syn* isomer, 62 %, selected resonances) δ 8.582 (s, $^1J_{CH}$ = 110 Hz, J_{HW} = 14 Hz, W=C*H*), 6.052 (s, 2H, Pyr*H*), 2.277 (s, 6H, MesCH_3), 2.228 (s, 6H, MesCH_3), 2.107 (s, 6H, MesCH_3), 1.685 (s, 3H, W=CHCMe_2Ph), 1.566 (s, 3H, W=CHCMe_2Ph), 0.823 (s, 9H, OCMe_3); ^{1}H NMR (C_6D_6, remaining resonances reported together) δ 7.224 (d, J_{HH} = 8 Hz), 7.174 – 7.132 (signals overlapping solvent), 7.034 (t, J_{HH} = 8 Hz), 6.997 (s), 6.931 (s), 6.873 (d, J_{HH} = 4 Hz), 6.844 (s), 6.737(s),1.937 (br s, Me_2pyr); ^{13}C{^{1}H} NMR (C_6D_6) δ 265.0, 256.0 (W=*C*H), 154.0, 152.8, 152.0, 139.8, 137.2, 137.2, 137.1, 137.0, 136.6, 136.5, 136.3, 136.2, 130.3, 129.9, 129.6, 129.2, 128.8, 127.3, 126.6, 126.2, 126.1, 125.4, 110.1, 85.4, 82.0, 51.4, 47.7, 34.5, 33.7, 33.6, 32.7, 31.6, 31.6, 21.8, 21.7, 21.6, 21.6, 21.4, 20.6. Anal. calcd for $C_{44}H_{54}N_2OW$: C, 65.18; H, 6.71; N, 3.46. Found: C, 65.02; H, 6.76; N, 3.59.

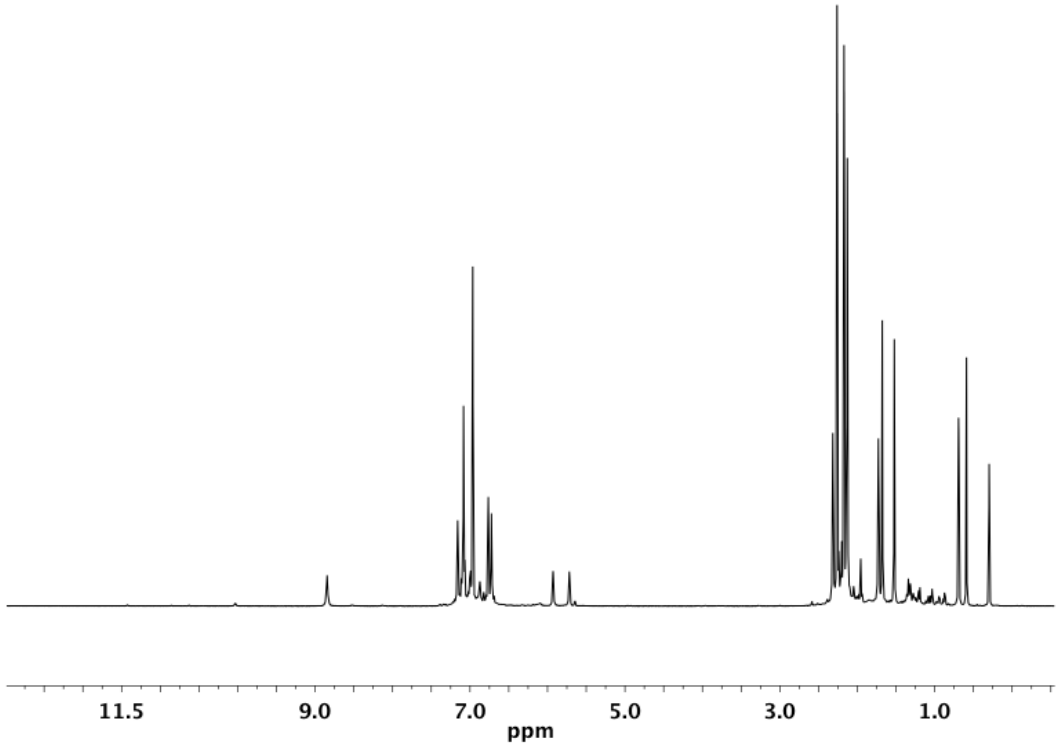
^{1}H NMR in C_6D_6:



W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$] (4b$_W$) HOCMe(CF$_3$)$_2$ (8.5 µL, 69 µmol) was added by microsyringe to a −25 °C, stirring solution of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$, **2$_W$** (57.9 mg, 69.6 µmol), in 2 mL Et$_2$O. The solution was stirred at ambient temperature for 16 h. The volatiles were removed *in vacuo*. The oil was extracted with pentane and filtered through a pipette filter. The volatiles were removed *in vacuo* from the filtrate. The dark yellow oil was dissolved in minimal MeCN and stored at −25 °C for 16 h over which time crystals formed. The mother liquor was removed by pipette and the crystals were washed with cold MeCN and dried under vacuum to give 43 mg, 68 % yield. ^{1}H NMR (C_6D_6) δ 8.846 (s, 1H, $^1J_{CH}$ = 113 Hz, W=C*H*), 7.114 – 7.067 (overlapping signals, 4H, Ar*H*), 6.999 (d, J_{HH} = 7 Hz, 1H), 6.964 (s, 3H), 6.764 (s, 2H), 6.724 (s, 2H), 5.927 (s, 1H, pyr*H*), 5.718 (s, 1H, pyr*H*), 2.315 (s, 3H, CH_3), 2.260 (s, 6H, MesCH_3), 2.171 (s, 6H, MesCH_3), 2.129 (s, 6H, MesCH_3), 1.727 (s, 3H, CH_3), 1.677 (s, 3H, CH_3), 1.522 (s, 3H, CH_3), 0.692 (s, 3H, OC(CF$_3$)$_2$CH_3); ^{13}C{^{1}H} NMR (C_6D_6) δ 263.1 (W=*C*H), 153.9, 150.9, 140.2, 137.0, 136.6, 136.2, 135.9, 130.6, 129.3, 128.9, 128.7, 128.7, 126.9, 126.7, 126.5, 111.1, 110.3 (Ar*C*), 52.6 (W=CH*C*Me$_2$Ph), 33.1, 31.0, 22.0, 21.6, 21.5,

19.6, 18.6, 16.0, 1.8, 0.4. ^{19}F NMR (C_6D_6) δ -76.98 (quartet, J_{FF} = 9 Hz), -77.22 (quartet, J_{FF} = 9 Hz). Anal. calcd for $C_{44}H_{48}F_6N_2OW$: C, 57.52; H, 5.27; N, 3.05. Found: C, 57.34; H, 5.36; N, 3.22.

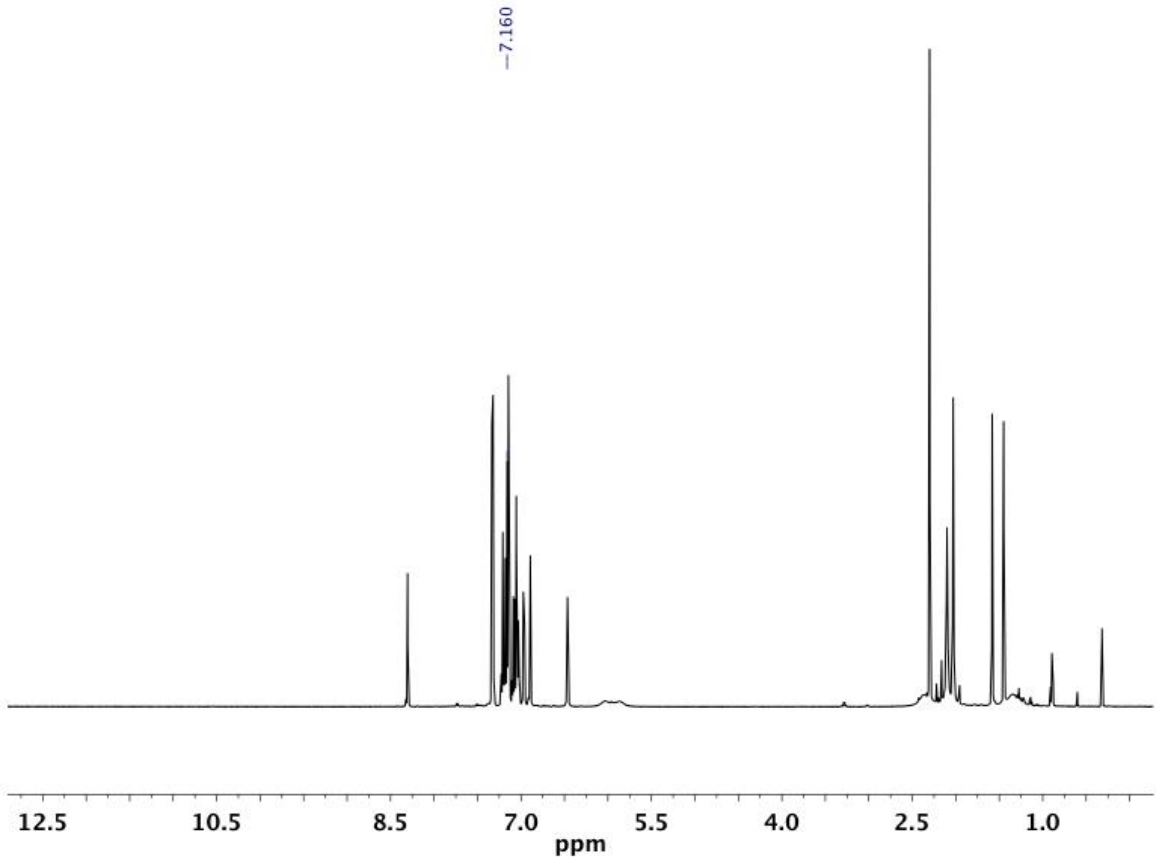
^{1}H NMR in C_6D_6:



W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OSiPh$_3$) (4c$_W$) Solid HOSiPh$_3$ (22.7 mg, 82.1 μmol) was added to a −25 °C, stirring solution of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$, **2$_W$** (75.7 mg, 91.0 μmol), and allowed to stir at ambient temperature for 16 h. The volatiles were removed *in vacuo*. The yellow oil was extracted with pentane, filtered through a pipette filter, and the volatiles removed *in vacuo* from the filtrate. The yellow oil was dissolved in 1 mL MeCN/0.1 mL Et$_2$O and stored at −25 °C for 16 h over which time yellow precipitate formed. The mother liquor was removed by pipette and the solid was washed with cold MeCN and dried under vacuum. The mother liquor was concentrated and cooled to −25 °C to collect a second crop for a combined yield of 81.6 mg, 89 %. ^{1}H NMR (C_6D_6) δ 8.286 (s, 1H, W=C*H*, $^1J_{HW}$ = 15 Hz), 7.309 (dd, 4H, J_{HH} = 8 Hz, J_{HH} = 1 Hz), 7.204 – 7.172 (overlapping signals, 3H), 7.141 (s, 2H), 7.126 (s, 3H), 7.112 (m, 1H), 7.084 – 6.992 (overlapping signals, 6H), 6.955 (m, 1H), 6.940 (s, 1H), 6.875 (s,

2H, $C_6H_2Me_3$), 6.446 (s, 2H, $C_6H_2Me_3$), 6.023 and 5.844 (overlapping br s, 2H, $Me_2C_4H_2N$), 2.343 (br s, 3H, $Me_2C_4H_2N$), 2.282 (s, 6H, $C_6H_2Me_3$), 2.082 (s, 6H, $C_6H_2Me_3$), 2.011 (s, 6H, $C_6H_2Me_3$), 1.563 (s, 3H, Mo=CHCMe_2Ph), 1.431 (s, 3H, Mo=CHCMe_2Ph), 1.334 (br s, 3H, $Me_2C_4H_2N$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 258.0, 153.7, 151.0, 139.4, 136.8, 136.7, 136.6, 136.2, 136.0, 135.8, 135.4, 130.6, 130.2, 128.9, 128.6, 128.4, 128.3, 126.1, 126.0, 126.0, 109.6, 51.1, 33.8, 32.3, 21.8, 21.3, 20.7. Anal. calcd for $C_{58}H_{60}N_2OSiW$: C, 68.77; H, 5.97; N, 2.77. Found: C, 68.48; H, 5.78; N, 2.86.

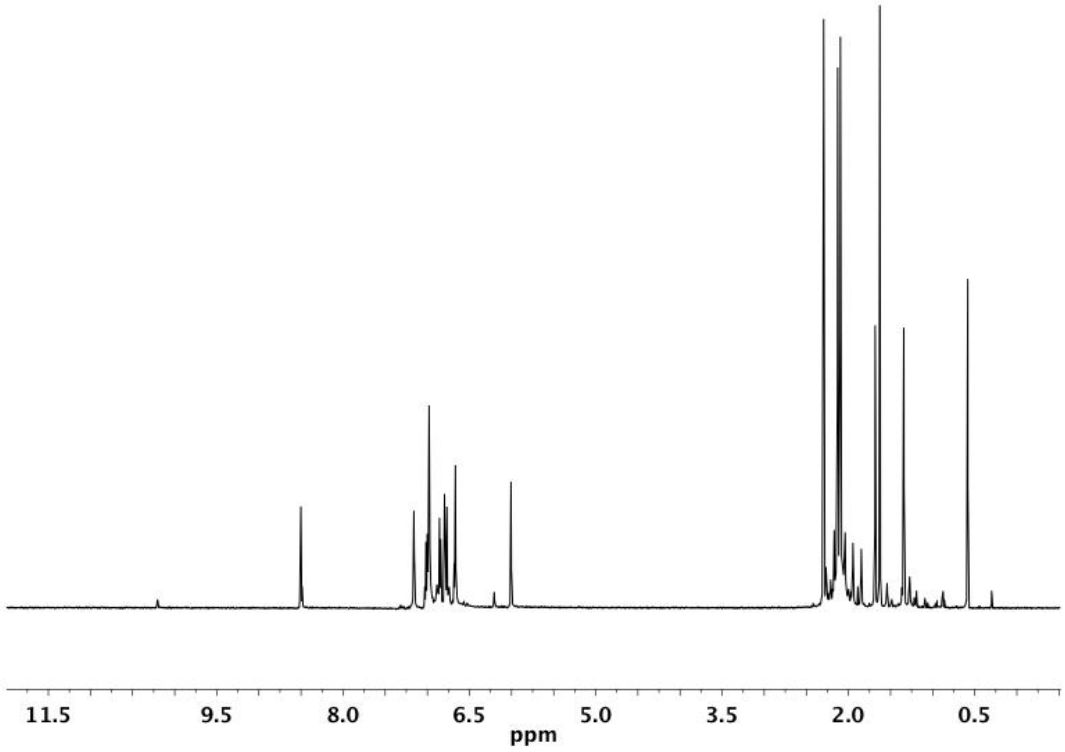
^1H NMR in C_6D_6:



W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-2,6-Me$_2$C$_6$H$_3$) (4d$_W$) Solid Ar'OH (13.2 mg, 0.108 mmol) was added to a −25 °C, stirring solution of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)$_2$, **2$_W$** (88.5 mg, 0.106 mmol), and allowed to stir at ambient temperature for 16 h. The volatiles were removed *in vacuo*. The yellow oil was extracted with pentane, filtered through a pipette filter, and the volatiles removed *in vacuo* from the filtrate. The yellow oil was dissolved in 1 mL

MeCN and stored at −25 °C for 16 h over which time yellow precipitate formed. The mother liquor was removed by pipette and the solid was washed with cold MeCN and dried under vacuum. The mother liquor was concentrated and cooled to −25 °C to collect three crops in the same manner, 65.0 mg, 71 %. ^{1}H NMR (C_6D_6, resonances reported for major isomer, about 85%) δ 8.501 (s, 1H, $^{1}J_{HW}$ = 14 Hz, W=C*H*), 7.030 – 6.961 (overlapping signals, Ar*H*, 6H), 6.859 – 6.842 (overlapping signals, 2H, Ar*H*), 6.796 – 6.768 (overlapping signals, 4H, Ar*H*), 6.681 – 6.651 (overlapping signals, 3H, Ar*H*), 6.007 (s, 2H, pyr*H*), 2.294 (s, 6H, MesCH_3), 2.127 (s, 6H, MesCH_3), 2.095 (s, 6H, MesCH_3), 1.682 (s, 3H, W=CHCMe_2Ph), 1.627(s, 6H), 1.342 (s, 3H, W=CHCMe_2Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, all visible peaks (both isomers) reported) δ 261.5 (W=*C*H), 162.8, 153.9, 151.0, 139.8, 137.1, 136.9, 136.0, 130.6, 129.0, 128.6, 128.6, 128.4, 126.7, 126.4, 126.1, 125.8, 122.2, 110.3, 51.8, 34.0, 32.6, 21.7, 21.4, 21.2, 21.1, 20.6, 18.1, 16.6. Anal. Calcd for $C_{48}H_{54}N_2OW$: C, 67.13; H, 6.34; N, 3.26. Found: C, 66.99; H, 6.47; N, 3.51.

^{1}H NMR in C_6D_6:



EXSY Studies Samples were prepared in C_6D_6 in teflon-stoppered NMR tubes. EXSY experiments were run at 21 °C with a mixing time of 1 s.

Photolysis Studies Samples were prepared in toluene-d_8 in teflon-stoppered NMR tubes and photolyzed at –78 °C in a Rayonet photolysis apparatus. The samples were kept at –78 °C until placed in a 500 MHz NMR spectrometer preequilibrated at the desired temperature. Data were collected over at least two half lives by observing the decay of the *anti* resonance with respect to an internal standard of poly(dimethylsiloxane).

General procedure for addition of $B(C_6F_5)_3$ to 3f and 3g. A solution of $B(C_6F_5)_3$ in ~0.2 mL C_6D_6 was added to a solution of **3** in ~ 0.4 mL C_6D_6 in a teflon-stoppered NMR tube. The tube was inverted to mix and ^{1}H and ^{19}F NMR spectra were obtained.

3f': 14.3 mg (0.0146 mmol) **3f** and 7.0 mg (0.0137 mmmol) $B(C_6F_5)_3$. ^{1}H NMR (C_6D_6, alkylidene resonances): δ 12.234 (W=C*H*, *anti*, $^1J_{CH}$ = 154 Hz, integration 51), 11.799 (W=C*H*, *syn*, $^1J_{CH}$ = 121 Hz, integration 100).

3g': 21.2 mg (0.0220 mmol) **3g** and 11.0 mg (0.0215 mmol) $B(C_6F_5)_3$. ^{1}H NMR spectra were obtained at 400 MHz, 500 MHz, and 600 MHz to distinguish the ^{13}C satellites from resonances due to trace impurities. ^{1}H NMR (C_6D_6, alkylidene resonances): δ 12.995 (W=C*H*, *anti*, $^1J_{CH}$ = 149 Hz, integration 44), 12.386 (W=C*H*, *syn*, $^1J_{CH}$ = 118 Hz, integration 100).

Crystallographic details. Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker-AXS X8 Kappa Duo diffractometer coupled to a Smart Apex2 CCD detector with Mo Kα radiation (λ = 0.71073 Å) from an Incoatec *IμS* micro-source. The structures were solved by direct methods using SHELXS[3] and refined against F^2 on all data by full-matrix least squares with SHELXL-97[4] following established refinement strategies[5]. All non-hydrogen atoms were refined anisotropically. Except for hydrogen on carbon atoms directly binding to the metal (for details see below), all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality, a summary of the residual values of the refinements as well as other pertinent parameters are listed in Tables S1 and S2.

Compound **10** crystallizes in the triclinic space group *P*-1 with one molecule of 10, one molecule of toluene and one-half molecule of Zn_2Cl_6 per asymmetric unit. The second half of the Zn_2Cl_6 is generated by the crystallographic inversion center. The tungsten-bound chlorine, the bipyridine ligand as well as the tungsten atom itself were treated as disordered over two positions. The ratio between the two components was refined freely and converged at 0.6824(15). The disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters for all atoms. Coordinates for the hydrogen atom on C1, that is the carbon atom directly binding to the tungsten, were taken from the difference Fourier synthesis. The hydrogen atom was subsequently refined semi-freely with the help of a distance restraint on the C—H-distance (target 0.95(2) Å). All bond lengths and angles specified and discussed throughout this publication are those of the major component of the disorder.

Compound $\mathbf{4a_w}$ crystallizes in the monoclinic space group $P2_1/c$ with one molecule per asymmetric unit and shows whole-molecule disorder. The ratio between the two components was refined freely and converged at 0.8979(13). The disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters for all atoms. The following pairs of almost overlapping atoms were constrained to show identical anisotropic displacement parameters: C1/C1A, C42/C42A, C43/C43A, C44/C44A, C33/C33A, C34/C34A, C35/C35A. Coordinates for the hydrogen atom on C1, that is the carbon atom directly binding to the tungsten, were taken from the difference Fourier synthesis. The hydrogen atom was subsequently refined semi-freely with the help of a distance restraint on the C—H-distance (target 0.95(2) Å). This approach did not work for the minor component of the whole-molecule disorder and H1A was introduced in its geometrically calculated position and refined using a riding model. All bond lengths and angles specified and discussed throughout this publication are those of the major component of the disorder.

Acknowledgements

The diffractometer used for diffraction data collection was purchased with the help of funding from the National Science Foundation (NSF) under Grant Number CHE-0946721.

Table S1. Crystal data and structure refinement for [W(NAr*)($CHCMe_2Ph$)Cl(bpy)]0.5[Zn_2Cl_6] (**10**).

Identification code	x12001	
Empirical formula	C_{51} H_{53} Cl_4 N_3 W Zn	
Formula weight	1098.98	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 9.8830(7) Å	α = 79.475(2)°.
	b = 11.6031(8) Å	β = 83.2370(10)°.
	c = 20.9756(15) Å	γ = 83.253(2)°.
Volume	2337.0(3) Å^3	
Z	2	
Density (calculated)	1.562 Mg/m^3	
Absorption coefficient	3.239 mm^{-1}	
F(000)	1104	
Crystal size	0.10 x 0.10 x 0.05 mm^3	
Theta range for data collection	1.79 to 30.31°.	
Index ranges	-14<=*h*<=14, -16<=*k*<=16, -29<=*l*<=29	
Reflections collected	100713	
Independent reflections	14002 [R_{int} = 0.0518]	
Completeness to theta = 30.31°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8548 and 0.7377	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14002 / 552 / 680	
Goodness-of-fit on F^2	1.039	
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0261, *wR*2 = 0.0630	
R indices (all data)	*R*1 = 0.0307, *wR*2 = 0.0644	
Largest diff. peak and hole	0.911 and -0.869 e.Å^{-3}	

Table S2. Crystal data and structure refinement for W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O^{t}Bu), **4a$_W$**

Identification code	x12104	
Empirical formula	C_{44} H_{54} N_2 O W	
Formula weight	810.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.6685(8) Å	α = 90°.
	b = 14.3088(9) Å	β = 91.113(2)°.
	c = 22.9645(16) Å	γ = 90°.
Volume	3833.5(4) Å^3	
Z	4	
Density (calculated)	1.405 Mg/m^3	
Absorption coefficient	3.048 mm^{-1}	
F(000)	1656	
Crystal size	0.05 x 0.04 x 0.03 mm^3	
Theta range for data collection	1.68 to 31.51°.	
Index ranges	-17<=h<=17, -21<=k<=21, -33<=l<=33	
Reflections collected	186081	
Independent reflections	12749 [R_{int} = 0.0546]	
Completeness to theta = 31.51°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9141 and 0.8625	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12749 / 1946 / 840	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2σ(I)]	R1 = 0.0273, wR2 = 0.0597	
R indices (all data)	R1 = 0.0395, wR2 = 0.0640	
Largest diff. peak and hole	1.028 and -0.570 e.Å^{-3}	

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