SYNTHESIS AND REACTIVITY OF TECHNETIUM HYDRIDES

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Abstract

CHAPTER 1. Several low valent technetium hydride complexes have been prepared. The trihydrides TcH_3L_4 (where L = PPh_2Me (**1**), PPh_3 (**2**)) were synthesized by treatment of $TcCl_4L_2$ with $NaBH_4$ in EtOH in the presence of excess L. Reaction of **1** with HBF_4 in EtOH affords the cationic species, $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**). The molecular structure for **3** was determined by X-ray diffraction to have the following parameters: a = b = 16.692 Å, c = 21.722 Å, $\alpha = \beta = \gamma = 90.000$ °, tetragonal, p4/ncc, Z = 4. The PPh_3 ligands in **2** are prone to substitution and upon treatment with 4.5 equiv. PPh_2Me $H_3Tc(PPh_2Me)_4$ (**1**) is obtained. Two equiv. of the bidentate phosphine dppe (dppe = diphenylphosphinoethane) react with **2** in the presence of N_2 to afford the known dinitrogen complex $HTc(N_2)(dppe)_2$ (**5**). Treatment of **5** with H_2 results in the formation of $H_3Tc(dppe)_2$ (**6**). Reaction of $H_3Tc(dppe)_2$ (**6**) with CO(g) and N_2 produces the Tc(I) complexes $HTc(CO)(dppe)_2$ (**7**) and $HTc(N_2)(dppe)_2$ (**5**), respectively. Treatment of **2** with CO(g) in benzene gives the monohydride complex *trans*- $HTc(CO)_3(PPh_3)_2$ (**8**).

CHAPTER 2. The reactivity of $H_3Tc(PPh_3)_4$ (**1**) with proton sources has been explored. Treatment of **1** with acetylacetone (Hacac) in the presence of N_2 gives the Tc(I) dinitrogen complex $Tc(N_2)(acac)(PPh_3)_3$ (**2**) as oranges crystals in 43% yield. A single crystal X-ray diffraction structure determination was performed on **2** (crystal data for $C_{59}H_{52}N_2O_2P_3Tc$: space group = $P2_1/n$, *a* = 10.659(6) Å, *b* = 22.324(5) Å, *c* = 21.466 Å, β = 101.26(3)°, *V* = 5009(6) Å^3 to give

Z = 4, R = 0.081, R_w = 0.095). Under similar conditions treatment of **1** with 2-mercaptopyridine (pySH) gives the Tc(I) monohydride complex $HTc(pyS)_2(PPh_3)_2$ (**3**).

CHAPTER 3. The chemistry of the technetium (I) monohydride complex *trans*-$HTc(CO)_3(PPh_3)_2$ (**1**) with electrophilic substrates has been investigated. Diazonium salts $[(p\text{-}^tBu(C_6H_4))N_2]PF_6$ react rapidly with **1** to give the diazene complex $[Tc(CO)_3(NHN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**) in 67% yield. The molecular structure for **2a** was determined by X-ray diffraction to have the following parameters: space group $P2_1/n$, a = 14.030(3) Å, b = 14.123(3) Å, c = 25.227(5) Å, β = 96.09(2) °, monoclinic, Z = 4. Addition of 1 equiv. DBU (DBU = 1,8-diazabicyclo[5.4.0]undecene) to MeCN solutions of **2a** gives the neutral diazene complex, $Tc(CO)_3(NN(p\text{-}^tBu(C_6H_4))(PPh_3)_2$ (**2b**). The heterocumulenes CS_2 and $N(CH_3)CS$, also readily insert into the Tc-H bond of **1** affording complexes $Tc(CO)_2(\eta^2\text{-}S_2CH)(PPh_3)_2$ (**3**) and $Tc(CO)_2(\eta^2\text{-}N(CH_3),SCH)(PPh_3)_2$ (**4**), respectively. Complex **1** also reacts with electron deficient acetylenes. When **1** is treated with 1 equiv. dimethylacetylenedicarboxylate (DMAD), $Tc(CO)_2[\text{-}C(CO_2Me)=CH(C(O)OMe)](PPh_3)_2$ (**5**) is obtained. Treatment with the less electrophilic acetylene methyl propiolate affords $Tc(CO)_3[\text{-}C(CO_2Me)=CH_2](PPh_3)_2$ (**6**) in 57% yield.

CHAPTER 4. Reactions of the Tc(I) monohydride complex *trans*-$HTc(CO)_3(PPh_3)_2$ (**1**) with proton sources have been employed for the synthesis of a variety of novel Tc(I) carbonyl compounds. In the presence of a coordinating ligand, L, treatment of **1** with HBF_4, yields the cation $[Tc(CO)_3L(PPh_3)_2]^+$ (where L = MeCN (**2**); CO (**3**)). When the protonation of **1** is carried out with HCl or CF_3SO_3H in the absence of a coordinating ligand, the neutral Tc(I) chloride **4** or triflate **5** complex is obtained. Reaction of **1** with formic acid and acetic acid affords the η^2-formate and acetate complexes $Tc(CO)_2(\eta^2\text{-}O_2CH)(PPh_3)_2$ (**6a**) and $Tc(CO)_2(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (**6b**). Weaker acids such as tropolone (Htrop) and acetylacetone (Hacac) also react with **1** to give $Tc(CO)_2(trop)(PPh_3)_2$ (**7**) and $Tc(CO)_2(acac)(PPh_3)_2$ (**8**). The molecular structure for **8** was determined by X-ray diffraction to have the following parameters: space group $P2_1/c$, a = 9.726(3) Å, b = 20.873(5) Å, c = 20.330(3) Å, β = 96.25(2)°, monoclinic, Z = 4. Reaction of **1** with 3-hydroxysalicylaldehyde or salicylaldehyde affords the complexes $Tc(CO)_2(\eta^2\text{-}3\text{-}hydroxysalicylaldehyde)(PPh_3)_2$ (**9a**) and $Tc(CO)_2(\eta^2\text{-}salicylaldehyde)(PPh_3)_2$ (**9b**) where the aldehyde ligand is coordinated in a bidentate fashion. Reaction

of **4** with NaCp (Cp = cyclopentadienyl) and NaL_{OEt} (L_{OEt} = {η^5-$CpCo(P(O)(OEt)_2)_3$}) affords (η^5-Cp)$Tc(CO)_2(PPh_3)$ (**10**) and $L_{OEt}Tc(CO)_2(PPh_3)$ (**11**).

CHAPTER 5. Several novel technetium nucleophile-carbonyl adducts have been synthesized and characterized. Treatment of the Tc(I) cation, *trans*-$[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) with $LiEt_3BH$ affords the Tc formyl complex $Tc(CO)_3(C(O)H)(PPh_3)_2$ (**2**) in 76% yield. Reaction of **2** with 1 equiv. $CH_3SO_3CF_3$ in toluene produces the Fischer carbene $[Tc(CO)_3(=C(OMe)H)(PPh_3)_2]SO_3CF_3$ (**3**). The nucleophile OH^- reacts with **1** to give the hydroxycarbonyl $Tc(CO)_3(C(O)OH)(PPh_3)_2$ (**4**). If this reaction is carried out in the presence of alkyl alcohols, ROH (R = Me (**5**), Et (**6**)) the corresponding alkoxycarbonyl complexes, $Tc(CO)_3(C(O)OR)(PPh_3)_2$ are obtained. The aryloxycarbonyl complex $Tc(CO)_3(C(O)OR)(PPh_3)_2$ (where R = (*p*-tolyl) (**7**) was prepared from the reaction of **1** with excess KOR in thf. Treatment of **1** with NaN_3 gives the isocyanate complex $Tc(CO)_3(NCO)(PPh_3)_2$ (**8**).

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Table of Contents

Abstract..3

Chapter 1. Synthesis and Characterization of Technetium Polyhydride Complexes

Introduction..12
Results and Discussion..13
Experimental...20
Notes and References..45

Chapter 2. Reactivity of $H_3Tc(PPh_3)_4$ with Proton Sources

Introduction..48
Results and Discussion..48
Experimental...51
Notes and References..64

Chapter 3. Insertion of Electrophilic Substrates in the Tc-H Bond of $HTc(CO)_3(PPh_3)_2$

Introduction..67
Results and Discussion..67
Experimental...72
Notes and References..92

Chapter 4. Protonation of the Tc-H Bond in $HTc(CO)_3(PPh_3)_2$

Introduction..95
Results and Discussion..95
Experimental..100
Notes and References..126

Chapter 5. Nucleophilic Attack on Coordinated Carbon Monoxide In the Cation $[Tc(CO)_4(PPh_3)_2]BF_4$

Introduction..129
Results and Discussion..129
Experimental..133
Notes and References..142

Acknowledgments..143
Biographical Note..144

List of Tables

Table **Page**

Chapter 1

I. Crystal and Data Collection Parameters for $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**). 30

II. Selected Intramolecular Distances for $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**). 32

III. Selected Intramolecular Bond Angles for $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**). 32

IV. Positional Parameters and Estimated Standard Deviations (Å^2) for $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**). 34

Chapter 2

I. Crystal and Data Collection Parameters for $Tc(N_2)(acac)(PPh_3)_2$ (**2**). 55

II. Selected Intramolecular Distances for $Tc(N_2)(acac)(PPh_3)_2$ (**2**). 57

III. Selected Intramolecular Bond Angles for $Tc(N_2)(acac)(PPh_3)_2$ (**2**). 58

IV. Positional Parameters and Estimated Standard Deviations (Å^2) for $Tc(N_2)(acac)(PPh_3)_2$ (**2**). 59

Chapter 3

I. Crystal and Data Collection Parameters for $[Tc(CO)_3(NHN(p\text{-}{}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**). 81

II. Selected Intramolecular Distances for $[Tc(CO)_3(NHN(p\text{-}{}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**). 82

III. Selected Intramolecular Bond Angles for $[Tc(CO)_3(NHN(p\text{-}{}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**). 83

IV. Positional Parameters and Estimated Standard Deviations (Å^2) for $[Tc(CO)_3(NHN(p\text{-}{}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**). 84

Chapter 4

I. Crystal and Data Collection Parameters for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**). 111

II. Selected Intramolecular Distances for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**). 113

III. Selected Intramolecular Bond Angles for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**). 114

IV. Positional Parameters and Estimated Standard Deviations ($Å^2$) for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**). 115

List of Figures

Figure **Page**

Chapter 1

1. ^1H NMR spectra of $H_3Tc(PPh_3)_4$ (**2**). 37
2. VT ^1H NMR spectra of $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**) in CD_2Cl_2. 39
3. ORTEP drawn diagram of $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**). 40
4. Stereochemical viewing of $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**). 41
5. VT ^1H NMR spectra of $H_3Tc(dppe)_2$ (**6**) in toluene (d_8). 43

Chapter 2

1. Chem 3D drawn diagram of $Tc(N_2)(acac)(PPh_3)_3$ (**2**). 62

Chapter 3

1. Chem 3D drawn diagram of $[Tc(CO)_3(NHN(p\text{-}{}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**). 88

Chapter 4

1. Chem 3D drawn diagram of $Tc(CO)_2(acac)(PPh_3)_2$ (**8**). 119

Chapter 1

Synthesis and Characterization of Technetium Polyhydride Complexes

Introduction

Transition metal hydride complexes have been intensely studied as a result of their fascinating structural features and unique reaction chemistry. The unusual reactivity of these complexes stems from their ability to form reactive intermediates *via* the loss of H_2. Of the transition metals, rhenium possesses the most diverse family of polyhydrides, encompassing the widest range of oxidation states and coordination numbers. Examples of known Re hydrides include K_2ReH_9,[1] $ReH_7(PR_3)_2$,[2] $ReH_5(PR_3)_3$,[2] $ReH_3(PR_3)_4$,[3] and $ReH(PMe_3)_5$.[4] Of particular interest is the heptahydride complex $ReH_7(PR_3)_2$ (where R = C_6H_5, C_6H_{10}) which undergoes C-H activation[5] as well as a number of other exciting reactions.[6]

Despite the extensive chemistry of rhenium polyhydrides, very little experimental information is available on the technetium analogs of these complexes. This is surprising since the lower M-H bond strength of second-row metals compared to that of their third-row congeners[6] is expected to result in enhanced reactivity. Reported technetium hydride compounds include K_2TcH_9,[2] $TcHN_2(dppe)_2$,[7] $[TcH(\eta^2\text{-tu}')(PMe_3)_4]PF_6$ (where tu'= $(NH)SC(NH_2)$),[8] $TcH_2(NO)(PPh_3)_3$[9] and $TcH_3(dppe)_2$.[10] Recently the first example of a Tc dihydrogen complex, $TcCl(H_2)(dppe)_2$[10] has been reported.

Although the enneahydrido complex K_2TcH_9 would seem to be the ideal starting material for the preparation of other technetium polyhydrides, the reported synthesis only produces low yields of impure product.[2] As part of our interest in the chemistry of technetium, several novel Tc trihydride complexes have been synthesized and characterized. The reactivity of these complexes is also explored.

Results and Discussion

Synthesis of Tc Polyhydrides

The neutral trihydrides H_3TcL_4 (where L = PPh_2Me (**1**), PPh_3 (**2**)) were prepared in high yield by the reduction of $TcCl_4L_2$ with $NaBH_4$ in EtOH in the presence of excess phosphine. This synthesis is not general and is only successful for PPh_3 and PPh_2Me. When smaller phosphines, such as $PPhMe_2$ are used, the corresponding Tc(III) halides, $TcCl_3L_3$ are formed. These complexes do not react further with $NaBH_4$ to yield Tc polyhydrides even at elevated temperatures. Complexes **1** and **2** may also be synthesized directly from NH_4TcO_4 under the same reaction conditions, however the resulting yields vary greatly and can be as low as 29%.

$H_3Tc(PPh_2Me)_4$ (**1**) is moderately stable in air as a solid, gradually decomposing over the course of several days. In solution, **1** is stable under H_2, N_2, and Ar atmospheres and may be purified in the dry box by recrystallization from CH_2Cl_2/pentane mixtures at -40° C. Unlike $H_3Tc(PPh_2Me)_4$ (**1**), the complex $H_3Tc(PPh_3)_4$ (**2**) is unstable in benzene or toluene solutions under Ar, N_2, and H_2 atmospheres. Chlorinated solvents react with **2** to give the Tc(IV) starting material $TcCl_4(PPh_3)_2$.

Characterization of Tc Trihydrides

The Tc-H resonance for $H_3Tc(PPh_2Me)_4$ (**1**) is observed in the ^1H NMR spectrum as a quintet at δ -5.06 (J_{P-H} = 20.8 Hz). The methyl resonance appears as a singlet at δ 0.99. Upon decreasing the temperature, the hydride and methyl resonances broaden, but the low-temperature limiting spectrum was not observed even at -80° C.

The ^1H NMR spectrum of $H_3Tc(PPh_3)_4$ (**2**) is unusual. In addition to showing the expected quintet for the hydride resonance at δ -7.15 (J_{P-H} = 36.9

Hz), a small quartet at δ -4.9 ($J_{P\text{-}H}$ = 19.5 Hz) is also visible. No other signals upfield of TMS are observed. The aryl region of the spectrum is complex and reveals a number of peaks corresponding to the PPh_3 protons. When the ^1H NMR spectrum of **2** is obtained in the presence of excess PPh_3 only the quintet at δ -7.15 is observed. This reaction is reversible and removal of the excess phosphine results in the reappearance of the quartet at δ -4.9.

The periodic monitoring by ^1H NMR spectroscopy of a C_6D_6 solution of **2** under an Ar(g) atmosphere shows the quartet at δ -4.9 broadening into the baseline over the course of several h. This is accompanied by the appearance of additional high field signals at δ -5.8, -8.5, and -9.3. These peaks are weak compared to the quintet at δ -7.15 and do not display any coupling to the phosphine ligands. After ~10 h. no peaks upfield of TMS are visible and a brown solid is deposited on the walls of the NMR tube.

Selective ^{31}P NMR decoupling experiments which have been used to confirm hydride multiplicity in transition metal polyhydrides[11,12] are not useful in the case of Tc. At room temperature both the ^{31}P and $^{31}P\{H\}$ NMR spectra of **1** and **2** exhibit extremely broad, flat peaks due to coupling of the ^{99}Tc quadrupolar nucleus (^{99}Tc: I = 9/2) and the phosphorus nuclei (^{31}P: I = 1/2). The linewidths (~10,000 Hz) of the observed peaks decrease as the temperature is lowered, however at -75° C the peaks are not fully decoupled from the Tc nucleus and exhibit linewidths of ~4000 Hz. This temperature dependent quadrapolar effect has been described for other ^{99}Tc complexes containing phosphine ligands (e.g.: $[TcH(\eta^2\text{-N,S-tu'})(PMe_3)_4]PF_6$).[8] It has also been observed in the $^{13}C\{H\}$ NMR spectra of Tc complexes which contain carbon atoms that are bound directly to the metal center.[13]

In the FAB(+) mass spectrum of **1** major peaks corresponding to the fragments at [Tc($PPh_2Me)_4$], [Tc($PPh_2Me)_3$], and [Tc($PPh_2Me)_2$] were observed at 899, 699 and 499 *m/z*, respectively. The FAB(+) mass spectrum of $H_3Tc(PPh_3)_4$ (**2**) only showed peaks corresponding to the fragments [Tc($PPh_3)_3$] (886 *m/z*) and [Tc($PPh_3)_2$] (623 *m/z*).

Protonation Reactions

$H_3Tc(PPh_3)_4$ (**2**) reacts rapidly with $HBF_4{\cdot}Et_2O$ in EtOH to give a number of unidentifiable products. However, treatment of $H_3Tc(PPh_2Me)_4$ (**1**) with $HBF_4{\cdot}OEt_2$ in EtOH at room temperature readily affords the cationic complex $[TcH_4(PPh_2Me)_4]BF_4$ (**3**) in 64% yield. Evolution of H_2 from the reaction mixture was not observed. This protonation is reversible and the subsequent addition of DBU (DBU = 1,8-diazabicyclo[5.4.0]undecene) or NEt_3 to MeCN solutions of **3** cleanly reforms **1**. This reaction was quantitative. An exact determination of the pKa of **3** is complicated by the low solubility of **1** in MeCN. Other solvents such as THF and CH_2Cl_2 which dissolve both complexes **1** and **3** suffer from problems associated with ion pairing in solution.[14] An approximate indication of the acidity of **3** can be obtained by a comparison to that reported for $[IrHCp^*(CO)_2]^+$.[15] Since both of these complexes are deprotonated by the weaker base (NEt_3) an approximate upper limit of their pKa can be placed at 18.5.[16] This indicates that complex **3** is more acidic than the related Re polyhydride, $[H_4Re(PPhMe_2)_4]BF_4$ whose pKa in MeCN was determined to be 25.5.[16] There are two effects which may account for the increase in the acidity of the Tc tetrahydride: 1) $PPhMe_2$ is a better donor than PPh_2Me, which should increase the acidity of the Tc complex; 2) second row transition metal hydrides appear to be more acidic than their third row congeners (pKa in MeCN: $CpMo(CO)_3H$ = 13.9; $CpW(CO)_3H$ = 16.1).[17]

The ^1H NMR spectrum of $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**) shows a quintet at δ -3.02 ($J_{P\text{-}H}$ = 17.5 Hz) for the hydride resonance. As was observed for $H_3Tc(PPh_2Me)_4$ (**1**) the quintet pattern is lost at -70 °C but the low-temperature limiting spectrum was not observed. The FAB(+) mass spectrum of **3** is identical to that of **1** showing major peaks at 899 $[Tc(PPh_2Me)_4]$, 699 $[Tc(PPh_2Me)_3]$, and 499 $[Tc(PPh_2Me)_2]$ *m/z*.

The observed $J_{P\text{-}H}$ coupling constants for $H_3Tc(PPh_2Me)_4$ (**1**) and $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**) are consistent with the presence of hydride ligands only.[18] For metal complexes which possess an η^2-dihydrogen ligand, the $J_{P\text{-}H}$ coupling between $^1(H_2)$ and ^{31}P nuclei is often less than 6 Hz and is usually zero.[18] Complexes **1** and **3** also show no signs of H_2 loss in solution and do not react with D_2 or CO. A lack of chemical reactivity was also reported for the similar Re polyhydrides $H_3Re(PPhMe_2)_4$ and $[H_4Re(PPhMe_2)_4]BF_4$.[19]

Since the protonation of transition metal hydrides is a common method for the preparation for dihydrogen complexes,[18] the molecular structure of $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**) was investigated further by a single crystal X-ray diffraction study. Diffusion of pentane into a CH_2Cl_2 solution at -40 °C resulted in the formation of colorless cubic crystals. Complex **3** crystallizes with a CH_2Cl_2 solvate molecule. Data and collection parameters are given in **Table I** and the experimental section. An ORTEP diagram is given in **Figure 3**. Bond lengths, angles and positional parameters are given in **Tables II, III,** and **IV**, respectively.

The geometry of **3** can best be described as distorted trigonal dodecahedron in which the nearly planar "TcP_4" fragment is intersected by a tetrahedron of hydride ligands. The Tc-H distance which was taken from the difference map and not refined (see Experimental Section). This value was determined to be closer to 1.87 Å than the usual values of 1.6 to 1.7 Å observed in other transition metal polyhydride X-ray crystal structures.[18] The long H···H distances of approximately 2.6 and 3.3 Å indicate that **3** is a classical (H···H > 1.6 Å) polyhydride.[18]

The molecular structure of **3** differs from those of the related complexes $[H_4Re(PPhMe_2)_4]BF_4$[19] and $H_4Mo(PPh_2Me)_4$.[20] In the Re compound the phosphine ligands are not planar and are arranged in a "flattened tetrahedral" geometry which is intermediate between the two extreme structures of tetrahedral and planar.[19] The hydride ligands were not located in this structure. The geometry of phosphines ligands in this Re complex is very similar to that determined for the Mo tetrahydride complex $H_4Mo(PPh_2Me)_4$.[20] The observed "flattened tetrahedron" of phosphine atoms in this molecule is intersected by an elongated tetrahedron containing the hydride ligands.[20] For **3** the four phosphine atoms and the Tc metal center are nearly planar rather than arranged into a "flattened tetrahedron".

Substitution Reactions of 2 with Phosphine Ligands

The behavior of $H_3Tc(PPh_3)_4$ (**2**) in solution led us to investigate the reactivity of this complex with other phosphine ligands. The addition of 4 equiv. of the monodentate phosphine PPh_2Me to toluene solutions of $H_3Tc(PPh_3)_4$ (**2**) leads to a complete substitution of the PPh_3 ligands. In 4.5 h., $H_3Tc(PPh_2Me)_4$ (**1**) is obtained in 58% yield. Although this reaction must be carried out using dry, non-chlorinated solvents under an inert atmosphere, it is not sensitive to the type atmosphere employed. Also the reaction yields do not significantly vary from N_2, H_2, or Ar atmospheres.

Smaller phosphines like $PPhMe_2$ (or PEt_3) also react with **3** giving $H_3Tc(PPhMe_2)_4$ (**4**). Due to the high solubility of **4** in alkane solvents the complex could not be separated from the liberated PPh_3. The signal for the hydride ligands is observed in the ^1H NMR spectrum of **4** as a quintet at δ -4.55 ($J_{P\text{-}H}$ = 20.5 Hz). No other peaks upfield of TMS were observed. The FAB(+) mass spectrum of **4** shows a parent peak at 652 *m/z* corresponding to the fragment $[Tc(PPhMe_2)_4]$. No peaks which could be attributed to mixed phosphine complexes of the type $H_3Tc(PPh_3)_x(PPhMe_2)_{4-x}$ were observed.

Reactions of $H_3Tc(PPh_3)_4$ (**2**) with bidentate phosphines are more complicated than was observed for the monodentate phosphines PPh_2Me and $PPhMe_2$. Treatment of **2** with 2 equiv. dppe (dppe = diphenylphosphino ethane) in toluene under N_2 produces the known dinitrogen complex $HTc(N_2)(dppe)_2$[7] (**5**) rather than the expected trihydride $H_3Tc(dppe)_2$. This reaction occurs readily at room temperature to give $HTc(N_2)(dppe)_2$ (**5**) in 85% yield. The dinitrogen stretch is observed in the IR spectrum at 2044 cm^{-1} and the hydride ligand appears in the ^1H NMR spectrum as a quintet at δ -10.1 ($J_{P\text{-}H}$ = 21.5 Hz).

The trihydride complex $H_3Tc(dppe)_2$[10] (**6**) was prepared by carrying out the reaction of $H_3Tc(PPh_3)_4$ (**2**) with dppe in toluene in the presence of 1 atm H_2. This reaction is quite slow and requires several d. for completion. Treatment of $HTc(N_2)(dppe)_2$ (**5**) with H_2 in C_6D_6 also affords $H_3Tc(dppe)_2$ (**6**) as observed by ^1H NMR spectroscopy. Removal of the H_2 atmosphere, followed by the addition of 1 atm N_2 for 24 h. regenerates the dinitrogen compound $HTc(N_2)(dppe)_2$ (**5**).

The ^1H NMR spectrum of $H_3Tc(dppe)_2$ (**6**) (obtained under 1 atm H_2) is identical to that reported by Burrell *et al.* [10] except that the phosphorus-hydride coupling for the hydride signal at δ -6.9 was not resolved. Lowering the temperature to -40 °C led to a splitting of this peak into two broad signals in a

1:2 ratio at δ -6.7 and -7.2, respectively. This ^{1}H NMR spectrum resembles that of the analogous Re complex $H_3Re(dppe)_2$ at -40 °C.[21]

Benzene solutions of $H_3Tc(dppe)_2$ (**6**) undergo a color change from pale yellow to colorless upon exposure to CO(g). The ^{1}H NMR spectrum shows a quintet at δ -5.54 ($J_{P\text{-}H}$ = 23 Hz) which corresponds to the hydride resonance of the known carbonyl complex $HTc(CO)(dppe)_2$[7] (**7**).

Reaction of Tc Trihydrides with π–Acceptors

The complex $H_3Tc(PPh_2Me)_4$ (**1**) does not react with CO(g), isonitriles, or pyridine. Treatment of $H_3Tc(PPh_3)_4$ (**2**) with with CO(g) in benzene, however, gives the Tc(I) monohydride complex $HTc(CO)_3(PPh_3)_2$ **8** in 71% yield. No evidence for the formation of the dicarbonyl complex $HTc(CO)_2(PPh_3)_3$ was observed. The FAB (+) mass spectrum of **8** shows two major peaks at 707 and 679 *m/z* which correspond to the fragments $Tc(CO)_3(PPh_3)_2$ and $Tc(CO)_2(PPh_3)_2$. The hydride ligand was observed in the ^{1}H NMR spectrum as a triplet at δ -4.8 ($J_{P\text{-}H}$ = 19.5 Hz).

The carbonyl resonances for **8** could only be observed by $^{13}C\{H\}$ NMR spectroscopy for the ^{13}C labeled complex $HTc(^{13}CO)_3(PPh_3)_2$. The carbonyl region of the $^{13}C\{H\}$ NMR spectrum shows one broad resonance at δ 209.5 which has a shoulder centered approximately at δ 208. The $^{31}P\{H\}$ NMR spectrum of **8** also shows an extremely broad peak at δ ~57.

Similar reactions carried out between (^{t}Bu)NC or pyridine and **2** did not yield the analogous complexes $HTcL_3(PPh_3)_2$ (where L = (^{t}Bu)NC, pyridine). The products of these reactions are currently under investigation.

Reactions with D_2

The treatment of $H_3Tc(PPh_2Me)_4$ (**1**) or $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**) with 1 atm of D_2 in C_6D_6 for 36 h. produces no discernible change in the ^{1}H NMR spectra of these complexes. The reaction of $H_3Tc(PPh_3)_4$ (**2**) with D_2 under similar conditions results in a change of color in the solution from yellow to red. This red complex has not yet been identified.

Conclusions

Several novel technetium polyhydride complexes have been synthesized and characterized. The complex $H_3Tc(PPh_3)_4$ (**2**) is a highly reactive species that can undergo ligand substitution reactions with a variety of phosphines. This differentiates **2** from most polyhydrides which undergo reactions with donor molecules which replace H_2 in the complex.[6]

Experimental

Caution! Technetium-99 is a weak β^--emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[22]

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Drybox solvents (toluene, THF, pentane, Et_2O) were distilled from sodium/benzophenone. A "bomb" refers to a cylindrical glass vessel sealed with a Kontes high vacuum stopcock. The complex $TcCl_4L_2$ (where L = PPh_3, PPh_2Me, $PPhMe_2$) was prepared according to the method of Mazzi *et al.*[23] Reagents and solvents were used as received unless otherwise stated. A Mattson Cynus 100 FTIR instrument was used to record all infrared spectra. Only representative IR data are given. Fast atom bombardment mass spectra (FABMS(+)) were obtained using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV and equipped with a Ion Tech B11N FAB gun. The FAB gun produces a beam of 6-8 keV xenon neutrals. All compounds were run in a matrix of neat 3-nitrobenzyl alcohol. ^1H, ^{13}C and ^{31}P NMR were recorded at 300.0 MHz, 75.429 MHz, and 121.421 MHz, respectively on a Varian Unity spectrometer unless otherwise noted. All $^{31}P\{H\}$ NMR are referenced to an external standard of 85% phosphoric acid in $CDCl_3$. The primary reference for ^{99}Tc NMR, $[NH_4][TcO_4]$ in D_2O resonates at 67.516 MHz and is designated as 0 ppm. The elemental analyses were performed by Atlantic Microlab, Norcross, GA.

$H_3Tc(PPh_2Me)_4$ (1). Method 1: To a round bottom flask containing $TcCl_4(PPh_2Me)_2$ (112 mg; 0.18 mmol), PPh_2Me (0.65 mL; 2.63 mmol) and 50 mL EtOH was slowly added $NaBH_4$ (40.0 mg; 1.05 mmol). The reaction mixture was stirred for 45 min. during which time a color change from green to bright yellow occurs. The yellow precipitate which formed was collected by filtration and washed copiously with H_2O, acetone, Et_2O and dried *in vacuo*. This complex was recrystallized in the dry box from CH_2Cl_2 /pentane mixtures stored at -40° C. Yield: (195.9 mg; 88%).

Method 2: An aqueous solution of $NH_4[TcO_4]$ (0.62 mL; 0.25 mmol) was evaporated to dryness and redissolved in 15 mL EtOH. To this solution was added 40 mL EtOH containing PPh_2Me (0.93 mL; 4.96 mmol), followed by $NaBH_4$ (95 mg; 2.50 mmol). The reaction mixture was stirred at room temperature for 45 min., during which time a yellow solid precipitated from the dark brown solution. The solid was collected onto a fritted disk(E), washed with H_2O, acetone, Et_2O and dried *in vacuo*. Yield: (148 mg; 65%).

Method 3: In the dry box, a Schlenk flask was charged with $H_3Tc(PPh_3)_4$ (**2**) (139 mg; 0.12 mmol), PPh_2Me (0.11 mL; 0.54 mmol) and 5 mL toluene. The reaction mixture was allowed to stir for 4.5 h. Removal of the volatiles under vacuum left a brownish/yellow oily residue. The flask was removed from the box, and 50 mL degassed EtOH was added. After stirring for 1 h., the bright yellow solid which precipitated was collected by filtration, washed with 5 mL EtOH, and 5 mL cold Et_2O, and dried *in vacuo*. This complex is spectroscopically identical to that which we previously reported. Yield: (50.0 mg; 58%).

Anal. Calcd. for $C_{52}H_{55}P_4Tc$: C, 69.18; H, 6.14. Found: C, 68.94; H, 6.14. ^1H NMR(CD_2Cl_2) δ (ppm): -5.06 (q, 3H, $J_{P\text{-}H}$ = 20.8 Hz, Tc-$\underline{H}$); 0.99 (s, 12H, P(C$\underline{H_3}$)); 7.14 (m, 24H, P(Ar$\underline{H}$)); 7.47 (m, 12H, P(Ar$\underline{H}$)). $^{31}P\{^1H\}$ NMR(CD_2Cl_2) δ (ppm): 40.1 (br). ^{99}Tc NMR(CD_2Cl_2) δ (ppm): -2070 (br). IR(KBr): ν 1956(w), 1885(w), 1772(m). FABMS(+)*m/z*: 899 $[Tc(PPh_2Me)_4]^+$; 699 $[Tc(PPh_2Me)_3]^+$; 499 $[Tc(PPh_2Me)_2]^+$.

$H_3Tc(PPh_3)_4$ (2). Method 1: To a round bottom flask containing $TcCl_4(PPh_3)_2$ (81 mg, 0.105 mmol) and triphenylphosphine (690 mg; 2.6 mmol) dissolved in 50 mL EtOH, was added $NaBH_4$ (40.0 mg; 1.1 mmol). The reaction mixture was stirred for 30 min. The yellow precipitate which formed was filtered onto a fritted disk (E) and washed copiously with acetone and Et_2O. The powder was then transferred to a round bottom flask containing 10 mL H_2O/10 mL MeOH and allowed to stir for 2 h. After this time the yellow powder was collected by filtration, washed with Et_2O, acetone, and dried *in vacuo*. Yield: (180 mg; 99%).

Method 2: An aqueous solution of $NH_4[TcO_4]$ (0.62 mL; 0.25 mmol) was evaporated to dryness and redissolved in 15 mL EtOH. To this solution was added 40 mL EtOH containing PPh_3 (1.3 g; 5.0 mmol). Next, $NaBH_4$ (95 mg; 2.5 mmol) was slowly added to the reaction flask. The reaction mixture was allowed to stir at room temperature for 45 min., during which time a yellow solid precipitated from the dark brown solution. The solid was collected on a fritted disk (E), washed with 25 mL of EtOH, acetone, Et_2O and dried *in vacuo.* Yield: (83.9 mg; 46%).

Anal. Calcd. for $C_{72}H_{63}P_4Tc$: C, 75.13; H, 5.52. Found: C, 74.77; H, 5.50. ^1H NMR (C_6D_6) δ (ppm): -7.15 (quintet, $J_{P\text{-}H}$ = 36.9 Hz, Tc-H); -4.9 (quartet, $J_{P\text{-}H}$ = 19.5 Hz); 6.75 (m, P(Ar$\underline{H}$)); 6.93 (m, P(Ar$\underline{H}$)); 7.04 (m, P(Ar$\underline{H}$)); 7.25 (br s, P(Ar$\underline{H}$)); 7.39 (m, P(Ar$\underline{H}$)); 7.75 (m, P(Ar$\underline{H}$)). IR(KBr): ν 2055(w), 1952(w), 1896(m), 1812(w). FABMS(+) m/z: 886 $[Tc(PPh_3)_3]^+$; 623 $[Tc(PPh_3)_2]^+$.

$[H_4Tc(PPh_2Me)_4]BF_4$ (3). To a stirred suspension of $H_3Tc(PPh_2Me)_4$ (**1**) (106 mg; 0.12 mmol) in 3.5 mL EtOH was slowly added 0.1 mL 85% $HBF_4{\cdot}Et_2O$. As the mixture was stirred for ~4 min., a brownish solution formed. The addition of 50 mL Et_2O precipitated a white solid which was collected by filtration, washed with benzene and Et_2O, and dried *in vacuo.* This complex was recrystallized in the dry box from CH_2Cl/pentane mixtures stored at -40° C. Yield: (75 mg; 64%).

Anal. Calcd. for $C_{52}H_{56}BF_4P_4Tc$: C, 63.05; H, 5.70. Found: C, 62.98; H, 5.74. ^1H NMR (CD_2Cl_2) δ (ppm): -3.02 (q, 4H, $J_{P\text{-}H}$ = 17.5 Hz, Tc-$\underline{H}$); 1.39 (s, 12H, P(C$\underline{H_3}$)); 7.35 (m, 48H, P(Ar$\underline{H}$)). $^{31}P\{H\}$ NMR(CD_2Cl_2) δ (ppm): ~29 (br). ^{99}Tc NMR(CD_2Cl_2) δ (ppm): -2269 (br). IR(KBr): ν 1967(w), 1843(w), 1815(w). FABMS(+) *m/z*: 899 $[Tc(PPh_2Me)_4]^+$; 699 $[Tc(PPh_2Me)_3]^+$; 499 $[Tc(PPh_2Me)_2]^+$; 299 $[Tc(PPh_2Me])^+$.

X-Ray Crystal Structure Determination of $[H_4Tc(PPh_2Me)_4]BF_4$ (3). Colorless cubic crystals were grown by slow vapor diffusion of pentane into a

CH_2Cl_2 solution of $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**) at -40 °C. Complex **3** crystallizes with a CH_2Cl_2 solvate molecule. A suitable crystal was selected and then transferred to an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $15.00 < 2\theta < 26.00$ °, corresponding to a tetragonal cell. Based on the systematic absences of 0kl: $l \neq 2n$; hk0: $h + k \neq 2n$; and hhl: $l \neq 2n$, the space group was determined to be P4/ncc. The final cell parameters are given in **Table I**.

The data were collected at a temperature of -86 °C using the ω–2θ scan technique to a maximum 2θ value of 49.7 °C. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.28° with a take-off angle of 2.8 °. Scans of $(0.80 + 0.35 \tan\theta)°$ were made at a speed ranging from 1.9 to 16.5 °/min (in omega). Moving-crystal moving counter background measurements were made by scanning an additional 25% above and below the scan range. The counter aperture consisted of a variable horizontal slit with a width ranging from 2.0 to 2.5 mm and a vertical slit set to 2.0 mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector.

Of the 10883 reflections which were collected, 30404 were unique (R_{int} = 0.155); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 min. of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied).

The linear absorption absorption coefficient for Mo Kα is 4.6 cm^{-1}. An empirical absorption correction, using the program DIFABS, was applied which resulted in transmission factors ranging from 0.59 to 1.46. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coeff. = 0.42792 x 10^{-7})

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 1085 observed reflections ($I>3.00\sigma(I)$) and 153 variable parameters and converged (largest parameter shift was 0.51 times its esd) with $R = 0.078$; $R_w = 0.076$. The standard deviation of an observation of unit weight was 2.35. The weighing scheme was based on counting statistics and included a factor (p = 0.02) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.24 and -0.51 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[24] Anomalous dispersion effects were included in F_{calc}; the values for Df$'$ and Df$''$ were those Cromer. All calculations were performed using TEXSAN crystallographic software package of Molecular Structure Corporation.

The peak assignment of the hydride ligand on the final difference Fourier map corresponded to 1.1 e$^-$/Å^3. Although there are two other peaks that are slightly larger (~1.2 e$^-$/Å^3), neither is located near the technetium metal center. Upon attempted refinement the peak associated with the hydride ligand merged with the electron density of the technetium atom.

Deprotonation of [H_4Tc(PPh_2Me)$_4$]BF_4 (3) with DBU. In the drybox, [H_4Tc(PPh_2Me)$_4$]BF_4 (3) (25.5 mg; 0.028 mmol) was dissolved in 5 mL MeCN.

The flask was removed from box and placed under a N_2 atmosphere. 0.10 mL DBU was added and the reaction mixture was allowed to stir for 2 h. The bright yellow precipitate which formed was filtered on a fritted disk, washed with 10 mL MeCN, 10 mL cold Et_2O, and dried *in vacuo.* Yield: (20.2 mg, 96%) of complex which is spectroscopically identical to $H_3Tc(PPh_2Me)_4$ (**1**).

$H_3Tc(PPhMe_2)_4$ (4). In the dry box, a Schlenk flask was charged with $H_3Tc(PPh_3)_4$ (**2**) (58.6 mg; 0.051 mmol), $PPhMe_2$ (33 μL; 0.23 mmol) and 5 mL toluene. The reaction mixture was allowed to stir for 4.5 h under 1 atm H_2. Removal of the volatiles under vacuum left a brownish/yellow oily residue. The reaction mixture was triturated with 5 x 10 mL portions Et_2O to yield a brownish/ yellow solid. The solid was collected onto a fritted funnel and dried *in vacuo*.

Complex **4** could not be isolated from the excess PPh_3 which is formed as a by-product in the reaction. ^1H NMR (C_6D_6) δ (ppm): -4.55 ppm (J_{P-H} = 20.5 Hz); 1.37 (s, P-C$\underline{H}_3$); 7.04 (m, P(Ar$\underline{H}$)); 7.95 (m, P(Ar$\underline{H}$)). FABMS(+) *m/z*: 653 [$Tc(PPhMe_2)_4$]; 514 [$Tc(PPhMe_2)_3$]; 375 [$Tc(PPhMe_2)_2$]; 262 [PPh_3].

$HTc(N_2)(dppe)_2$ (5). In a N_2 filled dry box, a flask was charged with $H_3Tc(PPh_3)_4$ (**2**) (108 mg; 0.094 mmol), dppe (76.8 mg; 0.194 mmol), and 20 mL toluene. The reaction mixture was stirred for 20 h. and then reduced to dryness under vacuum. The bright yellow residue was suspended in 25 ml Et_2O and stirred overnight. The product was collected by filtration and dried *in vacuo.* Yield: (59 mg; 85%). This complex is spectroscopically identical with that which was synthesized by Kaden *et al.*[7]

^1H NMR (CD_2Cl_2) δ (ppm): -10.1 (q, $J_{P\text{-}H}$ = 19.5 Hz, Tc-$\underline{H}$); 6.95 (P(Ar$\underline{H}$)); 7.70 (m, 24H, P(Ar$\underline{H}$)). $^{31}P\{H\}$ NMR (CD_2Cl_2) δ (ppm): ~75 ppm (br). IR(KBr): ν 2044 (s, N_2). FABMS(+) m/z: 896 [Tc(dppe)$_2$H]; 895 [Tc(dppe)$_2$].

$H_3Tc(dppe)_2$ (6). Method 1: In the dry box a concentrated solution of C_6D_6 and $HTc(N_2)(dppe)_2$ (**5**) was added to an NMR tube fitted with a PTFE valve. The tube was removed from the dry box, degassed by performing 3 freeze/pump/thaw cycles, and placed under 1 atm H_2(g). Monitoring by ^1H NMR spectroscopy showed the complete conversion of $HTc(N_2)(dppe)_2$ (**5**) to $H_3Tc(dppe)_2$ (**6**) in six h.

Method 2: In the dry box a bomb was charged with 20 mL toluene, dppe (81 mg; 0.204 mmol) and $H_3Tc(PPh_3)_4$ (**2**) (112 mg; 0.097 mmol). The bomb was removed from the dry box, degassed, and placed under 1 atm H_2. After stirring the reaction mixture at room temperature for 3 days, it was reduced in volume to ~1 mL under vacuum. To the resulting brown-yellow oil, approximately 50 mL Et_2O under H_2 was added. Stirring for 2 h. precipitates a yellow solid from solution. The solid material was collected by filtration and dried *in vacuo*. Yield: (36 mg; 53%).

^1H NMR (CD_2Cl_2) δ (ppm): -6.9 (br, Tc-$\underline{H}$); 2.09 (br s, 8H, C$\underline{H_2}$); 6.95 (m, 16H, P(Ar$\underline{H}$)); 7.70 (m, 24 H, P(Ar$\underline{H}$)). IR(KBr): ν 1961(w), 1889(w), 1806(w), 1735(m). FABMS(+) *m/z*: 896 [HTc(dppe)$_2$]; 895 [Tc(dppe)$_2$].

HTc(CO)(dppe)$_2$ (7). In the dry box a concentrated solution of C_6D_6 and $H_3Tc(dppe)_2$ (**6**) was added to an NMR tube fitted with a PTFE valve. The tube was removed from the dry box, degassed by performing 3 freeze/pump/thaw cycles, and placed under 1 atm CO(g) for 4 h. Monitoring by ^1H NMR spectroscopy showed the complete conversion of $H_3Tc(dppe)_2$ (**6**) to $HTc(CO)(dppe)_2$ (**8**) within six h. Addition of hexane to the C_6D_6 solution precipitated a white powder which collected by filtration and dried *in vacuo*.

^1H NMR (C_6D_6) δ (ppm): -5.5 (q, $J_{P\text{-}H}$ = 23 Hz, Tc-$\underline{H}$); 2.09 (br s, 8H, C$\underline{H_2}$); 6.95 (m, 16H, P(Ar$\underline{H}$)); 7.70 (m, 24 H, P(Ar$\underline{H}$)). IR(KBr): ν 1862 (s, C≡O). FABMS(+) *m/z*: 896 [$HTc(dppe)_2$]; 895 [$Tc(dppe)_2$].

$HTc(CO)_3(PPh_3)_2$ 8. $H_3Tc(PPh_3)_4$ (**2**) (101 mg, 0.088 mmol) was dissolved in 20 mL C_6H_6 under a CO(g) atmosphere. After stirring for approximately 1.5 h, the faint yellow solution was layered with 100 mL EtOH and allowed to stand overnight in a freezer(-20 °C). The colorless microcrystalline material which precipitated was collected by filtration, washed with EtOH and Et_2O, and dried *in vacuo*. The material can be recrystallized from CH_2Cl_2/pentane at -20 °C. Yield: (44 mg, 71%).

Anal. Calcd. for $C_{39}H_{31}O_3P_2Tc$: C, 66.11; H, 4.41. Found: C, 65.70; H, 4.49. IR(KBr): ν 2023 (m, C≡O); 1962 (sh); 1923 (br s, C≡O); 1859 (m, C≡O). ^1H NMR (CD_2Cl_2) δ (ppm): -4.8 (t, $J_{P\text{-}H}$ = 19.5 Hz, Tc-$\underline{H}$); 7.0 (m, 18 H, P($C_6\underline{H_5}$)); 7.8 (m, 12H, P($C_6\underline{H_5}$)). $^{13}C\{H\}$ NMR (CD_2Cl_2, $HTc(^{13}CO)_3(PPh_3)_2$) δ (ppm): 128.39 (t, $J_{P\text{-}C}$ = 4.5 Hz, $P(C_6H_5)_3$-ortho or meta); 129.89 (s, $P(C_6H_5)_3$-ortho); 133.82 (t, $J_{P\text{-}C}$ = 6.2 Hz, $P(C_6H_5)_3$-ortho or meta); 137.57 (t, $J_{P\text{-}C}$ = 20.4 Hz, $P(C_6H_5)_3$-ipso); 209.5 (br, s, *cis*- CO); 207 (shoulder, *trans*-CO). $^{31}P\{H\}$ NMR ($CDCl_3$) δ (ppm): ~57 (br, linewidth ~5000 Hz). FABMS(+) *m/z*: 707 $[Tc(CO)_3(PPh_3)_2]^+$; 679 $[Tc(CO)_2(PPh_3)_2]^+$.

Reaction of 1, 2, and 3 with D_2. The typical procedure for the reaction of Tc hydride complexes with D_2 is described below for $H_3Tc(PPh_2Me)_4$ (**1**). In the dry box an NMR tube fitted with a PTFE valve was charged with **1** (15 mg) and C_6D_6. The valve was closed and the tube was removed from the dry box and attached to a vacuum line. The sample was freeze-pump-thaw degassed 3 times and then pressurized to 1 atm with D_2(g). The valve was closed and the tube was allowed to warm to room temperature.

Table I. Crystal and Data Collection Parameters for $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**).

Empirical Formula: $C_{53}H_{56}BF_4P_4Cl_2Tc$

Crystal Parameters

a = 16.692(3) Å

b = 16.692(3) Å

c = 21.72(1) Å

$\alpha = \beta = \gamma = 90$ °

V = 6052(4) $Å^3$

T = -86 ± 1 °C

Space Group: P4/ncc

Formula Weight = 1071.63 amu

$Z = 4$

$D_{calc} = 1.176$ g/cm^3

$\mu_{calc} = 5.44$ cm^{-1}

Size = 0.28 x 0.28 x 0.28 mm

Data Measurements Parameters

Diffractometer: Enraf-Nonius CAD-4

Radiation: MoKα ($\lambda = 0.71069$ Å)

Scan Type: $\omega - 2\Theta$

Scan Rate: 1.9 - 16.5°/min (in omega)

Scan Width: $(0.80 + 0.35 \tan\Theta)°$

$2\Theta_{max}$: 49.7 °

No. of Reflections: Total = 10883 Unique = 3040 (R_{int} = 0.155)

Corrections: Lorentz Polarization Absorption (trans. factors: 0.59 - 1.46)

Secondary Ext. (coeff.: 0.42792 x 10^{-7})

Structure Solution and Refinement

Structure Solution: Direct Methods

Refinement: Full-matrix least-squares

Function Minimized: $\Sigma w (|F_o| - |F_c|)^2$

Least Squares Weight: $4F_o^2/\sigma^2(F_o^2)$

p-factor: 0.02

Anomalous Dispersion: All non-hydrogen atoms

No. Observations ($I > 3.00\ \sigma(I)$): 1085

No. Variables: 153

Residuals: $R = 0.078$; $R_w = 0.076$

Goodness of Fit: 2.345

Max. Peak in Diff. Map: 1.24 $e^-/Å^3$

Min. Peak in Diff. Map: -0.51 $e^-/Å^3$

Table II. Selected Intramolecular Distances for $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**).

Atom 1	Atom 2	Distance (Å)
Tc	P	2.447(2)
Tc	H	1.872
B	F	1.380(7)

Table III. Selected Intramolecular Bond Angles for $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**).

Atom 1	Atom 2	Atom 3	Angles(°)
P	Tc	P	90.138(7)
P	Tc	P	90.138(7)
P	Tc	P	174.4(1)
P	Tc	P	174.4(1)
P	Tc	P	90.138(7)
P	Tc	P	90.138(7)
P	Tc	H	129.98
P	Tc	H	68.23
P	Tc	H	107.47
P	Tc	H	55.12
P	Tc	H	107.47
P	Tc	H	129.98
P	Tc	H	55.12
P	Tc	H	68.23
P	Tc	H	68.23
P	Tc	H	55.12

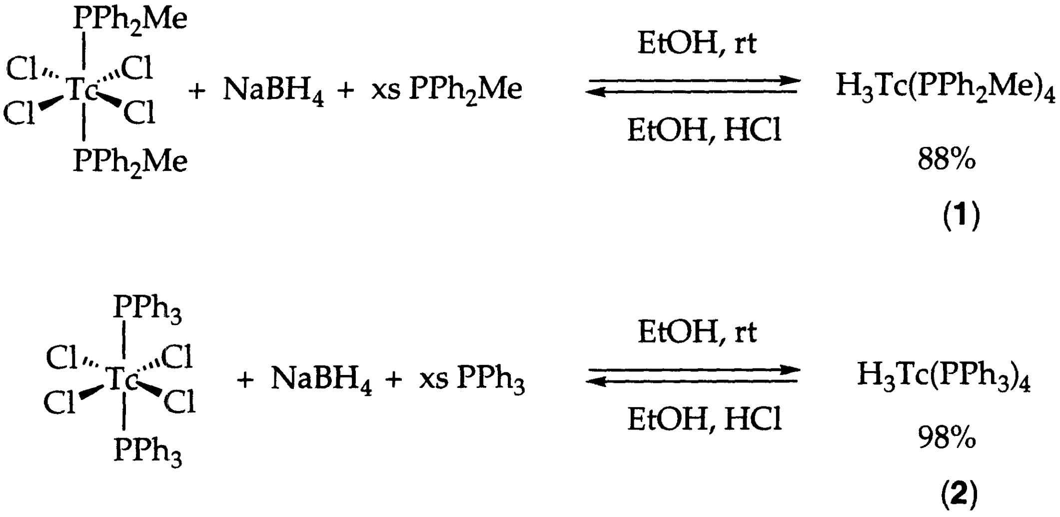
P	Tc	H	129.98
P	Tc	H	107.47
P	Tc	H	55.12
P	Tc	H	107.47
P	Tc	H	68.23
P	Tc	H	129.98
H	Tc	H	121.17
H	Tc	H	121.17
H	Tc	H	87.99
H	Tc	H	87.99
H	Tc	H	121.17
H	Tc	H	121.17

Table IV. Positional Parameters and Estimated Standard Deviations (Å^2) for [$H_4Tc(PPh_2Me)_4$]BF_4 (**3**).

atom	x	y	z	B(eq) (Å^2)
Tc	3/4	1/4	0	2.46(4)
P	0.7019(2)	0.1117(1)	-0.0055(1)	2.9(1)
C(1A)	0.6676(6)	0.0615(6)	0.0643(5)	2.9(5)
C(2A)	0.7001(6)	0.0837(7)	0.1220(5)	3.9(6)
C(3A)	0.6782(8)	0.0448(8)	0.1745(6)	5.2(7)
C(4A')	0.623(1)	-0.017(1)	0.1732(7)	7.0(1)
C(5A)	0.588(1)	-0.0401(8)	0.1184(7)	6.4(8)
C(6A)	0.6105(7)	0.0021(8)	0.0633(6)	5.0(7)
C(7A)	0.7658(5)	0.0323(6)	-0.0402(5)	2.6(5)
C(8A)	0.7921(7)	0.0431(6)	0.1014(5)	4.1(6)
C(9A)	0.8347(7)	-0.0197(8)	-0.1291(6)	5.1(7)
C(10A)	0.8535(7)	-0.0887(8)	-0.0989(8)	5.4(8)
C(11A)	0.8283(7)	-0.0995(8)	-0.0400(7)	4.7(7)
C(12A)	0.7845(6)	-0.0386(6)	-0.0094(5)	3.5(5)
C(13)	0.6175(6)	0.0983(6)	-0.0595(6)	4.0(6)
H	0.808	0.302	0.062	2.2
Cl(1)	0.8766(4)	0.0105(3)	0.2803(3)	5.7(4)
C(1S)	0.914(4)	-0.914	1/4	22(3)
F	0.7508(5)	0.1828(5)	0.2870(4)	7.2(4)
B	3/4	1/4	1/4	4.3(6)
H(1)	0.741	0.126	0.123	4.2
H(2)	0.703	0.062	0.213	5.4

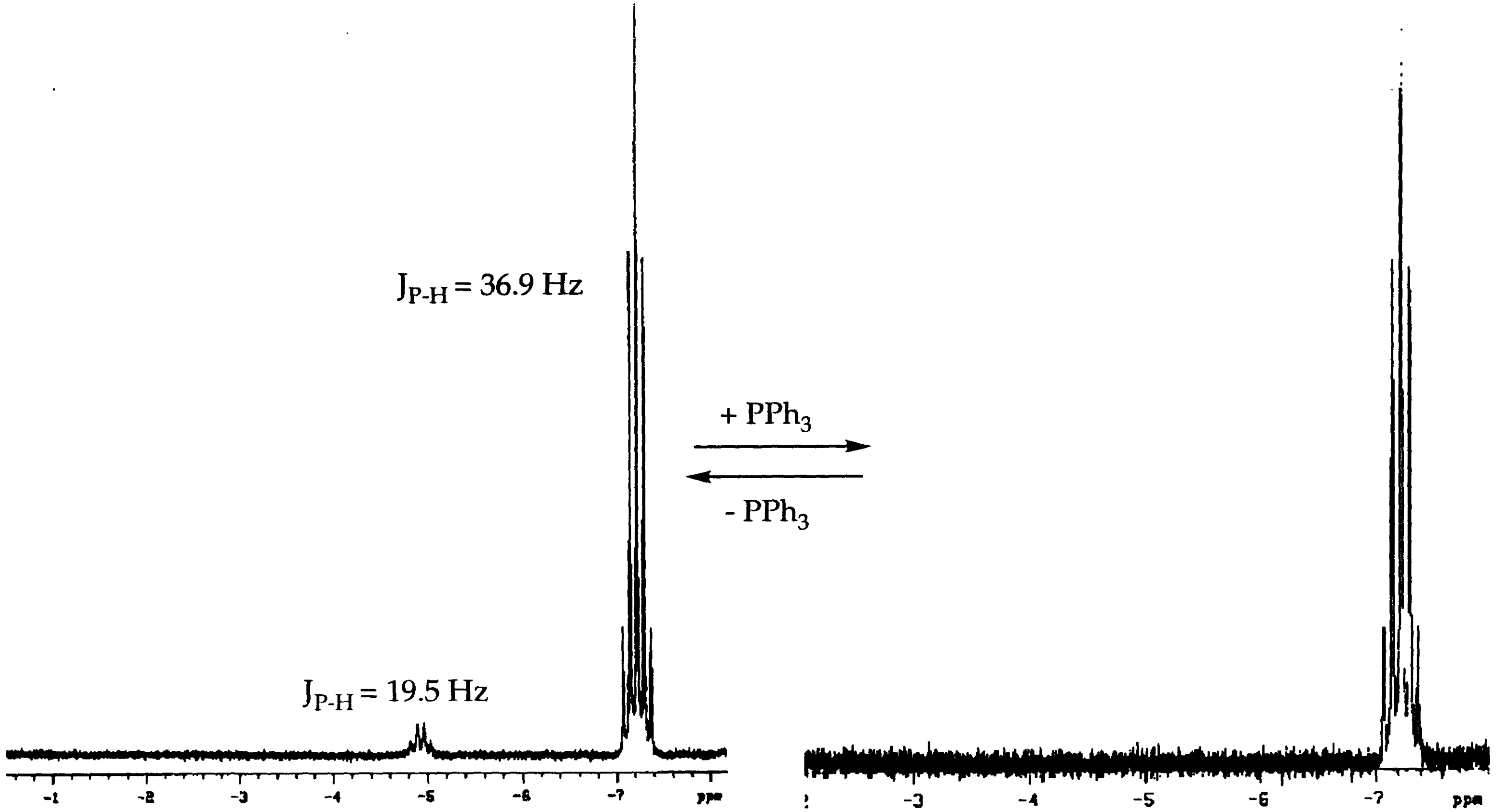
H(3)	0.601	-0.036	0.211	9.2
H(4)	0.553	-0.086	0.116	6.6
H(5)	0.584	-0.009	0.024	5.2
H(6)	0.777	0.097	-0.122	4.9
H(7)	0.853	-0.007	-0.173	6.0
H(8)	0.884	-0.129	-0.119	6.9
H(9)	0.838	-0.151	-0.017	6.0
H(10)	0.770	-0.042	0.034	4.5
H(11)	0.575	0.133	-0.051	4.6
H(12)	0.635	0.107	-0.102	4.6
H(13)	0.598	0.043	-0.058	4.6

Scheme I


(1)

(2)

Figure 1. ^1H NMR spectra of $H_3Tc(PPh_3)_4$ (**2**).



The ^1H NMR spectra of **2** were obtained in C_6D_6 under an Ar(g) atmosphere.

Scheme II

$$\mathrm{H_3Tc(PPh_2Me)_4} \underset{\text{DBU, MeCN}}{\overset{\mathrm{HBF_4}\text{, EtOH}}{\rightleftarrows}} \mathrm{[H_4Tc(PPh_2Me)_4]BF_4}$$

96%	64%
Bright yellow	White
(1)	(3)

Figure 2. VT ^{1}H NMR spectrum of $[H_4Tc(PPh_2Me)_4]BF_4$ (**3**) in CD_2Cl_2.

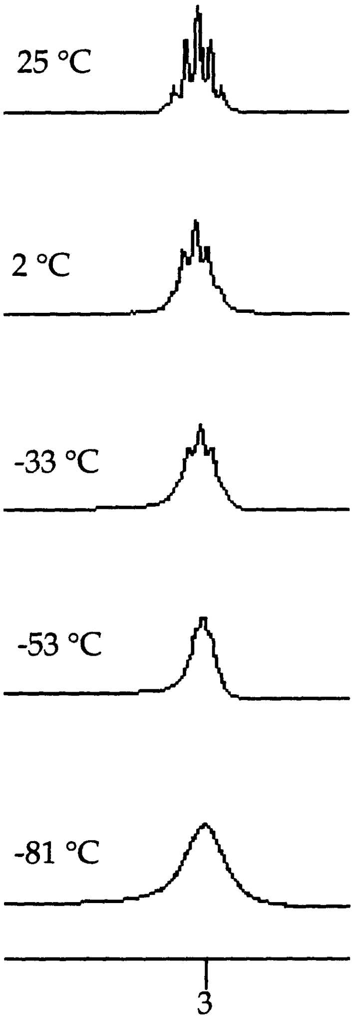


Figure 3. ORTEP diagram of **3** showing 35 % probability ellipsoids. The BF_4^- anion, the CH_2Cl_2 solvate molecule and the R groups on the phosphines ligands were omitted for the sake of clarity.

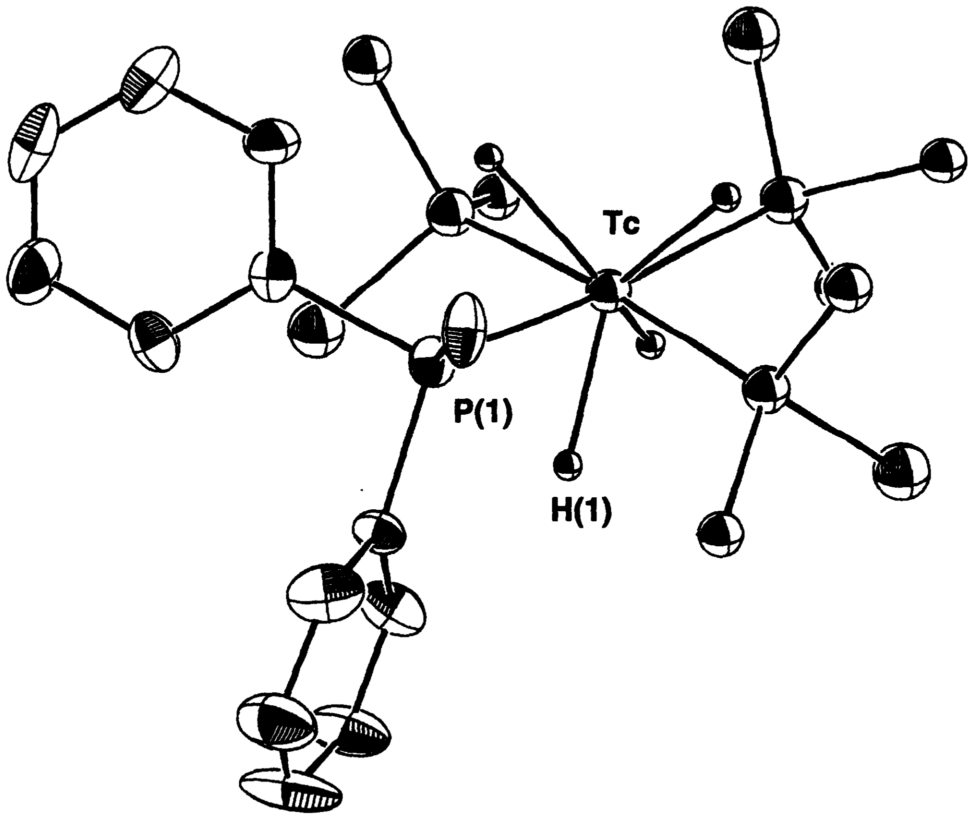
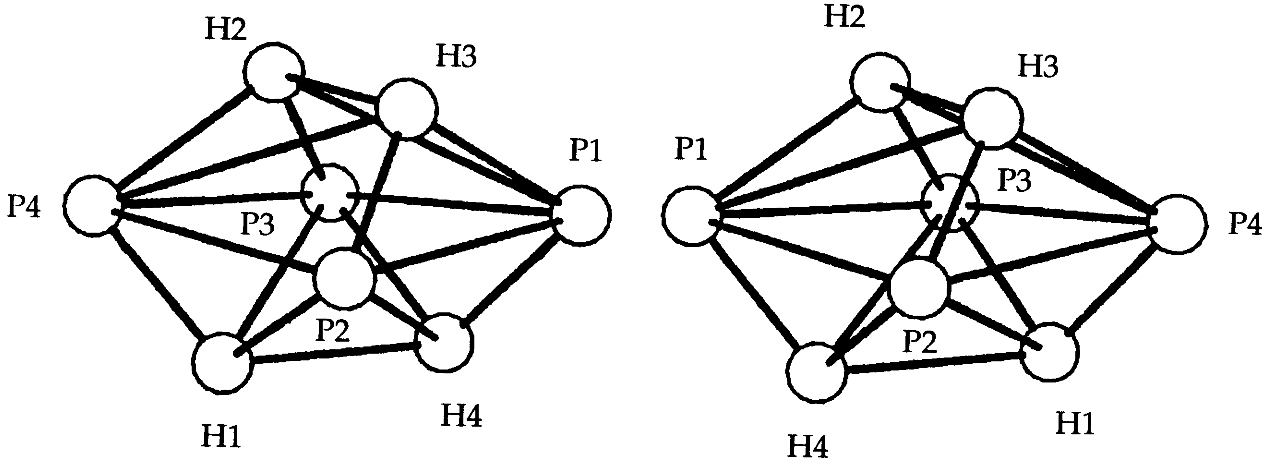


Figure 4. Stereochemical viewing of complex **3**.



Scheme III

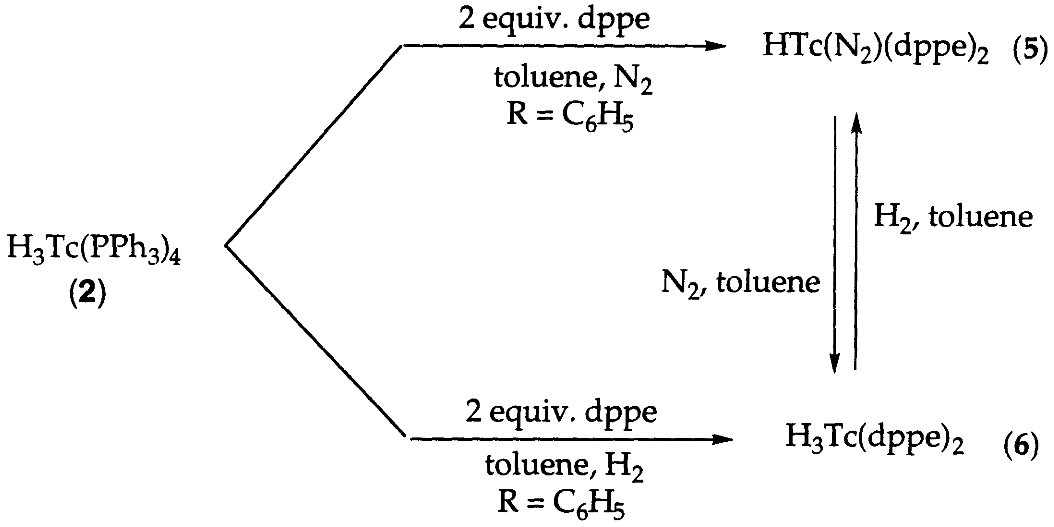
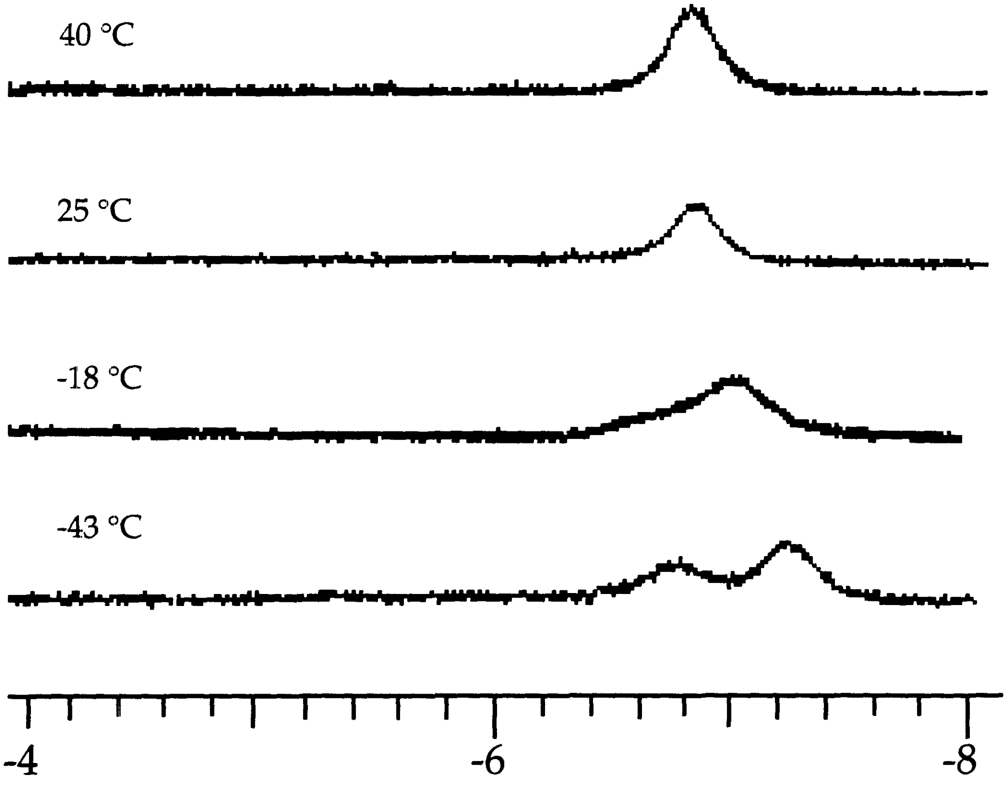
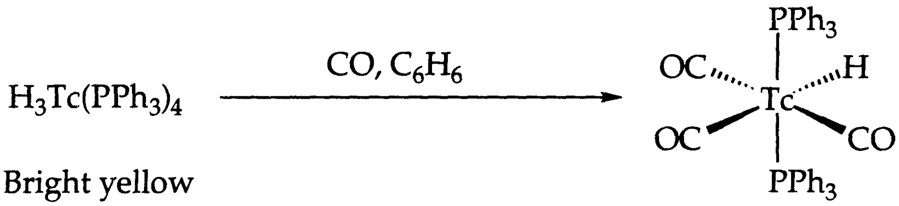

2 equiv. dppe
toluene, N_2
R = C_6H_5
$HTc(N_2)(dppe)_2$ (**5**)
$H_3Tc(PPh_3)_4$
(**2**)
H_2, toluene
N_2, toluene
2 equiv. dppe
toluene, H_2
R = C_6H_5
$H_3Tc(dppe)_2$ (**6**)

Figure 5. VT ^{1}H NMR spectrum of **6** in toluene (d_8).



Scheme IV



Bright yellow

(2)

Colorless

(3)

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Chapter 2

Reactions of $H_3Tc(PPh_3)_4$ with Proton Sources

Introduction

Since the initial discovery of $[Ru(N_2)(NH_3)_5]^{+2}$ by Allen and Senoff in 1965,[1] transition metal dinitrogen complexes have been intensely studied. Research in this area has focused on the mimicking of the enzyme nitrogenase which catalyzes the transformation of N_2 into NH_3.[2,3]

Although a number of Re dinitrogen complexes have been described in the literature,[4-6] $HTc(N)_2(dppe)_2$[7] (where dppe = bis(diphenylphosphinoethane) remains the only example of a Tc dinitrogen complex. In this chapter the synthesis of the new Tc(I) dinitrogen complex $Tc(acac)(N_2)(PPh_3)_3$ (**2**) is described. The molecular structure of this complex was also investigated by an X-ray crystal structure determination.

Results and Discussion

The complex $Tc(acac)(N_2)(PPh_3)_3$ (**2**) was prepared by the reaction of $H_3Tc(PPh_3)_4$ (**1**) with acetylacetone (Hacac) in toluene under an atmosphere of N_2. This complex is very stable as a solid and shows no signs of decomposition in air or under $N_2(g)$ or $Ar(g)$ atmospheres over a span of several months. In benzene solutions **2** is stable under an N_2 atmosphere. A strong stretch at 1952 cm^{-1} corresponding to $\nu(N\equiv N)$ was observed in the IR spectrum of **2**.

A single crystal X-ray diffraction study of $Tc(acac)(N_2)(PPh_3)_3$ (**2**) was undertaken. Diffusion of hexane into a toluene solution of **2** at room temperature resulted in the formation of orange crystals. Data and collection parameters are given in **Table I** and the experimental section. An ORTEP diagram is given in **Figure 1**. Bond lengths, angles and positional parameters are given in **Tables II, III,** and **IV**, respectively.

The complex Tc(acac)(N_2)(PPh_3)$_3$ (**2**) has a distorted octahedral geometry with meridionally arranged phosphine ligands, an "end-on" bound dinitrogen ligand and a planar acac ligand bound through both oxygen atoms to the Tc metal center. The N_2 ligand is nearly linear with a Tc-N(1)-N(2) bond angle of 177(1)°. The Tc-N(1) distance was determined to be 1.90(1) Å. This distance is shorter than that found for HTc(N_2)(dppe)$_2$[7] (where dppe = bis(diphenylphosphinoethane)) (Tc-N = 2.05(1) Å). This shortened bond distance reflects the strong *trans* influence of the hydride ligand relative to acac. Similar distances have been observed for a number of other structurally characterized transition metal N_2 complexes.[8] The N(1)-N(2) bond length of 1.14(1) Å is consistent with an N≡N triple bond,[8,9] being only slightly longer than that in molecular N_2[9] (1.098 Å).

The Tc-O(1) and Tc-O(2) distances in **2** were determined to be 2.140(9) and 2.12(1) Å. The Tc-O(1) and Tc-O(2) distances are longer than those found for the crystallographically characterized Tc acac complexes, Tc(acac)$_3$[10] (Tc-O_{avg} = 2.025 Å), [Tc(NO)(Cl)$_3$(acac)$^-$][11] (Tc-O_{avg} = 2.07 Å), and TcCl(acac)(PPh_3)$_3$[12] (Tc-O_{avg} = 2.01 Å). The longer Tc-O bonds lengths in **8** may reflect the larger size of the Tc(I) metal center and are in good agreement with that found for the Tc(I) acac complex *trans*-Tc(CO)$_2$(acac)(PPh_3)$_2$ (Tc-O = 2.152(7) and 2.135(7)Å).[13]

The displacement of N_2 by H_2 from transition metal-N_2 complexes is a common method of preparation for dihydrogen (η^2-H_2) complexes.[14] The IR spectra of the starting N_2 complexes have been correlated to the stability of the resulting dihydrogen complexes with respect to H_2 binding.[4,14] When $\nu(N_2)<2060$ cm^{-1} the meal center is very π-basic and will favor a dihydride complex due to excessive $d(M)\rightarrow\sigma^*(H_2)$ back bonding. Conversely when $2060<\nu(N_2)<2180$ cm^{-1} the transition metal center is weakly π-basic and will favor the formation of a dihydrogen complex. For **2** $\nu(N_2)$ is observed at 1952 cm^{-1} indicating a very π-basic metal center. Treatment of **2** with 1 atm H_2 in C_6D_6 gives a new complex with a broad peak at δ -8.37 as observed by ^1H NMR spectroscopy. Attempts to isolate and characterize this complex have been unsuccessful to date.

Unlike the above reaction with acetylacetone, treatment of $H_3Tc(PPh_3)_4$ (**1**) with 2-mercaptopyridine (pySH) in thf under an atmosphere of N_2 gives the Tc(III) orange-red monohydride complex $HTc(pyS)_2(PPh_3)_2$ (**3**). A strong absorption which could be attributed to the presence of a dinitrogen ligand was not observed in the IR spectrum of **3**. Peaks which could be attributed to $\nu(C{=}S)$, $\nu(N\text{-}H)$ or $\nu(SH)$ were also not observed, excluding the other possible modes of coordination for pyS.[15,16] In the ^1H NMR spectrum of **3** the Tc-H resonance is observed as a triplet at -0.99 ($J_{P\text{-}H}$ = 54 Hz).

In the reaction of $H_3Tc(PPh_3)_4$ (**1**) with 2 equivalents of 2-mercaptopyridine (pySH) the final product **3** is the result of two protonation reactions. Only one equivalent of acetylacetone (acacH) reacts with **1** under similar conditions to give the dinitrogen complex **2**. This is indicative that in the acacH reaction the reductive elimination of H_2 is favored to give a Tc(I) complex. The reason for the difference in the reactivity of **1** with pySH and acacH is not obvious. Both pySH and acacH are potentially bidentate, monoanionic ligands with similar acidities (pKa of pySH = 9.97;[6] pKa of acacH = 8.99[17]).

This unusual reactivity probably results from a combination of electronic and steric effects. The bite angle of ancillary ligands has been shown to play a significant role in the reactivity of hydride complexes. For example, dppf (where dppf = 1,1'-bis(diphenylphosphino)ferrocene) has a large bite angle of 106° which prevents octahedral coordination around Ru.[18]

This causes the formation of the seven-coordinate hydride $[RuH_3(dppf)_2]^+$ instead of the dihydrogen complex $[RuH(\eta^2\text{-}H_2)(dppf)_2]^+$ which is found for all other chelating phosphine ligands.[18] Bidentate coordination of pyS gives a four-membered chelate ring which is smaller and more strained than the six membered chelate ring which obtained from bidentate coordination of acac.

As previously described excessive $d(M) \rightarrow \sigma^*(H_2)$ back bonding favors a dihydrogen complex. This effect is nicely illustrated by the observation of Kubas *et. al.*[19] that $Mo(\eta^2\text{-}H_2)(CO)(dppe)_2$ is a dihydrogen complex whereas $MoH_2(CO)(P^iBu_2CH_2CH_2P^iBu_2)_2$ is a dihydride complex. The softer nature of the pyS ligand compared to that of acac ligand indicates that the Tc metal center is more π-basic when coordinated to the pyS ligand than when coordinated to the harder, more π–acidic ligand acac.

Conclusions

Complex **1** reacts with the potentially bidentate, monoanionic ligand acetylacetone to give a rare example of a Tc dinitrogen complex, **2**. In contrast a similar reaction with 2-mercaptopyridine gives the Tc monohydride complex **3**. These reactions illustrate how the reactivity of **1** can be influenced by subtle changes in the steric and electronic properties of a ligand. Other reactions of **1** with similar bidentate, monoanionic ligands of varying bite size, acidity (i.e.: tropolone, acetic acid) and π– and σ–donating ability may lead to a better understanding of the factors which result in reductive elimination of H_2 from **1**.

Experimental

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Drybox solvents (toluene, THF, pentane, Et_2O)

were distilled from sodium/benzophenone. A "bomb" refers to a cylindrical glass vessel sealed with a Kontes high vacuum stopcock. The complex $H_3Tc(PPh_3)_4$ was prepared as described in Chapter 1. Reagents and solvents were used as received unless otherwise stated. A Mattson Cynus 100 FTIR instrument was used to record all infrared spectra. Fast atom bombardment mass spectra (FABMS(+)) were obtained using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV and equipped with a Ion Tech B11N FAB gun. The FAB gun produces a beam of 6-8 keV xenon neutrals. All compounds were run in a matrix of neat 3-nitrobenzyl alcohol. ^1H spectra were recorded at 300.0 MHz on a Varian Unity spectrometer. The elemental analyses were performed by Atlantic Microlab, Norcross, GA.

$Tc(acac)(N_2)(PPh_3)_3$ (2). In a N_2 filled dry box, a flask was charged with $H_3Tc(PPh_3)_4$ (375 mg; 0.326 mmol), acac (70 μL; 0.684 mmol), and 10 mL toluene. The reaction mixture was allowed to stir at room temperature for 3.5 h., filtered through Celite and layered with 25 mL hexane. Storage overnight at 25 ° C results in the formation of bright orange crystals which were collected onto a fritted disk, washed 10 mL hexane and dried *in vacuo*. Yield: (125 mg; 43%).

Anal. Calcd. for $C_{59}H_{52}N_2O_2P_3Tc$: C, 69.96; H, 5.17; N, 2.77. Found: C, 69.59; H, 5.00; N, 2.67. IR(KBr): ν 3056 (m), 1952 (s, N_2), 1575 (s), 1515 (s), 1481 (m), 1403 (w), 1272 (w), 1192 (m), 1119 (m), 1090 (m), 1028 (w), 742 (m), 721 (m), 694 (s), 542 (m), 513 (s). FABMS(+)*m/z*: 984 [$Tc(acac)(PPh_3)_3$]; 722 [$Tc(acac)(PPh_3)_2$].

X-Ray Crystal Structure Determination of $Tc(acac)(N_2)(PPh_3)_3$ (2). Brown-orange prismatic crystals were grown by slow vapor diffusion of hexane into a toluene solution of **2** at room temperature. A suitable crystal was selected and then transferred to a Rigaku AFC6R diffractometer with graphite monochromated Mo-Kα radiation and a 12W rotating anode. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $12.57 < 2\theta < 18.75$ °, corresponding to a monoclinic cell. Based on the systematic absences of h0l: $h + l \neq 2n$ and 0k0: $k \neq 2n$, the space group was determined to be P21/n. The final cell parameters are given in **Table I**.

The data were collected at a temperature of 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0 °C. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.27° with a take-off angle of 6.0°. Scans of $(1.47 + 0.30 \tan\theta)°$ were made at a speed of 16.0°/min (in omega). The weak reflections ($I < 6.0 \sigma(I)$) were rescanned (maximum of 8 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Of the 12422 reflections which were collected, 11802 were unique ($R_{int} = 0.353$); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption absorption coefficient for Mo Kα is 4.1 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4281 observed reflections ($I>3.00\sigma(I)$) and 604 variable parameters and converged (largest parameter shift was 0.03 times its esd) with $R = 0.081$; $R_w = 0.095$. The standard deviation of an observation of unit weight was 1.94. The weighing scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.39 and -0.97 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[20] Anomalous dispersion effects were included in F_{calc}; the values for Df' and Df" were those Cromer. All calculations were performed using TEXSAN crystallographic software package of Molecular Structure Corporation.

$HTc(\eta^2\text{-pyrS})_2(PPh_3)_2$ (3). In the dry box 2.1 equiv. pyrSH (30.5 mg; 0.260 mmol) was added to a solution containing **1** (150 mg; 0.130 mmol) and 10 mL THF. The reaction mixture was stirred for 4.5 h, filtered through Celite and reduced in volume to ~ 4 mL. The red/orange solution was layered with 15 mL hexane and stored overnight to afford metallic red crystals. The crystals were collected by filtration and dried *in vacuo*. Yield: (51.5 mg; 64%).

Anal. Calcd. for $C_{46}H_{39}N_2P_2S_2Tc$: C, 65.40; H, 4.65; N, 3.32; S, 7.59. Found: C, 65.18; H, 4.95; N, 3.12; S, 7.33. IR(KBr): ν 3012 (w), 1954 (w), 1820 (w), 1574 (s), 1541 (m), 1478 (m), 1433 (s), 1415 (m), 1254 (m), 1135 (s), 1086 (s), 742 (vs), 694 (vs), 519 (vs). ^1H NMR (C_6D_6) δ (ppm): -0.99 (t, 1 H, $J_{P\text{-}H}$ = 54 Hz); 6.07 (t, $J_{P\text{-}H}$ = 7.9 Hz); 6.40 (d, $J_{P\text{-}H}$ = 7.9 Hz); 6.88 (t, $J_{P\text{-}H}$ = 7.3 Hz); 7.17 (m, PAr-$\underline{H}$); 7.19 (m, PAr-$\underline{H}$); 7.35 (PAr-$\underline{H}$). One of the resonances from the 2-mercaptopyridine ligand is obscured by the PPh_3 resonances. $^{31}P\{H\}$ (C_6D_6) δ (ppm): ~ 40 (br). FABMS(+)*m/z*: 844 [$HTc(pyS)_2(PPh_3)_2$]; 702 [$HTc(C_4H_4N)(PPh_3)_2$].

Table 1. Crystal and Data Collection Parameters for $Tc(acac)(N_2)(PPh_3)_3$ (**2**).

Empirical Formula: $C_{59}H_{52}N_2O_2P_3Tc$

Crystal Parameters

a = 10.659(6) Å	Space Group: P21/n
b = 22.324(5) Å	Formula Weight = 1010.99 amu
c = 21.466(5) Å	Z = 4
β = 101.26(3)°	D_{calc} = 1.340 g/cm^3
V = 5009(6) Å^3	Size = 0.120 x 0.120 x 0.180 mm
T = 23 °C	

Data Measurements Parameters

Diffractometer: Rigaku AFC6R

Radiation: MoKα (λ = 0.71069 Å)

Scan Type: ω - 2Θ

Scan Rate: 16.0 °/min (in omega) (8 rescans)

Scan Width: $(1.47 + 0.30 \tan\Theta)°$

$2\Theta_{max}$: 55.0°

No. of Reflections: Total = 12422 Unique = 11802 (R_{int} = 0.353)

Corrections: Lorentz Polarization

Structure Solution and Refinement

Structure Solution: Direct Methods

Refinement: Full-matrix least-squares

Function Minimized: $\Sigma w (|F_o| - |F_c|)^2$

Least Squares Weight: $4F_o^2/\sigma^2(F_o^2)$

p-factor: 0.03

No. Observations ($I>3.00\ \sigma(I)$): 4281

No. Variables: 604

Residuals: $R = 0.081$; $R_W = 0.095$

Goodness of Fit: 1.94

Max. Shift/Error in Final Cycle: 0.30

Max. Peak in Diff. Map: 1.39 $e^-/Å^3$

Min. Peak in Diff. Map: -0.97 $e^-/Å^3$

Table II. Selected Intramolecular Distances for Tc(acac)(N_2)(PP_3)$_3$ (**2**).

Atom	Atom	Distance (Å)
Tc	P(1)	2.399(4)
Tc	P(2)	2.483(4)
Tc	P(3)	2.434(4)
Tc	O(1)	2.140(9)
Tc	O(2)	2.12(1)
Tc	N(1)	1.90(1)
O(1)	C(3)	1.28(2)
O(2)	C(1)	1.29(2)
N(1)	N(2)	1.14(1)
C(1)	C(2)	1.36(2)
C(1)	C(4)	1.51(2)
C(2)	C(3)	1.37(2)
C(3)	C(5)	1.52(2)

Table III. Selected Intramolecular Bond Angles for Tc(acac)(N_2)(PP_3)$_3$ (**2**).

Atom	Atom	Atom	Angle (deg)
Tc	N(1)	N(2)	177(1)
P(1)	Tc	P(2)	100.3(1)
P(1)	Tc	P(3)	99.3(1)
P(1)	Tc	O(1)	82.8(3)
P(1)	Tc	O(2)	167.4(3)
P(1)	Tc	N(1)	98.2(3)
P(2)	Tc	P(3)	159.5(1)
P(2)	Tc	O(1)	95.0(3)
P(2)	Tc	O(2)	81.7(3)
P(2)	Tc	N(1)	84.6(3)
P(3)	Tc	O(1)	93.4(3)
P(3)	Tc	O(2)	80.4(3)
P(3)	Tc	N(1)	86.8(3)
O(1)	Tc	O(2)	84.7(3)
O(1)	Tc	N(1)	179.0(4)
O(2)	Tc	N(1)	94.4(4)

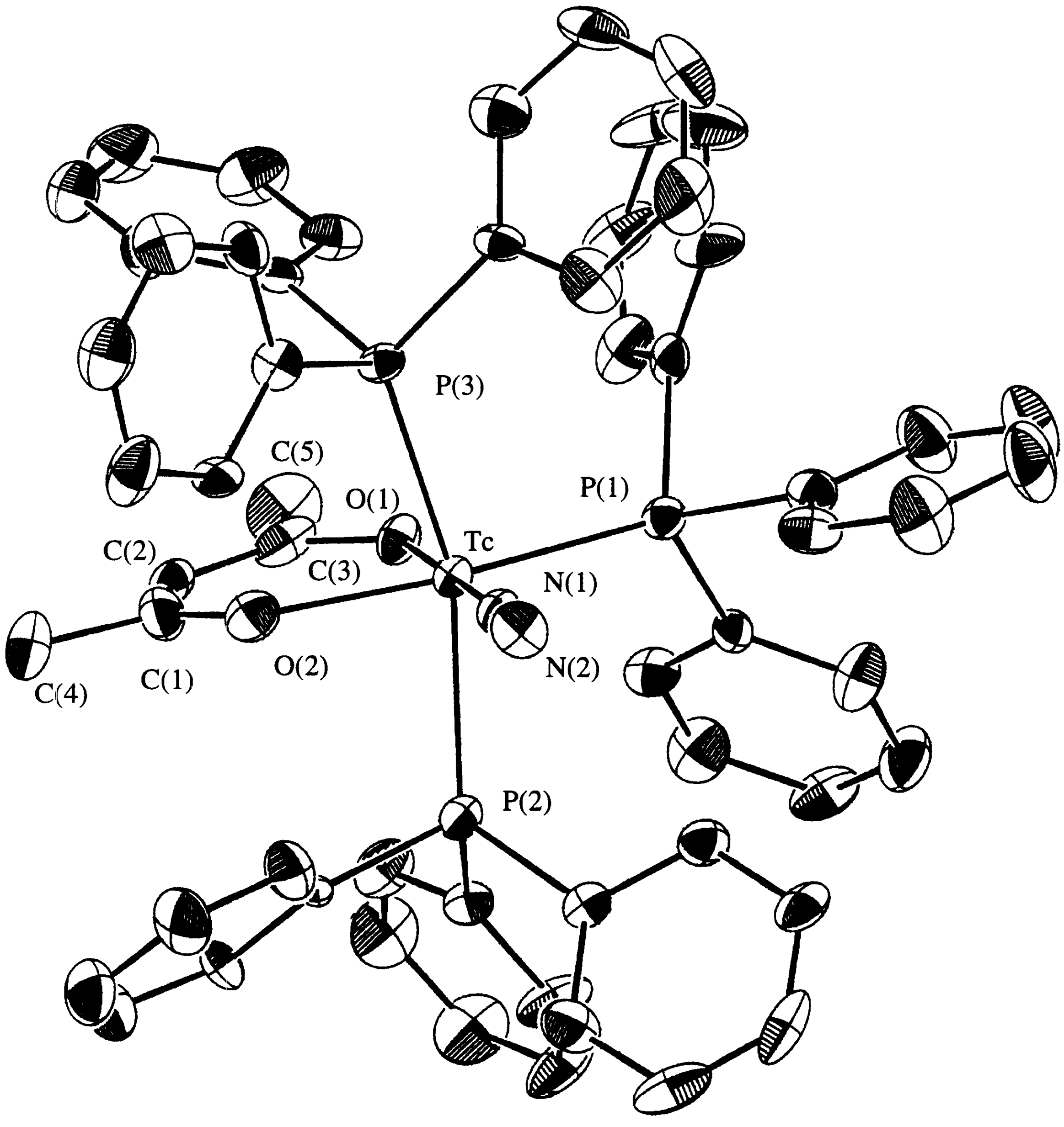
Table IV. Positional Parameters and Estimated Standard Deviations (Å^2) for Tc(acac)(N_2)(PP_3)$_3$ (**2**).

Atom	x	y	z	B(eq)
Tc	0.0699(1)	0.17054(5)	0.73465(5)	2.08(4)
P(1)	0.0500(3)	0.1762(2)	0.8439(2)	2.5(1)
P(2)	0.1752(3)	0.2680(2)	0.7231(2)	2.6(2)
P(3)	-0.0046(3)	0.0684(2)	0.7115(2)	2.3(1)
O(1)	-0.1197(8)	0.2065(4)	0.7189(4)	2.8(4)
O(2)	0.0449(8)	0.1718(5)	0.6341(4)	3.5(4)
N(1)	0.239(1)	0.1390(5)	0.7473(5)	2.5(5)
N(2)	0.339(1)	0.1186(6)	0.7519(6)	3.5(6)
C(1)	-0.053(1)	0.1909(7)	0.5944(7)	3.8(7)
C(2)	-0.165(1)	0.2125(6)	0.6065(7)	3.2(6)
C(3)	-0.195(1)	0.2170(7)	0.6659(8)	3.7(7)
C(4)	-0.038(2)	0.1841(9)	0.5264(8)	6(1)
C(5)	-0.323(1)	0.2428(9)	0.673(1)	6(1)
C(11)	0.034(1)	0.2532(6)	0.8745(6)	2.4(6)
C(12)	-0.053(1)	0.2933(6)	0.8370(7)	3.3(7)
C(13)	-0.075(2)	0.3502(8)	0.8580(9)	5(1)
C(14)	-0.009(2)	0.3697(7)	0.916(1)	4.8(9)
C(15)	0.079(2)	0.3325(8)	0.9528(8)	5.1(8)
C(16)	0.099(1)	0.2744(8)	0.9324(8)	4.7(8)
C(21)	0.333(1)	0.2808(6)	0.7744(6)	2.3(6)
C(22)	0.357(1)	0.2554(7)	0.8343(7)	3.2(7)
C(23)	0.475(1)	0.2645(6)	0.8748(8)	3.7(7)
C(24)	0.569(1)	0.2963(8)	0.8559(9)	4.6(8)

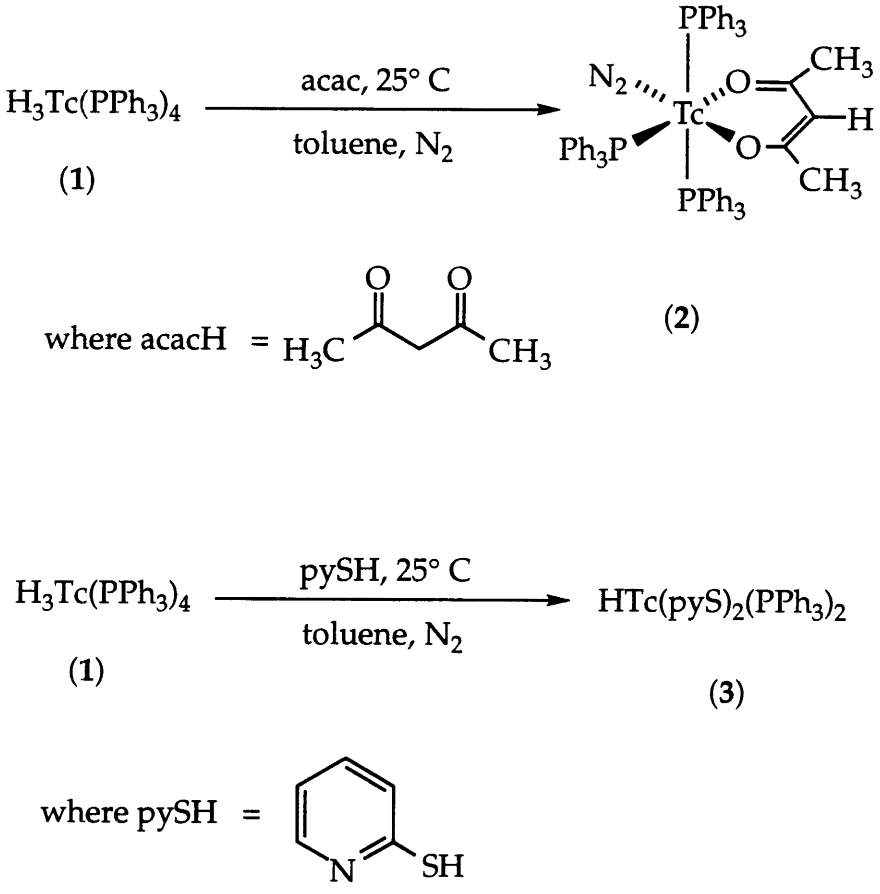
C(25)	0.546(1)	0.3216(8)	0.799(1)	5.0(9)
C(26)	0.430(2)	0.3123(7)	0.7563(8)	4.2(8)
C(31)	0.015(1)	0.0124(6)	0.7749(6)	2.5(6)
C(32)	0.134(1)	0.0065(8)	0.8131(8)	4.5(8)
C(33)	0.158(2)	-0.035(1)	0.8618(9)	6(1)
C(34)	0.065(2)	-0.0715(9)	0.8719(9)	5(1)
C(35)	-0.052(2)	-0.0693(7)	0.8342(9)	4.7(9)
C(36)	-0.078(1)	-0.0280(7)	0.7854(8)	4.1(8)
C(41)	0.166(1)	0.1440(7)	0.9128(7)	3.3(7)
C(42)	0.286(1)	0.1241(6)	0.9042(8)	3.5(7)
C(43)	0.373(2)	0.102(1)	0.956(1)	6(1)
C(44)	0.344(2)	0.098(1)	1.0135(9)	6(1)
C(45)	0.226(2)	0.118(1)	1.0212(9)	6(1)
C(46)	0.136(2)	0.141(1)	0.9738(8)	5(1)
C(51)	0.099(1)	0.3417(6)	0.7272(7)	2.9(6)
C(52)	-0.021(1)	0.3514(7)	0.6928(8)	4.1(8)
C(53)	-0.081(2)	0.4065(9)	0.693(1)	5(1)
C(54)	-0.019(2)	0.4517(8)	0.730(1)	6(1)
C(55)	0.099(2)	0.4446(7)	0.766(1)	5(1)
C(56)	0.158(1)	0.3884(7)	0.7633(9)	4.6(8)
C(61)	-0.173(1)	0.0619(6)	0.6723(7)	2.8(6)
C(62)	-0.265(1)	0.0799(7)	0.7051(8)	3.8(7)
C(63)	-0.395(1)	0.0789(8)	0.675(1)	5(1)
C(64)	-0.431(1)	0.060(1)	0.614(1)	6(1)
C(65)	-0.341(2)	0.0432(9)	0.5829(8)	5(1)
C(66)	-0.211(1)	0.0420(7)	0.6101(7)	3.9(8)
C(71)	-0.098(1)	0.1401(7)	0.8610(6)	2.9(6)

C(72)	-0.216(1)	0.168(1)	0.8449(7)	5.2(9)
C(73)	-0.326(2)	0.1408(8)	0.853(1)	5(1)
C(74)	-0.322(2)	0.0846(8)	0.877(1)	7(1)
C(75)	-0.210(2)	0.0542(9)	0.894(1)	7(1)
C(76)	-0.096(2)	0.0823(7)	0.8858(9)	4.6(8)
C(81)	0.221(1)	0.2716(6)	0.6457(6)	2.3(6)
C(82)	0.304(1)	0.2286(7)	0.6287(7)	3.9(8)
C(83)	0.342(2)	0.2280(9)	0.5715(8)	5(1)
C(84)	0.295(2)	0.270(1)	0.5252(9)	6(1)
C(85)	0.211(2)	0.312(1)	0.5389(8)	6(1)
C(86)	0.177(2)	0.3143(7)	0.5978(7)	4.7(8)
C(91)	0.076(1)	0.0271(7)	0.6552(7)	2.9(6)
C(92)	0.052(1)	-0.0337(7)	0.6456(7)	3.6(7)
C(93)	0.102(2)	-0.0651(7)	0.6026(8)	4.4(8)
C(94)	0.174(2)	-0.0368(9)	0.5660(8)	5(1)
C(95)	0.201(2)	0.022(1)	0.5730(8)	5(1)
C(96)	0.151(1)	0.0546(6)	0.6171(7)	2.8(6)

Figure 1. ORTEP diagram of $Tc(acac)(N_2)(PPh_3)_3$ (**2**) showing 35% probability ellipsoids.



Scheme 1


H3Tc(PPh3)4
(1)
acac, 25° C
toluene, N2
PPh3
N2
Tc
O
CH3
H
Ph3P
PPh3
(2)
where acacH =
H3C
CH3
H3Tc(PPh3)4
(1)
pySH, 25° C
toluene, N2
HTc(pyS)2(PPh3)2
(3)
where pySH =
N
SH

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Chapter 3

Insertion of Electrophilic Substrates in the Tc-H Bond of $HTc(CO)_3(PPh_3)_2$

Introduction.

Some of the more significant reactions displayed by terminal transition metal hydride complexes include intra- and intermolecular hydride transfers, reductive elmination reactions, exchange reactions with H_2, H_2O, ROH, and hydrogen migration reactions.[1] This latter reaction involving the insertion of an electrophilic substrate into a metal hydride bond, has many industrial applications.[2] For example such insertions are believed to be important steps in hydrogenation reactions,[3] Fischer Tropsch chemistry,[4] and hydrosilation reactions.[5]

Although the Re analog[6] of the monohydride complex $HTc(CO)_3(PPh_3)_2$ **1** has been known for some time, few reports regarding its insertion chemistry have appeared.[7,8] This is surprising since the insertion chemistry of $HW(CO)_2(NO)(PR_3)_2$ (where R=Ph, Me, Et) has received a great deal of attention.[9,10] As part of our interest in the chemistry of technetium hydride complexes, we have developed a simple synthetic route for **1** and explored its reactivity with heterocumulenes, electron deficient acetylenes, and diazonium salts.

Results and Discussion

The Tc(I) monohydride $HTc(CO)_3(PPh_3)_2$ **1** undergoes a number of insertion reactions when treated with unsaturated substrates. Phenyl diazonium salts react rapidly with **1** to produce the phenyldiazene cation, **2a** in 67 %. The formation of an α-insertion product is consistent with the terminal N atom in $R\text{-}N{=}N^+$ being electrophilic. In the ^1H NMR spectrum of

2a the N-H proton is observed as a singlet at 12.3 ppm. The ν(N=N) stretches are tentatively assigned to weak peaks at 1487, 1445 cm^{-1} in the IR spectrum.

A single crystal X-ray diffraction study of **2a** was undertaken. Diffusion of pentane into a CH_2Cl_2 solution at -40 °C results in the formation of yellow parallelepiped crystals. The complex crystallizes with one CH_2Cl_2 solvate molecule. Data and collection parameters are given in **Table I** and the experimental section. An ORTEP diagram is given in **Figure 1**. Bond lengths, angles and positional parameters are given in **Tables II, III,** and **IV**, respectively. One of the phenyl groups of the triphenylphosphine ligands is disordered; this is described in the experimental section.

Complex **2a** has a slightly distorted octahedral geometry with two axial PPh_3 ligands, three meridionally arranged CO ligands and a bent organohydrazide ligand with a TcN(1)N(2) angle of 124.2(5) °. The long Tc-N(1) distance of 2.157(6) Å indicates that there is very little multiple bond character between Tc-N(1). Typically M=N(1) bond lengths for M=N(1)=NHR species are ~1.7 Å.[11,12] Also there is a short N(1)-N(2) distance of 1.243(8) Å which is consistent with a double bond between the nitrogen atoms. Based on the bond lengths and angles and spectroscopic data, the organohydrazide moiety in **2a** is best described as a (1-) aryldiazene ligand.[11]

Addition of excess DBU (DBU = 1,8-diazabicyclo[5.4.0]undecene) to MeCN solutions of **2a** results in the rapid precipitation of the yellow complex **2b**. In the IR spectrum of **2b** ν(N=N) is tentatively assigned to peaks at 1481, 1434 cm^{-1}. There were no peaks which could be assigned to a ν(Tc=N) stretch. Also the N-H peak at 12.3 ppm is no longer observed in the ^1H NMR spectrum of **2b**.

The heterocumulenes, CS_2 and $(CH_3)NCS$, react with **1** to give the yellow complexes $Tc(CO)_2(\eta^2\text{-}S_2CH)(PPh_3)_2$ (**3**) and $Tc(CO)_2(\eta^2\text{-}(CH_3)NSCH)(PPh_3)_2$ (**4**) in 72% and 45% yield, respectively. These reactions occur with the hydride ligand being transferred to the electronically deficient carbon atom of X=C=Y (where X = S; Y = S, $N(CH_3)$). The hydrogen atom resonance is observed in the ^1H NMR spectra at δ 10.13 for **3** and δ 7.38 for **4**. As was described in Chapter 2, the carbonyl resonances could only be observed for the ^{13}CO enriched complexes. The $^{13}C\{H\}$ NMR spectrum of **3** shows the β-carbon atom at δ 236.12 and the carbonyl resonance as a broad peak at δ 202. For **4** the β-carbon atom resonance occurs at δ 180.61 and the two unique carbonyl ligand resonances occur in a 1:1 ratio at δ 219 and 211. Mass spectrometry also supports η^2-coordination of the CS_2 and $(CH_3)NCS$ ligands showing parent ion peaks at 756 *m/z* for **3** and 753 *m/z* for **4**. The bidentate nature of these ligands is preserved even when complexes **3** and **4** are heated in the presence of a potential ligand like CO. When **1** is treated with other heterocumulenes such as CO_2 and COS only starting material is isolated from the reaction mixture. This lack of reactivity is attributed to the low pressures (1 atm) under which the reactions were attempted.[13]

Activated acetylenes also insert into the Tc-H bond of $HTc(CO)_3(PPh_3)_2$. Treatment of **1** with 1 equiv. $MeO_2CC{\equiv}CCO_2Me$ affords the bright yellow complex **5**. The two unique methoxy resonances appear in the ^1H NMR spectrum of **5** as singlets at 2.78 and 3.32 ppm. The vinylic H atom is clearly observed as a sharp triplet at 6.71 ppm with $J_{P\text{-}H}$ = 2.65 Hz. The presence of both a non-coordinating and a coordinating C=O group is confirmed by IR spectroscopy where ν(C=O) occurs at 1702 and 1593 cm^{-1}, respectively.

In the ^{1}H-coupled-^{13}C NMR spectra of **5**, the β–vinylic carbon atom appears at δ 178 as a doublet with $J_{C\text{-}H}$ = 166 Hz confirming the presence of the vinylic H atom. The α–vinylic carbon occurs as a slightly broadened singlet at 229 ppm. The absence of any resolved phosphorus-carbon coupling is attributed to the influence of the quadrupolar ^{99}Tc (I=9/2) nucleus which is also responsible for the severe broadening of the carbonyl resonances.

The high chemical shift values of the α–vinylic carbon atom is attributed to contributions from the resonance structure $\overline{\mathrm{M{=}C{-}C{=}C{-}O}}$. This imparts more carbenoid character to the α–vinyl carbon and results in a low field shift of the resonance. A similar effect has been observed in other complexes containing five-membered rings of the type $\overline{\mathrm{M{-}C{=}C{-}C{=}O}}$.[10,14,15]

Compound **1** reacts much slower with less electrophilic acetylenes. The addition of excess $HC{\equiv}CCO_2Me$ to toluene solutions of **1** followed by stirring for 4.5 hours affords **6** in 57 % yield. The length of reaction time is critical; longer times result in a significantly lower yield. This is in contrast to the reaction of **1** with DMAD which occurs rapidly and shows no decomposition with time. In agreement with the proposed η^1-coordination of the acetylene ligand, ν(C=O) occurs at 1675 cm^{-1} in the IR spectrum. If the carboxylate oxygen atom was coordinated to the technetium center, ν(C=O) would be expected to occur at much lower wavenumber than that observed for free methyl propiolate (1724 cm^{-1}). Also the observed ν(C≡O) stretches at 2042 (m), 1956 (s) and 1905 (s) cm^{-1} are typical of three meridionally arranged CO ligands.[16] The mass spectrometry data which shows a parent peak at 791 amu also supports η^1-coordination of the acetylene ligand.

In the ^{1}H NMR spectrum of **6** two unique doublets for the β–vinylic protons are observed at δ 6.79 and 5.51 with $J_{H\text{-}H}$ = 4.2 Hz. These doublets are not sharp as the phosphorus coupling is not resolved. This value is characteristic of a geminal rather than cis or trans coupling constant.[17] The methoxy resonance is observed as a singlet at 3.13 ppm. The ^{13}C{H} NMR spectrum shows the α–vinylic carbon as a broadened singlet at 166 ppm. No discernible change in the this peak was observed in the proton-coupled ^{13}C NMR spectrum. As was seen for **5**, phosphorus coupling to the α-carbon atom is not resolved. The β–vinylic carbon atom was obscured by resonances corresponding to the phenyl rings of the phosphine ligands.

In the ^{1}H NMR spectrum of the product resulting from the insertion of methylpropiolate into the Tc-D bond of $DTc(CO)_3(PPh_3)_2$[18] the signal at δ 6.79 is absent. Cleavage of the vinyl ligand with CH_3CO_2H resulted in the formation of $Tc(CO)_2(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$[19] and deuterated methylacrylate. The location of the deuterium atom as being *cis* to the CO_2Me group is confirmed in the ^{1}H NMR spectrum by the appearance of 2 sharp doublets at δ 5.93 and 6.45 for the *cis*-coupled olefin protons ($J_{H\text{-}H}$ = 10.9 Hz). No reactivity of **1** with bulkier acetylenes such as $PhC{\equiv}CCO_2Me$ was observed.

Conclusions

The complex *trans*-$HTc(CO)_3(PPh_3)_2$ (**1**) shows a wide range of reactivity with a variety of unsaturated substrates including heterocumulenes, electron deficient acetylenes, and diazonium salts. These reactions proceed via transfer of the hydride ligand to the most electrophilic atom of the substrate. This behavior is consistent with the hydride ligand of **1** being hydridic rather than acidic.

Experimental Section

Caution! Technetium-99 is a weak β^--emitter (E = 0.292 MeV, $t_{1/2}$ = 2.12×10^5 years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[20]

Reagents and solvents were used as received unless otherwise stated. Drybox solvents (toluene, THF, pentane, Et_2O) were distilled from sodium/benzophenone. The complex $HTc(CO)_3(PPh_3)_2$ (**1**) was prepared as described in Chapter 2. A "bomb" refers to a cylindrical glass vessel sealed with a Kontes high vacuum stopcock. A Mattson Cynus 100 FTIR instrument was used to record all infrared spectra. Only representative IR data are given. Fast atom bombardment mass spectra (FABMS(+)) were obtained using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV and equipped with a Ion Tech B11N FAB gun. The FAB gun produces a beam of 6-8 keV xenon neutrals. All compounds were run in a matrix of neat 3-nitrobenzyl alcohol. ^1H, ^{13}C, and ^{31}P NMR were recorded at 300.0 MHz, 75.429 MHz, and 121.421 MHz, respectively on a Unity Varian spectrometer unless otherwise noted. All $^{31}P\{H\}$ NMR are referenced to an external standard of 85% phosphoric acid in $CDCl_3$. The elemental analyses were performed by Atlantic Microlab, Norcross, GA.

$[Tc(CO)_3(NHN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (2a). In the drybox, a solution containing $[p\text{-}^tBu(C_6H_4)N_2]PF_6$ (49.5 mg; 0.16 mmol) in 5 mL THF was added to a solution containing $HTc(CO)_3(PPh_3)_2$ (**1**) (104.12 mg; 0.15 mmol) in 15 mL THF. After stirring for 6 h., the yellow/brown reaction mixture was filtered through Celite. The volume of the reaction mixture was reduced to ~3 mL under vacuum. The addition of 3 mL heptane followed by storage overnight at -40 °C yielded bright yellow crystals. The crystals were collected by filtration, washed with 10 mL heptane and dried *in vacuo*. Yield: (142 mg, 67%).

Anal. Calcd. for $C_{49}H_{44}F_6N_2O_3P_3Tc$: C, 58.00; H, 4.43; N, 2.76. Found: C, 57.52; H, 4.29; N, 2.70. IR(KBr): ν 2071 (w, C≡O); 1987 (s, C≡O); 1929 (s, C≡O); 1487, 1445 (N=N). ^1H NMR(CD_2Cl_2) δ (ppm): 1.32 (s, 9H, ^{t}Bu); 6.77 (AA'BB', 2H, J = 8.8 Hz, $N(C_6\underline{H}_4)$); 7.37 (m, 12H, $P(C_6\underline{H}_5)$); 7.49 (m, 18H, $P(C_6\underline{H}_5)$); 12.30 (s, 1H, $N\underline{H}NR$). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ (ppm): 31.11 (s, $C(\underline{C}H_3)_3$); 35.76 (s, $\underline{C}(CH_3)_3$); 121.22 (s, $\underline{C}_6H_4$-Bu); 126.52 (s, $\underline{C}_6H_4$-Bu); 129.63 (t, $J_{P\text{-}C}$ = 6.0 Hz, $P(C_6H_5)_3$-ortho or meta); 131.29 (s, $P(C_6H_5)_3$-para); 132.58 (t, $J_{P\text{-}C}$ = 21.3 Hz, $P(C_6H_5)_3$-ipso); 132.95 (s, $\underline{C}_6H_4$-Bu); 133.35 (t, $J_{P\text{-}C}$ = 6.1 Hz, $P(C_6H_5)_3$-ortho or meta); 150.10 (s, $\underline{C}_6H_4$-Bu). $^{31}P\{H\}$ NMR (CD_2Cl_2) δ (ppm): ~44 (br). FABMS(+) *m/z*: 869 $[Tc(CO)_3(NHN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]^+$; 841 $[Tc(CO)_2(NHN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]^+$; 679 $[Tc(CO)_2(PPh_3)_2]^+$.

X-Ray Crystal Structure Determination of 2a. Yellow parallelepiped crystals were grown by slow vapor diffusion of pentane into a CH_2Cl_2 solution of $[Tc(CO)_3(NHN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]PF_6$ at -40 °C. A suitable crystal was selected and mounted on a glass fiber under a stream of N_2. The mounted crystal was then transferred to an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $14.00 < 2\theta < 27.00°$ corresponded to a monoclinic cell. Based on the systematic absences the space group was determined to be $P2_1/n$. The final cell parameters are given in **Table I.**

The data were collected at a temperature of -72±1 °C using the ω-2θ scan technique to a maximum 2θ value of 45.0 °C. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 2.8°. Of the 7139 reflections which were collected, 6814 were unique ($R_{int} = 0.032$); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 minutes of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption absorption coefficient for Mo Kα is 5.4 cm^{-1}. An empirical absorption correction, using the program DIFABS, was applied which resulted in transmission factors ranging from 0.94 to 1.13. The data were corrected for secondary extinction was applied (coeff. = 0.80004×10^{-7}).

The structure was solved by direct methods. The non-hydrogen atoms were refined either anisotropically or isotropically. The final cycle of full-matrix least-squares refinement was based on 4404 observed reflections ($I > 3.00\sigma(I)$) and 375 variable parameters and converged with $R = 0.059$; $R_w = 0.055$. The standard deviation of an observation of unit weight was 2.02. The weighing scheme was based on counting statistics and included a factor (p =

0.01) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.98 and -0.80$e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_{calc}; the values for Df' and Df'' were those of Cromer. All calculations were performed using TEXSAN crystallographic software package of Molecular Structure Corporation.

This structure was troublesome in that disorder was discovered in one of the phenyl groups of the triphenylphosphine ligands. The problem was modeled as an eleven carbon moiety where both phenyls share a common atom. This atom is meta to the phosphorus atoms of one of the groups and para to the same atom in the other ring. A figure of the observed disorder is included in the Supplementary Data. As a result of the disorder and the sharp cutoff of observed data, only those atoms with atomic number seven or greater were refined anisotropically.

$Tc(CO)_3(NN(p\text{-}^tBu(C_6H_4))(PPh_3)_2$ (2b). In the drybox, DBU (0.17 mL) was added to a solution of $[Tc(CO)_3(NHN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**) (83.1 mg; 0.082 mmol) dissolved in 5 mL MeCN. The yellow reaction mixture was stirred for 2 h. during which time a orange-yellow solid precipitated. The solid was filtered on a fritted disk, washed with 10 mL Et_2O and dried *in vacuo*. Yield: (52.4 mg, 85%).

Anal. Calcd. for $C_{49}H_{43}N_2O_3P_2Tc$: C, 67.75; H, 4.99; N, 3.22. Found: C, 67.25; H, 4.79; N, 3.01. IR(KBr); ν 1925 (C≡O); 1850 (C≡O); 1481, 1434 (N=N). ^1H NMR(CD_2Cl_2) δ (ppm): 1.25 (s, 9H, ^tBu); 6.45 (AA'BB', 2H, J = 8.8Hz,

$N(C_6\underline{H}_4)$); 6.96 (AA'BB', 2H, J = 8.4Hz, $N(C_6\underline{H}_4)$); 7.32 (m, 12H, $P(C_6\underline{H}_5)$); 7.48 (m, 18H, $P(C_6\underline{H}_5)$). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ (ppm): 31.52 (s, $C(\underline{C}H_3)_3$); 51.24 (s, $\underline{C}(CH_3)_3$); 119.86 (s, $\underline{C}_6H_4$-Bu); 125.38 (s, $\underline{C}_6H_4$-Bu); 128.58 (t, $J_{P\text{-}C}$ = 6.2 Hz, $P(C_6H_5)_3$-ortho or meta); 130.11 (s, $P(C_6H_5)_3$-para); 130.56 (s, $\underline{C}_6H_4$-Bu); 134.16 (t, $J_{P\text{-}C}$ = 6.0 Hz, $P(C_6H_5)_3$-ortho or meta); 135.49 (t, $J_{P\text{-}C}$ = 21.3 Hz, $P(C_6H_5)_3$-ipso); 150.99 (s, $\underline{C}_6H_4$-Bu). $^{31}P\{H\}$ NMR (CD_2Cl_2) δ (ppm): ~54 (br). FABMS(+) *m/z*: 868 $[Tc(CO)_3(NN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]^+$; 841 $[Tc(CO)_2(NN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]^+$; 679 $[Tc(CO)_2(PPh_3)_2]^+$.

$Tc(CO)_2(\eta^2\text{-}S_2CH)(PPh_3)_2$ (3). A solution containing 10 mL CS_2 and $HTc(CO)_3(PPh_3)_2$ (**1**) (58.4 mg; 0.082 mmol) was allowed to reflux for 1.5 hours. The volume of the reaction mixture was reduced to 3 mL CS_2 under a stream of N_2 and combined with 50 mL EtOH. A bright yellow precipitate was isolated on a fritted disk washed with 10 mL EtOH and allowed to dry *in vacuo*. Recrystallization was effected by the slow evaporation of a benzene/EtOH mixture at room temperature. Yield: (45.1 mg, 72%).

Anal. Calcd. for $C_{39}H_{31}O_2P_2S_2Tc$: C, 61.91; H, 4.13; S, 8.47. Found: C, 61.50; H, 4.19; S, 8.03. IR(KBr): ν 1934 (s, C≡O); 1865 (s, C≡O). ^1H NMR(CD_2Cl_2) δ (ppm): 7.39 (m, 18H, $P(C_6\underline{H}_5)$); 7.62 (m, 12H, $P(C_6\underline{H}_5)$); 10.13 (br, 1H, $S_2C\underline{H}$). $^{13}C\{H\}$ NMR(CD_2Cl_2, $Tc(^{13}CO)_2(\eta^2\text{-}S,SCH)PPh_3)_2$, 125.697 MHz) δ (ppm): 128.18 (t, $J_{P\text{-}C}$ = 4.0 Hz, $P(C_6H_5)_3$-ortho or meta); 129.92 (s, $P(C_6H_5)_3$-para); 134.42 (t, $J_{P\text{-}C}$ = 6.0 Hz, $P(C_6H_5)_3$-ortho or meta); 135.23 (t, $J_{P\text{-}C}$ = 19.8 Hz, $P(C_6H_5)_3$-ipso); 202 (br, ~500 Hz wide, CO); 236.12 (s, $\eta^2\text{-}S,S\underline{C}H$). ^{13}C NMR(CD_2Cl_2) δ (ppm): 236.12 (d, $J_{C\text{-}H}$ = 181 Hz, $\eta^2\text{-}S,S\underline{C}H$). $^{31}P\{H\}$ NMR(CD_2Cl_2) δ (ppm): ~48 (br). FABMS(+) *m/z*: 756 [Tc(CO)$_2$(η^2-S,SCH)(PPh$_3$)$_2$]; 728 [Tc(CO)(η^2-S,SCH)(PPh$_3$)$_2$]; 700 [Tc(η^2-S,SCH)(PPh$_3$)$_2$].

Tc(CO)$_2$(η^2-(CH$_3$)NSCH)(PPh$_3$)$_2$ (4). In the drybox a bomb was charged with HTc(CO)$_3$(PPh$_3$)$_2$ (1) (142.3 mg, 0.21 mmol), 1 mL (CH$_3$)NCS, and 10 mL toluene. It was removed from the drybox and heated at 40 °C for 24 h. As the reaction proceeded the initially colorless solution turned a pale yellow. After this period the reaction mixture was filtered through Celite to remove a small amount of black insoluble material. All volatiles were removed using a vacuum pump leaving a bright yellow solid. The residue was dissolved in 20 mL CH$_2$Cl$_2$ and layered with 20 mL MeOH. Slow evaporation at room temperature yielded pale yellowish crystals which were filtered on a fritted disk, washed with Et$_2$O, MeOH and dried *in vacuo*. Yield: (68.3 mg; 45%).

Anal. Calcd. for C$_{40}$H$_{34}$NO$_2$P$_2$STc: C, 63.75; H, 4.55; N, 1.86; S, 4.25. Found: C, 62.42; H, 4.53; N, 1.95; S, 4.29. IR (KBr): ν 1927 (s, C≡O); 1839 (s, C≡O). ^{1}H NMR (CD$_2$Cl$_2$) δ (ppm): 0.40 (s, 3H, NC$\underline{H_3}$); 7.05 (m, 18H, P(C$_6\underline{H_5}$)); 7.38 (s, 1H, (CH$_3$)NC$\underline{H}$S); 7.99 (m, 12H, P(C$_6\underline{H_5}$)). ^{13}C{H} NMR (CD$_2$Cl$_2$, Tc(^{13}CO)$_2$(η^2-(CH$_3$)NSCH)PPh$_3$)$_2$, 125.697 MHz) δ (ppm): 45.41 (s, N$\underline{C}$H$_3$); 128.13 (t, $J_{P\text{-}C}$ = 4.5 Hz, P(C$_6$H$_5$)$_3$-ortho or meta); 129.82 (s, P(C$_6$H$_5$)$_3$-para); 134.26 (t, $J_{P\text{-}C}$ = 6.2 Hz, P(C$_6$H$_5$)$_3$-ortho or meta); 135.36 (t, $J_{P\text{-}C}$ = 19.9 Hz, P(C$_6$H$_5$)$_3$-ipso); 180.61 (s, (CH$_3$)N$\underline{C}$HS); 211 (br, ~600 Hz, CO); 219 (br, ~600 Hz, CO). ^{31}P{H} NMR (CD$_2$Cl$_2$) δ (ppm): ~45 (br). FABMS(+) *m/z*: 753 [Tc(CO)$_2$(η^2-(CH$_3$)NSCH)(PPh$_3$)$_2$]; 725 [Tc(CO)$_2$(SCH)(PPh$_3$)$_2$]; 679 [Tc(CO)$_2$(PPh$_3$)$_2$]$^+$.

$\overline{Tc(CO)_2[-C(CO_2Me)=CH(C(O}OMe)](PPh_3)_2$ (5). In the drybox a flask was charged with $HTc(CO)_3(PPh_3)_2$ (1) (149.3 mg, 0.21 mmol), $MeO_2CC{\equiv}CCO_2Me$ (26 μL, 0.21 mmol) and 10 mL toluene. The reaction mixture was stirred for 1.5 h., filtered through Celite, and evaporated to dryness under vacuum. The bright yellow viscous residue was combined with 10 mL MeCN and stirred overnight. The resulting yellow solid was collected by filtration, washed with Et_2O, MeCN and dried *in vacuo*. Yield: (81.6 mg; 41%).

Anal. Calcd for $C_{44}H_{37}O_6P_2Tc$: C, 64.24; H, 4.53. Found: C, 63.87; H, 4.52. IR(KBr): ν 1930 (s, C≡O); 1848 (s, C≡O); 1702 (C=O, non-coord.); 1593 (C=O, coord.). ^1H NMR(C_6D_6) δ (ppm): 2.78 (s, 3H, $CO_2\underline{Me}$); 3.32 (s, 3H, $CO_2\underline{Me}$); 6.71 (t, 1H, vinylic H, $J_{P\text{-}H}$ = 2.65 Hz); 7.0 (m, 18 H, $P(C_6\underline{H}_5)$); 7.9 (m, 12 H, $P(C_6\underline{H}_5)$). ^{13}C NMR (CD_2Cl_2) δ (ppm): 127.8 (d, β-vinylic C, $J_{C\text{-}H}$ = 166 Hz). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ (ppm): 50.4 (s, $CO_2\underline{Me}$); 52.0 (s, $CO_2\underline{Me}$); 127.8 (s, β-vinylic C); 128.75 (t, $J_{P\text{-}C}$ = 4.2 Hz, $P(C_6H_5)_3$-ortho or meta); 130.60 (s, $P(C_6H_5)_3$-para); 132.45 (t, $J_{P\text{-}C}$ = 20.0 Hz, $P(C_6H_5)_3$-ipso); 134.03 (t, $J_{P\text{-}C}$ = 5.4 Hz, $P(C_6H_5)_3$-ortho or meta); 174.5 (s, $\underline{C}O_2Me$); 180.8 (s, $\underline{C}O_2Me$); 214 (br, CO); 220 (br, CO); 229 (s, α-vinylic C). $^{31}P\{H\}$ NMR(CD_2Cl_2) δ (ppm): 53 (br). FABMS(+) *m/z*: 823 [$Tc(CO)_2[-C(CO_2Me)=CH(C(O)OMe)](PPh_3)_2$]; 795 [$Tc(CO)[-C(CO_2Me)=CH(C(O)OMe)](PPh_3)_2$].

$Tc(CO)_3(-C(CO_2Me)=CH_2)(PPh_3)_2$ (6). In the drybox a flask was charged with $HTc(CO)_3(PPh_3)_2$ (1) (112 mg, 0.16 mmol), $HC{\equiv}CCO_2Me$ (0.70 mL; 7.9 mmol) and 10 mL toluene. The reaction mixture was stirred for 5 h., filtered through Celite, and evaporated to dryness under vacuum. The pale pink material was suspended in 15 mL Et_2O, collected by filtration, washed with Et_2O, and dried *in vacuo*. Yield: (79.2 mg; 57%).

Repeated attempts failed to give a satisfactory analysis of this complex; results were consistently $\geq$2% low for carbon. IR(KBr): ν 2042 (m, C≡O); 1956 (s, C≡O); 1905 (s, C≡O); 1675 (C=O, non-coord.). ^1H NMR(C_6D_6) δ (ppm): 3.13 (s, 3H, $CO_2\underline{Me}$); 5.51 (1H, vinylic H, $J_{H\text{-}H}$ = 4.2 Hz); 6.79 (1H, vinylic H, $J_{H\text{-}H}$ = 4.2 Hz); 6.95 (m, 18 H, $P(C_6\underline{H_5})$); 7.5 (m, 12 H, $P(C_6\underline{H_5})$). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ (ppm): 49.8 (s, $CO_2\underline{Me}$); 128.45 (t, $J_{P\text{-}C}$ = 4.5 Hz, $P(C_6H_5)_3$-ortho or meta); 129.99 (s, $P(C_6H_5)_3$-para); 133.61 (t, $J_{P\text{-}C}$ = 19.4 Hz, $P(C_6H_5)_3$-ipso); 134.53 (t, $J_{P\text{-}C}$ = 6.0 Hz, $P(C_6H_5)_3$-ortho or meta); 166 (br s, α–vinylic C); 173.4 (s, $\underline{C}O_2Me$). $^{31}P\{H\}$ NMR(CD_2Cl_2) δ (ppm): 45 (br). FABMS(+) *m/z*: 791 $[Tc(CO)_3[\text{-}C(CO_2Me)=CH_2](PPh_3)_2]$; 763 $[Tc(CO)_2[\text{-}C(CO_2Me)=CH_2](PPh_3)_2]$; 707 $[Tc(CO)_3(PPh_3)_2]$.

Reaction of $DTc(CO)_3(PPh_3)_2$ with HC≡CCO_2Me. This reaction was carried out as described for **6** with the substitution of $DTc(CO)_3(PPh_3)_2$ for **1**.

^1H NMR(C_6D_6) δ (ppm): 3.18 (s, 3H, $CO_2\underline{Me}$); 5.54 (t, vinylic H, $J_{P\text{-}H}$ = 2.8 Hz); 6.95 (m, 18 H, $P(C_6\underline{H_5})$); 7.5 (m, 12 H, $P(C_6\underline{H_5})$).

Reaction of $Tc(CO)_3(\text{-}C(CO_2Me)=CHD)(PPh_3)_2$ with CH_3CO_2H. To $Tc(CO)_3(\text{-}C(CO_2Me)=CHD)(PPh_3)_2$ (45.9 mg; 0.058 mmol) dissolved in C_6D_6 (~3 mL) was added 1.0 equiv. CH_3CO_2H (0.058 mmol; 3.3 μL). Approximately 1 mL of this solution was withdrawn and added to an NMR tube containing 3 mL C_6D_6.

^{1}H NMR(C_6D_6) δ (ppm): Tc(CO)$_2$(η^2-O_2CCH_3)(PPh_3)$_2$^{19} and $H_1DC=C(CO_2Me)H_2$: 0.59 (s, η^2-$O_2CC\underline{H_3}$); 3.35 (s, $CO_2\underline{Me}$); 5.93 (d, J_{H1H2} = 10.9 Hz); 6.45 (d, J_{H1H2} = 10.9 Hz); 7.38 (m, 30 H, P(C_6H_5)).

Table 1. Crystal and Data Collection Parameters for $[Tc(CO)_3(NHN(p\text{-}{}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**).

Empirical Formula: $C_{50}H_{46}N_2O_3F_6P_3Cl_2Tc$

Crystal Parameters

a = 14.030(3) Å
b = 14.123(3) Å
c = 25.227(5) Å
β = 96.09(2) °
V = 4971(3) Å^3
T = -72±1 °C

Space Group: $P2_1/n$
Formula Weight = 1097.74 amu
Z = 4
D_{calc} = 1.467 g/cm^3
μ_{calc} = 5.44 cm^{-1}
Size = 0.25 x 0.30 x 0.43 mm

Data Measurements Parameters

Diffractometer: Enraf-Nonius CAD-4
Radiation: MoKα (λ = 0.71069 Å)
Scan Type: ω - 2Θ
Scan Rate: 1.9 - 16.5°/min (in omega)
Scan Width: (0.80 + 0.35 tanΘ)°
2Θ_{max}: 45.0°
No. of Reflections: Total = 7139 Unique = 6814 (R_{int} = 0.032)
Corrections: Lorentz Polarization Absorption (trans. factors: 0.94 - 1.13)
Secondary Ext. (coeff.: 0.80004 x 10^{-07})

Structure Solution and Refinement

Structure Solution: Direct Methods
Refinement: Full-matrix least-squares

Function Minimized: $\Sigma w (|F_o| - |F_c|)^2$

Least Squares Weight: $4F_o^2/\sigma^2(F_o^2)$

p-factor: 0.01

No. Observations ($I>3.00\sigma(I)$): 4404

No. Variables: 375

Residuals: R = 0.059; R_w = 0.055

Goodness of Fit: 2.02

Max. Peak in Diff. Map: 0.98 $e^-/Å^3$

Min. Peak in Diff. Map: -0.80 $e^-/Å^3$

Table II. Selected Intramolecular Distances for $[Tc(CO)_3(NHN(p\text{-}{}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**).

Atom 1	Atom 2	Distance (Å)
Tc	P(1)	2.453(2)
Tc	P(2)	2.461(2)
Tc	N(1)	2.157(6)
Tc	C(1)	1.999(9)
Tc	C(2)	1.910(8)
Tc	C(3)	1.985(8)
C(1)	O(1)	1.127(9)
C(2)	O(2)	1.156(9)
C(3)	O(3)	1.131(8)
N(1)	N(2)	1.243(8)

Table III. Selected Intramolecular Bond Angles for [Tc(CO)$_3$(NHN(*p*-^{t}Bu(C$_6$H$_4$))(PPh$_3$)$_2$]PF$_6$ (**2a**).

Atom 1	Atom 2	Atom 3	Angles(deg)
Tc	N(1)	N(2)	124.2(5)
P(1)	Tc	P(2)	173.37(8)
P(1)	Tc	N(1)	86.9(2)
P(1)	Tc	C(1)	94.2(2)
P(1)	Tc	C(2)	91.7(2)
P(1)	Tc	C(3)	84.9(2)
P(2)	Tc	N(1)	86.8(2)
P(2)	Tc	C(1)	88.3(2)
P(2)	Tc	C(2)	94.5(2)
P(2)	Tc	C(3)	92.8(2)
N(1)	Tc	C(1)	92.6(3)
N(1)	Tc	C(2)	178.0(3)
N(1)	Tc	C(3)	89.7(3)
C(1)	Tc	C(2)	86.1(3)
C(1)	Tc	C(3)	177.5(3)
C(2)	Tc	C(3)	91.6(3)

Table IV. Positional Parameters and Estimated Standard Deviations (Å^2) for $[Tc(CO)_3(NHN(p\text{-}^tBu(C_6H_4))(PPh_3)_2]PF_6$ (**2a**).

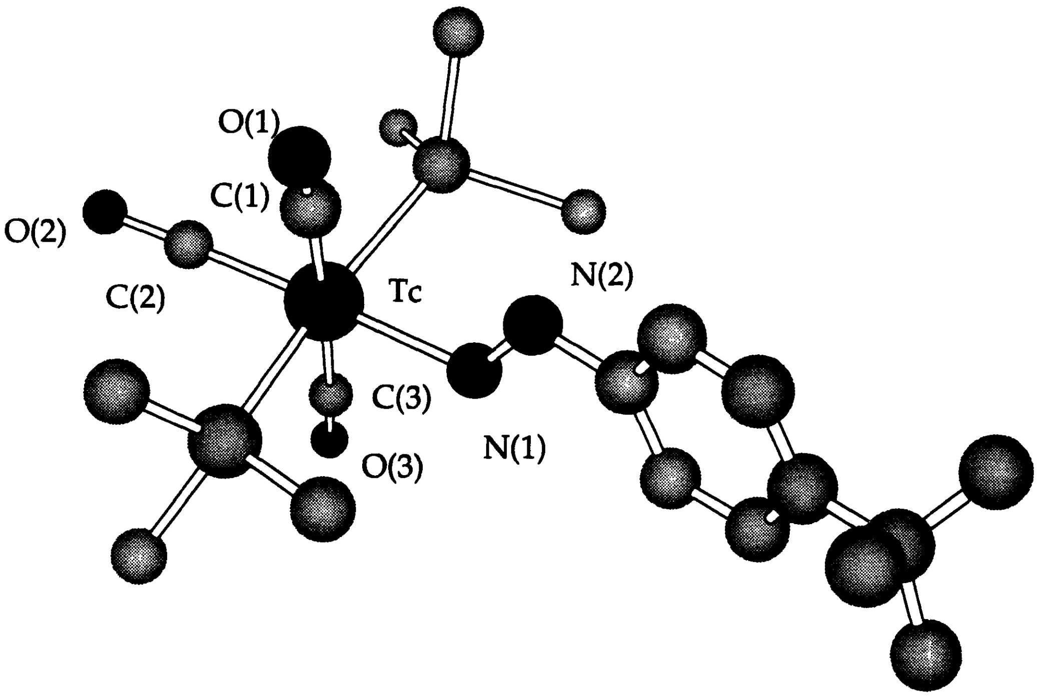
Atom	x	y	z	B(eq)
Tc	0.26762(5)	0.18858(5)	0.15795(2)	1.91(3)
P(1)	0.4426(1)	0.2045(1)	0.17139(8)	2.2(1)
P(2)	0.0915(2)	0.1927(2)	0.14322(8)	2.3(1)
O(1)	0.2628(5)	0.0754(4)	0.0515(2)	5.7(4)
O(2)	0.2784(4)	-0.0081(4)	0.2096(2)	4.2(3)
O(3)	0.2759(4)	0.2861(4)	0.2691(2)	3.5(3)
N(1)	0.2654(4)	0.3256(4)	0.1201(2)	2.0(3)
N(2)	0.2384(5)	0.3996(5)	0.1405(2)	2.8(3)
C(1)	0.2673(6)	0.1205(6)	0.0885(3)	3.2(2)
C(2)	0.2730(5)	0.0660(6)	0.1901(3)	2.4(2)
C(3)	0.2703(6)	0.2513(5)	0.2285(3)	2.3(2)
C(11)	0.4745(5)	0.3238(5)	0.1540(3)	2.1(1)
C(12)	0.4990(5)	0.3479(5)	0.1044(3)	2.5(2)
C(13)	0.5118(6)	0.4423(6)	0.0901(3)	3.6(2)
C(14)	0.5016(6)	0.5122(6)	0.1265(3)	4.0(2)
C(15)	0.4775(6)	0.4911(6)	0.1767(3)	3.5(2)
C(16)	0.4636(6)	0.3970(6)	0.1905(3)	2.9(2)
C(21)	0.0458(5)	0.2732(5)	0.0893(3)	2.5(2)
C(22)	-0.0294(6)	0.3347(6)	0.0952(3)	3.7(2)
C(23)	-0.0648(7)	0.3914(7)	0.0524(4)	4.3(2)

C(24)	-0.0280(6)	0.3853(6)	0.0051(3)	3.8(2)
C(25)	0.0449(6)	0.3260(6)	-0.0014(3)	3.6(2)
C(26)	0.0829(6)	0.2693(6)	0.0406(3)	3.0(2)
C(31)	0.5005(5)	0.1901(6)	0.2396(3)	2.3(1)
C(32)	0.4618(6)	0.1301(6)	0.2746(3)	3.3(2)
C(33)	0.5102(7)	0.1135(7)	0.3258(4)	4.3(2)
C(34)	0.5955(6)	0.1591(6)	0.3407(3)	3.9(2)
C(35)	0.6337(6)	0.2188(6)	0.3063(3)	3.8(2)
C(36)	0.5877(6)	0.2344(6)	0.2556(3)	3.4(2)
C(41)	0.0305(5)	0.2326(5)	0.1933(3)	2.3(2)
C(42)	-0.0442(6)	0.1821(6)	0.2187(3)	3.4(2)
C(43)	-0.0885(6)	0.2151(6)	0.2618(3)	4.0(2)
C(44)	-0.0598(6)	0.2993(7)	0.2853(3)	4.0(2)
C(45)	0.0112(6)	0.3513(6)	0.2660(3)	3.6(2)
C(46)	0.0562(5)	0.3190(6)	0.2238(3)	2.8(2)
C(51A)	0.531(1)	0.130(1)	0.1413(7)	1.7(4)
C(51B)	0.503(1)	0.122(1)	0.1289(7)	1.7(4)
C(52A)	0.498(1)	0.037(1)	0.1261(6)	2.1(3)
C(52B)	0.580(1)	0.069(1)	0.1500(7)	3.7(4)
C(53A)	0.567(1)	-0.023(1)	0.1082(6)	2.2(3)
C(54C)	0.6455(8)	0.0044(8)	0.1087(4)	6.1(3)
C(53B)	0.597(1)	-0.001(1)	0.0648(8)	4.7(4)
C(55A)	0.687(1)	0.094(1)	0.1165(6)	2.3(3)
C(55B)	0.522(1)	0.054(1)	0.0411(7)	3.7(4)
C(56A)	0.623(1)	0.157(1)	0.1360(6)	2.1(3)

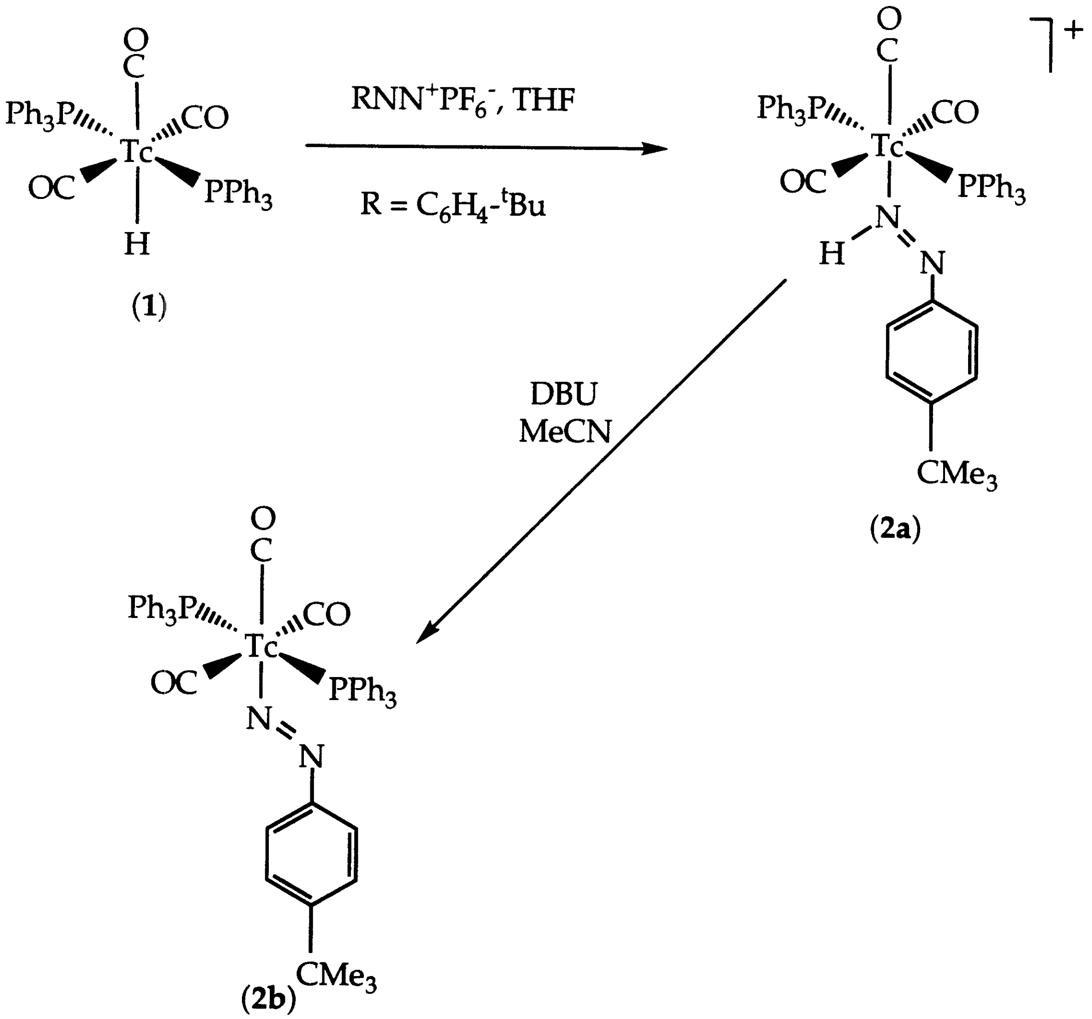
C(56B)	0.473(1)	0.116(1)	0.0741(7)	3.2(4)
C(61)	0.0334(5)	0.0803(5)	0.1239(3)	2.3(2)
C(62)	0.0515(6)	0.0018(6)	0.1567(3)	3.3(2)
C(63)	0.0083(6)	-0.0850(6)	0.1447(3)	3.7(2)
C(64)	-0.0553(7)	-0.0929(7)	0.0995(4)	4.7(2)
C(65)	-0.0732(7)	-0.0161(8)	0.0665(4)	5.3(2)
C(66)	-0.0292(7)	0.0711(7)	0.0786(4)	4.5(2)
C(71)	0.2458(5)	0.4873(5)	0.1131(3)	2.1(2)
C(72)	0.2663(6)	0.4970(6)	0.0610(3)	2.7(2)
C(73)	0.2776(6)	0.5865(6)	0.0405(3)	2.9(2)
C(74)	0.2701(6)	0.6678(6)	0.0701(3)	2.7(2)
C(75)	0.2483(6)	0.6562(6)	0.1221(3)	3.6(2)
C(76)	0.2358(6)	0.5676(6)	0.1431(3)	3.5(2)
C(741)	0.2841(7)	0.7669(6)	0.0478(4)	3.8(2)
C(742)	0.1934(8)	0.8213(8)	0.0468(4)	6.4(3)
C(743)	0.318(1)	0.765(1)	-0.0059(6)	10.0(4)
C(744)	0.3596(8)	0.8198(8)	0.0844(4)	6.4(3)
Cl(1)	0.7574(2)	0.3782(3)	0.1620(1)	9.5(2)
Cl(2)	0.7193(3)	0.4726(2)	0.2584(2)	10.6(3)
C(1S)	0.750(1)	0.481(1)	0.1959(6)	11.4(5)
H(1)	0.8061	0.5194	0.1935	12.0
H(2)	0.6977	0.5223	0.1735	12.0
P(3)	0.8307(2)	0.2057(2)	0.45121(8)	2.8(1)
F(1)	0.7444(4)	0.2755(4)	0.4349(2)	5.8(3)
F(2)	0.7573(4)	0.1194(4)	0.4475(2)	5.7(3)

F(3)	0.8149(3)	0.2183(3)	0.5130(2)	3.9(2)
F(4)	0.9147(4)	0.1349(4)	0.4686(2)	5.5(3)
F(5)	0.9018(4)	0.2907(4)	0.4563(2)	6.9(4)
F(6)	0.8440(4)	0.1920(4)	0.3902(2)	6.1(3)

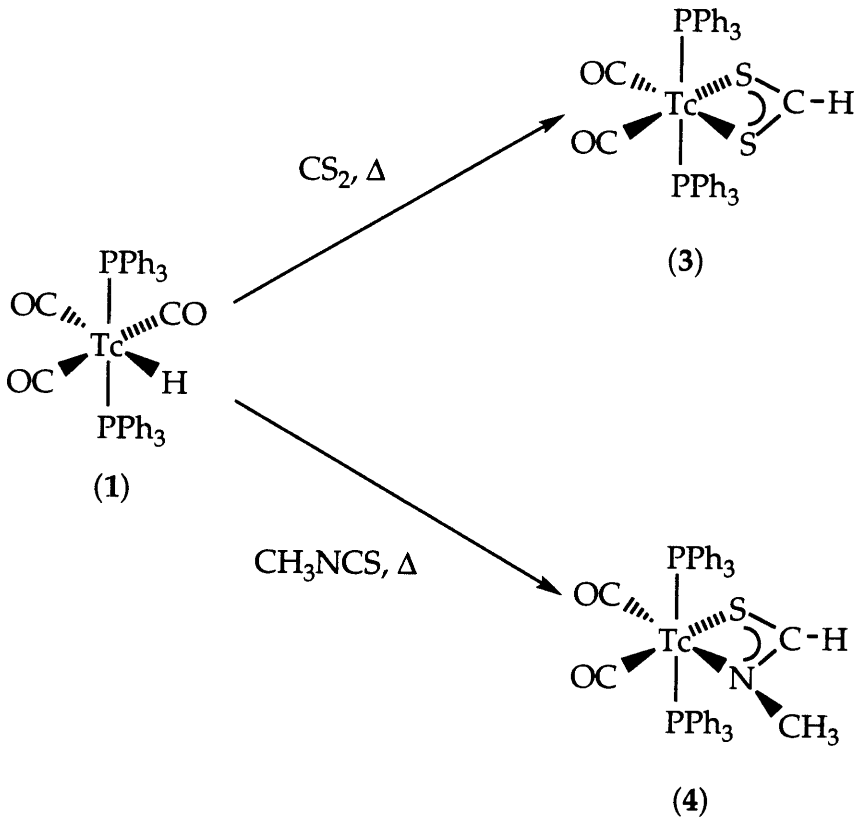
Figure 1. Chem 3D representation of **2a**. The phenyl rings of the PPh_3 ligands, the PF_6^- counterion. and the CH_2Cl_2 solvate molecule were omitted for clarity.



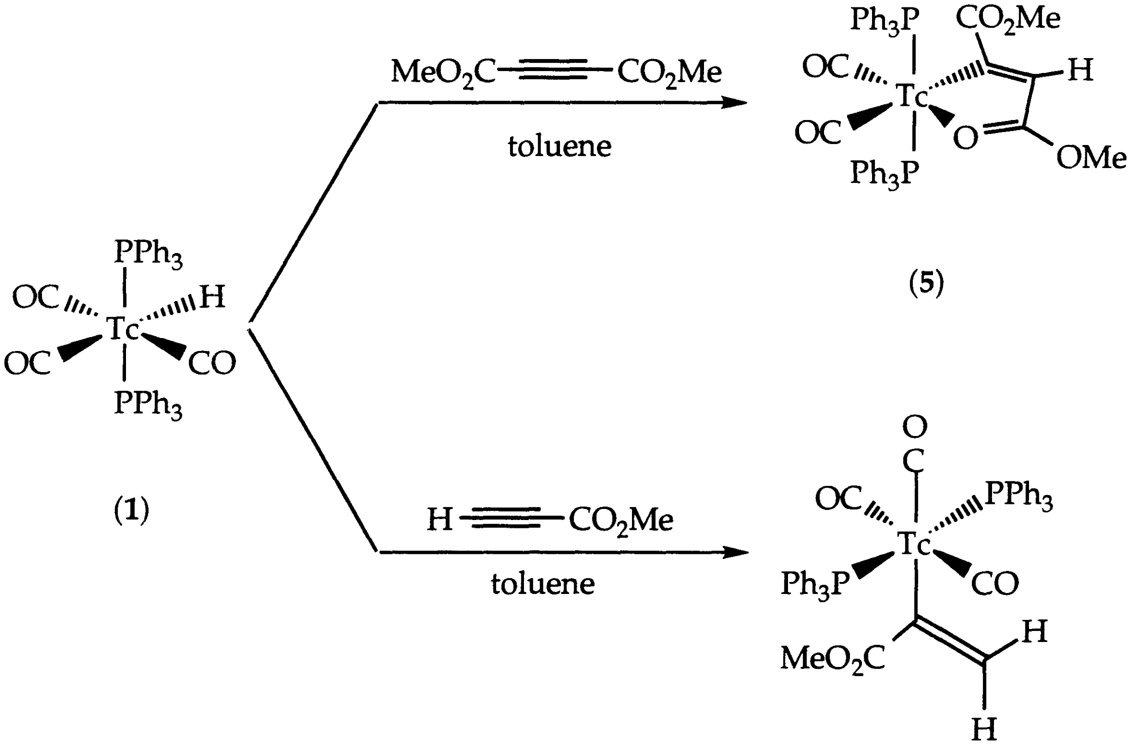
Scheme I



Scheme II


PPh3
OC
CO
Tc
OC
H
PPh3
(1)
CS2, Δ
PPh3
OC
Tc
S
C-H
OC
S
PPh3
(3)
CH3NCS, Δ
PPh3
OC
Tc
S
C-H
OC
N
PPh3
CH3
(4)

Scheme III



PPh3
OC
H
Tc
OC
CO
PPh3
(1)
MeO2C
CO2Me
toluene
Ph3P
CO2Me
OC
Tc
H
OC
O
OMe
Ph3P
(5)
H
CO2Me
toluene
O
C
OC
PPh3
Tc
Ph3P
CO
MeO2C
H
H
(6)

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(19) The synthesis of this complex is fully described in Chapter 4.

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Chapter 4

Protonation of the Tc-H Bond in $HTc(CO)_3(PPh_3)_2$

Introduction

The synthesis of transition metal complexes which behave as strong Lewis acids has received considerable attention.[1,2] The low valent metal center in these complexes is bound to strong π-acceptors and a labile anionic or neutral ligand. Such complexes have been postulated as intermediates in many catalytic pathways[2,3] and are excellent starting materials for preparative organometallic chemistry.

A variety of synthetic routes have been used for the preparation of Lewis acidic transition metal complexes.[2] One commonly used method involves the elimination of H_2 from a transition metal complex by reaction of a metal hydride with a strong acid.[1,4] The reactivity of the Tc(I) hydride, *trans*-$HTc(CO)_3(PPh_3)_2$ (**1**) with proton sources has been investigated for the preparation a variety of Tc(I) carbonyl complexes.

Results and Discussion

Treatment of **1** with HBF_4 in the presence of a neutral ligand L (where L = MeCN (**2**); CO (**3**)) affords the cationic Tc(I) complexes $[Tc(CO)_3L(PPh_3)_2]BF_4$. The FAB(+) mass spectra for **2** and **3** show peaks corresponding to the cationic fragments $[Tc(CO)_3(MeCN)(PPh_3)_2]$ and $[Tc(CO)_4(PPh_3)_2]$ at 748 and 735 *m/z*, respectively. The meridional arrangement of the carbonyl ligands in **2** was confirmed by a characteristic IR spectrum showing two strong bands (1986, 1957 cm^{-1}) and a higher energy band of lower intensity (2074 cm^{-1}).[5] Also visible are weak peaks at 2317 and 2283 cm^{-1} which are assigned to $\nu(C{\equiv}N)$.

In support of a *trans* arrangement of phosphine ligands, only one broad peak at $\delta \sim 199$ is visible in the carbonyl region of the $^{13}C\{H\}$ NMR spectrum of $[Tc(CO)_3(^{13}CO)(PPh_3)_2]BF_4$. As described in Chapter 2 the carbonyl resonances could only observed by ^{13}C NMR spectroscopy when complex **3** was prepared using $^{13}CO(g)$.

In the absence of a neutral ligand, reaction of **1** with $HOSO_2CF_3$ results in anion coordination to the metal center affording the Tc(I) triflate complex $Tc(CO)_3(OSO_2CF_3)(PPh_3)_2$ (**5**). The IR spectrum of **5** shows two strong bands at 1231 and 1324 cm^{-1} which can be assigned to the monodentate bound $CF_3SO_3^-$ ligand.[1,2] The Tc(I) chloride **4** may be prepared similarly by treating **1** with HCl. Several high yield syntheses of **4** have been previously reported.[6,7]

Organic acids, HCO_2R, ($R = H, CH_3$) react with **1** to yield the η^2-formate **6a** and acetate **6b** complexes. The IR spectra of **6a** and **6b**, show $\nu(OCO)$ at 1547, 1434 and 1518, 1464 cm^{-1} respectively.[8] Consistent with η^2-coordination of the formate ligand the $^{13}C\{H\}$ NMR spectrum of $Tc(^{13}CO)_2(O_2CH)(PPh_3)_2$ (**6a**) shows one broad peak at δ 204 for the carbonyl ligands. The FAB(+) mass spectrum of **6a** also support an η^2-formate ligand showing a parent peak at 725 *m/z* corresponding to $[Tc(CO)_2(\eta^2\text{-}O_2CH)(PPh_3)_2]$. The bidentate nature of the acetate and formate ligands is preserved even when the complexes are heated in the presence of a potential ligand like CO.

The acids, acetylacetone (Hacac) and tropolone (Htrop), which form anions as a result of enolization and ionization, also react with **1** to give stable chelate complexes. Treatment of **1** with excess tropolone affords the bright yellow complex, $Tc(CO)_2(trop)(PPh_3)_2$ (**7**). The major peaks in the FAB(+) mass spectrum of **7** occur at 800 $[Tc(CO)_2(trop)(PPh_3)_2]$ and 772 [Tc(CO) (trop)$(PPh_3)_2$] *m/z* . Similar to that found in uncoordinated tropolone,[9] the $^{13}C\{H\}$ NMR spectrum of **7** shows 4 resonances at δ 122.97, 125.50, 135.83, and 182.99. The upfield peak at δ 182.99 is assigned to the carbon atoms bound to the chemically equivalent oxygen atoms of the tropolonato ligand.

Acetylacetone reacts with **1** in a similar fashion to tropolone, affording the pale pink complex **8**. In accordance with a monoanionic, bidentate O,O-coordinated acetylacetonato ligand, the ^1H NMR spectrum of **8** shows a singlet at δ 1.3 which is assigned to the equivalent methyl groups and a singlet at δ 4.25 that is due to the unique vinylic proton of the acetylacetonato ligand.

The structure of **8** was confirmed by a single crystal X-ray diffraction study. Diffusion of pentane into a CH_2Cl_2 solution at 0 °C resulted in the formation of colorless parallelepiped crystals. Complex **8** crystallizes with a CH_2Cl_2 solvate molecule. Data and collection parameters are given in **Table I** and the experimental section. An ORTEP diagram is given in **Figure 1.** Bond lengths, angles and positional parameters are given in **Tables II, III,** and **IV**, respectively.

Complex **8** has slightly distorted octahedral geometry with a bidentate acetylacetonato ligand, two axial PPh_3 ligands and two *cis* CO ligands. The acetylacetonato ligand is planar and binds the metal center through both oxygen atoms to form a six-membered chelate ring. The Tc-O(1) and Tc-O(2) distances were determined to be 2.152(7) and 2.135(7)Å, respectively. These distances, although significantly longer than found for the crystallographically characterized Tc acac complexes $Tc(acac)_3$[10] ($Tc\text{-}O_{avg}$ = 2.025 Å), $[Tc(NO)(Cl)_3(acac)^-]$[11] ($Tc\text{-}O_{avg}$ = 2.07 Å), and $TcCl(acac)(PPh_3)_3$[12] ($Tc\text{-}O_{avg}$ = 2.01 Å), are within the range of M-O bond lengths reported for other transition metal acetylacetone complexes.[13] The longer Tc-O bonds lengths in **8** may reflect the larger size of the Tc(I) metal center.

Salicylaldehyde and 3-hydroxysalicylaldehyde react with **1** to afford the complexes **9a** and **9b**. These reactions occur readily at room temperature with a slight excess of the aldehyde. When the reaction is carried out with only one equiv. of 3-hydroxysalicylaldehyde the reaction mixture contains primarily starting materials as seen by ^{1}NMR spectroscopy (48 h.). The ^{1}H NMR spectrum of **9a** shows the aldehyde proton at δ 7.95 and the OH proton at δ 6.56. In the proton-coupled ^{13}C NMR spectrum of **9a** the aldehyde carbon atom is observed as a doublet (J_{C-H} = 168 Hz) at δ 191, a 10 ppm downfield shift from that of the free ligand. Also, two unique signals at δ 150.97 and 160.44 are observed for the phenyl carbon atoms bound to oxygen atoms. The IR spectrum of **9a** shows ν(C≡O) at 1932 and 1848 cm^{-1} and ν(C=O) at 1608 cm^{-1}. A weak peak corresponding to ν(OH) is observed at 3395 cm^{-1}. The FAB(+) mass spectrum of **9a** shows a parent peak at 816 *m/z* and a peak at 788 *m/z* corresponding to the loss of CO from the complex.

The ability to form phenolate bonds to Tc^{I} is very dependent upon the nature of the added aryloxide. Other potentially bidentate aldehyde ligands such as 2-aminobenzaldehyde,[17] 2-methoxybenzaldehyde and 2-pyridinecarboxaldehyde as well as monodentate aldehydes (e.g. benzaldehyde) do not react with **1** under similar conditions. Also **1** shows no reactivity towards phenol or 2-hydroxy-methylbenzoate. Berke's group has demonstrated that the isoelectronic system *trans, trans*-$WH(CO)_2(NO)(PMe_3)_2$ reacts with aldehydes to form tungsten alkoxides by insertion into the W-H bond.[18] These compounds rapidly loose CO and can be trapped by the addition of pyridine for a mondentate alkoxide. No intermediates were observed during the reaction of **1** and salicylaldehyde. In the presence of 1 atm CO(g) the reaction does not proceed and only starting material is isolated after 24 h.

As shown in **Scheme VI**, complex **4** is a useful synthon. Treatment of **4** with NaCp in THF, under reflux conditions yields the colorless cyclopentadienyl complex (η^5-Cp)Tc(CO)$_2$(PPh$_3$) (**10**) in 54% yield. The η^5-Cp ligand is observed as a singlet in the ^{1}H NMR at δ 4.57 and in the ^{13}C{H} NMR spectrum at δ 86.3. A FAB(+) mass spectrum of **10** shows peaks at 482 and 453 *m/z* which correspond to the fragments CpTc(CO)$_2$(PPh$_3$) and CpTc(CO)(PPh$_3$), respectively.

Other tridentate monoanionic ligands react with **4**. The complex {HB(py)$_3$}Tc(CO)$_2$(PPh$_3$) ({HB(py)$_3$} = hydridotrispyrazolylborate) can be prepared by refluxing **4** with 1 equiv. {HB(py)$_3$}.[6] Similarly, **11** is formed by refluxing NaL$_{OEt}$ (L$_{OEt}$ = {η^5-CpCo(P(O)(OEt)$_2$)$_3$}) with **4**. Like {HB(py)$_3$}Tc(CO)$_2$(PPh$_3$), complexes **10** and **11** are both 18 electron species in which the Tc metal center is coordinated to a 6e-, monoanionic face capping ligand, two carbonyl ligands, and a PPh$_3$ ligand.

The ^{1}H NMR spectrum of **11** supports the proposed structure showing three well-resolved triplets at δ 0.88 , 1.27, and 1.34, which correspond to the methyl groups of L$_{OEt}$. Two complex multiplets at δ 3.45 and 4.29 are observed for the methylene groups. In the FAB(+) mass spectrum of **11** peaks occurring at 952, 924 and 896 *m/z* were assigned to the fragments [L$_{OEt}$Tc(CO)$_2$(PPh$_3$)], [L$_{OEt}$Tc(CO)(PPh$_3$)] and [L$_{OEt}$Tc(PPh$_3$)].

Conclusion

The Tc(I) monohydride complex *trans*-$HTc(CO)_3(PPh_3)_2$ (**1**) is a synthetically useful precursor to a number of Tc(I) carbonyl compounds. In addition to reacting with strong acids like HBF_4, HCl, and triflic acid, treatment of **1** with weaker acids like tropolone and acetylacetone also results in loss of H_2 affording complexes **10** and **11**.

Experimental Section

Caution! Technetium-99 is a weak β^--emitter (E = 0.292 MeV, $t_{1/2}$ = 2.12×10^5 years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[16]

Reagents and solvents were used as received unless otherwise stated. Drybox solvents (toluene, THF, pentane, Et_2O) were distilled from sodium/benzophenone. The complex $HTc(CO)_3(PPh_3)_2$ **1** was prepared as described in Chapter 1. The ligand NaL_{OEt} ($L_{OEt} = \{\eta^5\text{-}CpCo(P(O)(OEt)_2)_3\}$) was prepared according to the method of Kläui.[17] A "bomb" refers to a cylindrical glass vessel sealed with a Kontes high vacuum stopcock. A Mattson Cynus 100 FTIR instrument was used to record all infrared spectra. Only representative IR data is presented. Fast atom bombardment mass spectra (FABMS(+)) were obtained using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV and equipped with a Ion Tech B11N FAB gun. The FAB gun produces a beam of 6-8 keV xenon neutrals. All compounds were run in a matrix of neat 3-nitrobenzyl alcohol. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR were recorded at 300.0 MHz, 75.429 MHz, 19.000 MHz, and 121.421 MHz, respectively on a Unity Varian spectrometer unless otherwise noted. All $^{31}P\{H\}$ NMR are referenced to an external standard of 85% phosphoric acid in $CDCl_3$. The ^{19}F NMR spectrum is referenced to an external standard of $CFCl_3$ in $CDCl_3$. The elemental analyses were performed by Atlantic Microlab, Norcross, GA.[18]

$[Tc(CO)_3(CH_3CN)(PPh_3)_2]BF_4$ (2). To $HTc(CO)_3(PPh_3)_2$ (**1**) (30.4 mg; 0.043 mmol) suspended in 5 mL CH_3CN was added 0.05 mL 85% $HBF_4{\cdot}Et_2O$. After the reaction mixture was stirred for 30 minutes, 25 mL Et_2O and 70 mL pentane were added to the reaction mixture. Storage at 0 °C overnight yielded colorless crystals which were collected by filtration, washed with C_6H_6, Et_2O, and dried *in vacuo*. This cation is spectroscopically identical with that which was synthesized by Kaden *et al.*[19] Yield: (27.7 mg; 65%).

Anal. Calcd. for $C_{41}H_{33}BNO_3F_4P_2Tc$: C, 58.95; H, 3.98; N, 1.68. Found: C, 57.97; H, 4.12; N, 1.67. IR(KBr): ν 2317 (m, C≡N); 2283 (m, C≡N); 2074 (m, C≡O); 1989 (s, C≡O); 1957 (s, C≡O). FABMS(+) *m/z*: 748 $[Tc(CO)_3(MeCN)(PPh_3)_2]^+$; 707 $[Tc(CO)_3(PPh_3)_2]^+$; 678 $[Tc(CO)_2(PPh_3)_2]^+$.

$[Tc(CO)_4(PPh_3)_2]BF_4$ (3). To $HTc(CO)_3(PPh_3)_2$ (**1**) (52.9 mg; 0.075 mmol) dissolved in 25 mL C_6H_6 under positive CO(g) pressure was added 0.30 mL 85% $HBF_4{\cdot}Et_2O$. The reaction mixture was stirred for 15 minutes and then combined with 75 mL Et_2O. After standing overnight at 0 °C, a white solid had precipitated. It was collected on a fritted funnel and washed with 15 mL Et_2O. This compound was crystallized from CH_2Cl_2/pentane to yield colorless crystals which were collected by filtration, washed with C_6H_6, Et_2O, and dried *in vacuo.* Yield: (42.2 mg; 59%).

Anal. Calcd. for $C_{40}H_{30}BF_4O_4P_2Tc$: C, 58.42; H, 3.68. Found: C, 58.00; H, 3.63. IR (KBr): ν 2119 (w, C≡O); 2073 (m, C≡O); 2005 (br, C≡O); 1052 (br, BF_4). ^1H NMR (CD_2Cl_2) δ (ppm): 7.5 (m, br, $P(C_6H_5)_3$). $^{13}C\{H\}$ NMR (CD_2Cl_2, $[Tc(CO)_3(^{13}CO)(PPh_3)_2]BF_4$, 125.697 MHz) δ (ppm): 129.78 (t, $J_{P\text{-}C}$ = 5.3 Hz, $P(C_6H_5)_3$-ortho or meta); 132.99 (s, $P(C_6H_5)_3$-para); 133.21 (partially obscured, $P(C_6H_5)_3$-ipso); 133.96 (t, $J_{P\text{-}C}$ = 6.6 Hz, $P(C_6H_5)_3$-ortho or meta); ~199 (broad hump, ~800 Hz, C≡O). $^{31}P\{H\}$ (CD_2Cl_2) δ (ppm): ~45 (br, ~4050 Hz, flat). FABMS(+) *m/z*: 735 $[Tc(CO)_4(PPh_3)_2]^+$; 707 $[Tc(CO)_3(PPh_3)_2]^+$; 679 $[Tc(CO)_2(PPh_3)_2]^+$.

$TcCl(CO)_3(PPh_3)_2$ (4). To a solution containing $HTc(CO)_3(PPh_3)_2$ (**1**) (111.2 mg; 0.157 mmol) dissolved in 20 mL C_6H_6 was added 1.0 mL $HCl{\cdot}Et_2O$ (1M solution). The reaction mixture was refluxed for 15 min. and then reduced in volume to ~5 mL on a vacuum line. The addition of 50 mL EtOH, followed by storage overnight at 0 °C resulted in the precipitation of a white solid. The solid was collected by filtration, washed with EtOH, Et_2O and dried *in vacuo.* This complex is spectroscopically identical to that which was synthesized by Alberto *et al.*[6] Yield: (63.5 mg, 52%).

Anal. Calcd. for $C_{39}H_{30}ClO_3P_2Tc$: C, 63.05; H, 4.07, Cl, 4.77. Found: C, 62.55; H, 4.39; Cl, 4.36. IR(KBr): ν 2055 (m, C≡O); 1964 (s, C≡O); 1922 (s, C≡O). FABMS(+) *m/z*: 742 $[TcCl(CO)_3(PPh_3)_2]$; 716 $[TcCl(CO)_2(PPh_3)_2]$.

$Tc(CO)_3(\eta^1\text{-}OSO_2CF_3)(PPh_3)_2$ (5). To a solution containing $HTc(CO)_3(PPh_3)_2$ (**1**) (138.8 mg; 0.196 mmol) dissolved in 20 mL C_6H_6 was added 0.10 mL $HOSO_2CF_3$. Addition of the triflic acid resulted in immediate loss of H_2 from **1**. The reaction mixture was stirred for an additional 2 min. and reduced in volume on a vacuum line to ~3 mL. Addition of 100 mL Et_2O caused the rapid precipitation a colorless microcrystalline material which was collected by filtration and dried *in vacuo*. The white solid was redissolved in 5 mL of C_6H_6, filtered through Celite, layered with 50 mL pentane, and stored at 0 °C overnight. The resulting colorless crystals were collected by filtration and dried *in vacuo*. Yield: (108.7 mg; 54%).

Anal. Calcd. for $C_{40}H_{40}O_6F_3P_2STc$: C, 56.09; H, 3.53; S, 3.74. Found: C, 55.55; H, 3.54; S, 3.46. ^1H NMR (C_6D_6) δ (ppm): 7.01 (m, 18H, $P(C_6H_5)$); 7.46 (m, 12 H, $P(C_6H_5)$). ^{19}F NMR (CD_2Cl_2) δ (ppm): 77.2 (s, CF_3). IR(KBr): ν 2080 (m, C≡O); 1965 (s, C≡O); 1922 (s, C≡O); 1324, 1231 (s, η^1-SO_2). FABMS(+) *m/z*: 856 [$Tc(CO)_3(OSO_2CF_3)(PPh_3)_2$]; 707 [$Tc(CO)_3(PPh_3)_2$]; 679 [$Tc(CO)_3(PPh_3)_2$].

$Tc(CO)_2(\eta^2\text{-}O_2CH)(PPh_3)_2$ (6a). To a solution containing 10 mL CH_2Cl_2 and $HTc(CO)_3(PPh_3)_2$ (**1**) (125.6 mg; 0.177 mmol) was added 3 mL formic acid followed by 10 mL 2-propanol. The reaction mixture was refluxed for 20 minutes, reduced in volume to ~3 mL on a vacuum line, and combined with 10 mL 2-propanol. The resulting white precipitate was collected by filtration, washed with 10 mL Et_2O, and dried *in vacuo*. The solid material was extracted into a minimum volume C_6H_6 (~5 mL), filtered through a bed of Celite, and layered with pentane. Storage at 0 °C overnight produced an off-white microcrystalline material which was collected on a fritted disk and dried *in vacuo*. Yield: (68.6 mg; 52%).

Anal. Calcd. for $C_{39}H_{31}O_4P_2Tc$: C, 64.65; H, 4.31. Found: C, 64.20; H, 4.40. IR(KBr): ν 1946 (s, C≡O); 1866 (s, C≡O); 1547, 1434 (OCO). ^1H NMR (CD_2Cl_2) δ (ppm): 6.99 (s, 1H, $O_2C\underline{H}$); 7.48 (m, 30 H, $P(C_6\underline{H}_5)$). $^{13}C\{H\}$ NMR (CD_2Cl_2, $Tc(^{13}CO)_2(\eta^2\text{-}O_2CH)(PPh_3)_2$, 125.697 MHz) δ (ppm): 128.54 (t, $J_{P\text{-}C}$ = 4.5 Hz, $P(C_6H_5)_3$-ortho or meta); 130.40 (s, $P(C_6H_5)_3$-para); 132.95 (t, $J_{P\text{-}C}$ = 20.0 Hz, $P(C_6H_5)_3$-ipso); 134.43 (t, $J_{P\text{-}C}$ = 5.4 Hz, $P(C_6H_5)_3$-ortho or meta); 173.79 (s, η^2-O,O$\underline{C}$H); 204 (br, ~400 Hz, CO). $^{31}P\{H\}$ (CD_2Cl_2) δ (ppm): ~50 (br, flat). FABMS(+) *m/z*: 725 $[Tc(CO)_2(\eta^2\text{-}O_2CH)(PPh_3)_2]$; 679 $[Tc(CO)_2(PPh_3)_2]$.

$Tc(CO)_2(\eta^2\text{-}O_2CCH_3)(PPh_3)_2$ (6b). To a solution containing 10 mL CH_2Cl_2 and $HTc(CO)_3(PPh_3)_2$ **(1)** (87.0 mg; 0.123 mmol) was added 4 mL CH_3COOH followed by 10 mL 2-propanol. The reaction mixture was refluxed for 20 minutes. Reducing the volume of the reaction mixture to ~3 mL on a vacuum line yielded a colorless microcrystalline material which was collected by filtration, washed with 10 mL Et_2O, and dried *in vacuo*. The complex was recrystallized as described for **6a**. Yield: (56.7 mg; 63%).

Anal. Calcd. for $C_{40}H_{33}O_4P_2Tc$: C, 65.05; H, 4.50. Found: C, 64.69; H, 4.62. IR(KBr): ν 1937 (s, C≡O); 1864 (s, C≡O); 1518, 1464 (OCO). ^1H NMR (CD_2Cl_2) δ (ppm): 0.51 (s, 3H, $O_2CC\underline{H}_3$); 7.43 (m, 30 H, $P(C_6H_5)$). $^{13}C\{^1H\}$ (CD_2Cl_2) δ (ppm): 22.54 (s, η^2-O,OC$\underline{C}H_3$); 128.49 (t, $J_{P\text{-}C}$ = 4.5 Hz, $P(C_6H_5)_3$-ortho or meta); 130.19 (s, $P(C_6H_5)_3$-para); 132.89 (t, $J_{P\text{-}C}$ = 19.2 Hz, $P(C_6H_5)_3$-ipso); 134.40 (t, $J_{P\text{-}C}$ = 6.4 Hz, $P(C_6H_5)_3$-ortho or meta); 206.5 (s, η^2-O,O$\underline{C}CH_3$). $^{31}P\{H\}$ (CD_2Cl_2) δ (ppm): ~47 (br, flat).

$Tc(CO)_2(trop)(PPh_3)_2$ (7). In the drybox a bomb was charged with $HTc(CO)_3(PPh_3)_2$ (**1**) (90.6 mg; 0.128 mmol), tropolone (781 mg; 6.40 mmol), and 10 mL toluene. The reaction mixture was heated at 45 °C for 24 h. and then taken back into the drybox. The yellow solution was filtered through a bed of Celite and reduced to dryness under vacuum. The residue was suspended in 5 mL Et_2O and stirred overnight. The bright yellow solid which formed was filtered onto a fritted disk, washed with Et_2O, and dried *in vacuo.* Yield: (38.7 mg; 33%).

Anal. Calcd. for $C_{45}H_{35}O_4P_2Tc$: C, 67.51; H, 4.41. Found: C, 67.01; H, 4.35. IR(KBr): ν 1923 (C≡O); 1846 (br, C≡O); 1365 (s, C=O). ^1H NMR (C_6D_6) δ (ppm): 5.88 (d, 1H, $C_7\underline{H}_5$, J = 9.15 Hz); 6.41 (d, 2H, $C_7\underline{H}_5$, J = 10.8 Hz); 6.50 (t, 2H, $C_7\underline{H}_5$, J = 9.9 Hz); 7.15 (m, 12 H, $P(C_6\underline{H}_5)$); 7.70 (m, 18 H, $P(C_6\underline{H}_5)$). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ (ppm): 122.97 (s, trop); 125.50 (s, trop); 128.28 (t, $J_{P\text{-}C}$ = 4.5 Hz, $P(C_6H_5)_3$-ortho or meta; 129.87 (s, $P(C_6H_5)_3$-para); 133.41 (t, $J_{P\text{-}C}$ = 18.4 Hz, $P(C_6H_5)_3$-ipso); 134.56 (t, $J_{P\text{-}C}$ = 6.0 Hz, $P(C_6H_5)_3$-ortho or meta); 135.83 (s, trop); 182.96 (s, trop). $^{31}P\{H\}$ (CD_2Cl_2) δ (ppm): ~41 (br, flat). FABMS(+) *m/z*: 800 $[Tc(CO)_2(trop)(PPh_3)_2]$; 772 $[Tc(CO)(trop)(PPh_3)_2]$.

$Tc(CO)_2(acac)(PPh_3)_2$ (8). In the drybox a bomb was charged with $HTc(CO)_3(PPh_3)_2$ (**1**) (104.4 mg; 0.147 mmol), acetylacetone (0.76 mL; 7.26×10^{-3} mol), and 5 mL toluene. The reaction mixture was heated at 40 °C for 18 h. and then brought back into the drybox. The solution was filtered through Celite and evaporated to dryness under vacuum. The resulting white solid was redissolved in 5 mL CH_2Cl_2, layered with 10 mL pentane and stored at -40

°C overnight. The pink microcrystalline material which formed was collected by filtration, washed with pentane, and dried *in vacuo*. Yield: (65.1 mg, 52%).

Anal. Calcd. for $C_{43}H_{37}O_4P_2Tc$: C, 66.33; H, 4.79. Found: C, 65.89; H, 4.77. IR(KBr): ν 1929 (C≡O); 1850 (br, C≡O); 1580 (s, C=O). ^1H NMR (C_6D_6) δ (ppm): 1.30 (s, 6 H, $C\underline{H}_3$); 4.25 (s, 1H, $OC(CH_3)C\underline{H}C(CH_3)O$); 7.14 (m, 18 H, $P(C_6\underline{H}_5)$); 7.83 (m, 12 H, $P(C_6\underline{H}_5)$). FABMS(+) *m/z*: 778 $[Tc(CO)_2(acac)(PPh_3)_2]$; 750 $[Tc(CO)(acac)(PPh_3)_2]$.

X-Ray Crystal Structure Determination of $Tc(CO)_2(acac)(PPh_3)_2$ (8). Pale pink parallelepiped crystals were grown by slow vapor diffusion of pentane into a CH_2Cl_2 solution of **8** at 0 °C. Complex **8** crystallizes with a CH_2Cl_2 solvate molecule. A suitable crystal was selected and then transferred to an Rigaku AFC6R diffractometer with graphite monochromated Mo-Kα radiation and a 12W rotating anode. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $11.84 < 2\theta < 14.61$ °, corresponding to a monoclinic cell. Based on the systematic absences of h0l: $l \neq 2n$ and 0k0: $k \neq 2n$, the space group was determined to be $P2_1/c$. The final cell parameters are given in **Table I**.

The data was collected at a temperature of 23±1 °C using the ω–2θ scan technique to a maximum 2θ value of 45.0 °C. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a take-off angle of 6.0°. Scans of $(1.05 + 0.35 \tan\theta)°$ were made at a speed of 16.0°/min (in omega). The weak reflections ($I < 6.0\ \sigma(I)$) were rescanned (maximum of 8 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 310.0 mm.

Of the 5625 reflections which were collected, 5244 were unique (R_{int} = 0.117); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption absorption coefficient for Mo $K\alpha$ is 5.8 cm^{-1}. An empirical absorption correction, using the program DIFABS, was applied which resulted in transmission factors ranging from 0.90 to 1.20. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods. The non-hydrogen atoms were refined either isotropically or anisotropically. The final cycle of full-matrix least-squares refinement was based on 3359 observed reflections ($I>3.00\sigma(I)$) and 479 variable parameters and converged (largest parameter shift was 0.33 times its esd) with R = 0.054; R_w = 0.067. The standard deviation of an observation of unit weight was 2.24. The weighing scheme was based on counting statistics and included a factor (p = 0.03) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.66 and -0.78$e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber. Anomalous dispersion effects were included in F_{calc} [20]; the values for Df' and

Df" were those Cromer.[21] All calculations were performed using TEXSAN crystallographic software package of Molecular Structure Corporation.

$Tc(CO)_2(\eta^2$-3-hydroxysalicylaldehyde)$(PPh_3)_2$ (9a). In the drybox $HTc(CO)_3(PPh_3)_2$ (**1**) (51.4 mg; 0.073 mmol) was added to a flask containing 5 mL toluene and 3-hydroxysalicylaldehyde (30 mg; 0.219 mmol). The reaction mixture was stirred overnight. The yellow solution was then filtered through Celite and evaporated to dryness. The residue was suspended in 5 mL Et_2O and stirred for 30 minutes. The yellow solid was collected by filtration and dried *in vacuo*. Yield: (44.8 mg; 66%).

Anal. Calcd. for $C_{45}H_{35}O_5P_2Tc$: C, 66.19; H, 4.32. Found: C, 65.57; H, 4.18. IR(KBr): ν 3395 (OH); 1932 (s, C≡O); 1888 (s, C≡O); 1608 (s, C=O). ^{1}H NMR (C_6D_6) δ (ppm): 5.76 (d, 1 H, $J_{H\text{-}H}$ = 3.6 Hz; $C_6\underline{H}_3$); 5.91 (t, 1 H, $J_{H\text{-}H}$ = 6.2 Hz, $C_6\underline{H}_3$); 6.56 (s, 1 H, O$\underline{H}$); 6.68 (d, 1 H, $J_{H\text{-}H}$ = 3.8 Hz; $C_6\underline{H}_3$); 6.95 (m, 18 H, $P(C_6\underline{H}_5)_3$); 7.72 (m, 12 H, $P(C_6\underline{H}_5)_3$); 7.95 (s, 1 H, C$\underline{H}$O). ^{13}C NMR (CD_2Cl_2) δ (ppm): 191 (d, $J_{C\text{-}H}$ = 168 Hz, $\underline{C}$(O)H). ^{13}C{H} NMR (CD_2Cl_2) δ (ppm): 113.87 (s, $\underline{C}_6H_3$); 116.09 (s, $\underline{C}_6H_3$); 126.43 (s, $\underline{C}_6H_3$); 129.36 (t, $J_{P\text{-}C}$ = 6.1 Hz, $P(C_6H_5)_3$-ortho or meta); 131.02 (s, $\underline{C}_6H_3$); $P(C_6H_5)_3$-para); 134.34 (t, $J_{H\text{-}H}$ = 18.4 Hz, $P(C_6H_5)_3$-ipso); 135.24 (t, $J_{P\text{-}C}$ = 5.4 Hz, $P(C_6H_5)_3$-ortho or meta); 150.97 (s, C-OH); 160.44 (s, C-OH); 192.27 (s, $\underline{C}$(O)H). FABMS(+) *m/z*: 816 [$Tc(CO)_2(\eta^2$-(3-hydroxysalicylaldehyde)$(PPh_3)_2$]; 788 [$Tc(CO)(\eta^2$-(3-hydroxysalicylaldehyde)$(PPh_3)_2$].

$Tc(CO)_2(\eta^2$-salicylaldehyde)$(PPh_3)_2$ (9b). This complex was prepared using the same method as described above with the substitution of salicylaldehyde for 3-hydroxysalicylaldehyde. Yield: (36.2 mg; 51%).

Anal. Calcd. for $C_{45}H_{35}O_4P_2Tc$: C, 67.51; H, 4.41. Found: C, 66.98; H, 4.38. IR(KBr): ν 1931 (s, C≡O); 1849 (s, C≡O); 1609 (s, C=O). ^1H NMR (C_6D_6) δ (ppm): 5.89 (t, 1 H, J_{H-H} = 7.5 Hz; $C_6\underline{H}_4$); 6.03 (d, 1 H, J_{H-H} = 6.3 Hz; $C_6\underline{H}_4$); 6.63 (d, 1 H, J_{H-H} = 8.4 Hz; $C_6\underline{H}_4$); 6.82 (t, 1 H, J_{H-H} = 6.6 Hz; $C_6\underline{H}_4$); 6.95 (m, 18 H, $P(C_6\underline{H}_5)_3$); 7.78 (m, 12 H, $P(C_6\underline{H}_5)_3$); 7.91 (s, C(O)$\underline{H}$). FABMS(+) *m/z*: 800 [$Tc(CO)_2(\eta^2$-salicylaldehyde)$(PPh_3)_2$]; 772 [$Tc(CO)(\eta^2$-salicylaldehyde)$(PPh_3)_2$].

$(\eta^5$-Cp)$Tc(CO)_2(PPh_3)$ (10). In the drybox, a Schlenk flask was charged with $Tc(CO)_3Cl(PPh_3)_2$ (**4**) (128.4 mg; 0.173 mmol), NaCp (0.11 mL as a 2M THF solution, 0.225 mmol) and THF (20 mL). The flask was removed from the box and allowed to stir at 50 °C for 30 h. under N_2. The solution was filtered in the air through a bed of Celite and then evaporated to dryness on a vacuum line. The off-white residue was extracted into 50 mL Et_2O, filtered again through a bed of Celite and reduced in volume to ~3 mL on a vacuum line. Addition of 10 mL EtOH caused the precipitation of an off-white solid which was collected by filtration and dried *in vacuo*. Recrystallization was effected by the slow-evaporation of Et_2O solutions of **10** at 0 °C. Yield: (29.2 mg; 54%).

Anal. Calcd. for $C_{25}H_{20}O_2PTc$: C, 62.26; H, 4.18. Found: C, 61.66; H, 4.18. IR(KBr): ν 1937 (s, C≡O); 1868 (s, C≡O). ^1H NMR (C_6D_6) δ (ppm): 4.57 (s, 5 H, η^5-Cp); 6.99 (m, 9 H, $P(C_6\underline{H}_5)_3$); 7.55 (m, 6 H, $P(C_6\underline{H}_5)_3$). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ (ppm) (125.697 MHz): 138.4 (d, J_{P-C} = 45.0 Hz, $P(C_6H_5)_3$-ipso); 133.3 (d, J_{P-C} = 11.4 Hz, $P(C_6H_5)_3$-ortho or meta); 129.9 (s, $P(C_6H_5)_3$-para); 128.4 (d, J_{P-C} = 9.9

Hz, $P(C_6H_5)_3$-ortho or meta); 86.3 (s, η^5-Cp). FABMS(+) *m/z*: 482 $[CpTc(CO)_2(PPh_3)]$; 454 $[CpTc(CO)(PPh_3)]$; 426 $[CpTc(PPh_3)]$.

$L_{OEt}Tc(CO)_2(PPh_3)$ (11). In the drybox, a Schlenk flask was charged with $Tc(CO)_3Cl(PPh_3)_2$ (**4**) (118.4 mg; 0.173 mmol), NaL_{OEt} (98.1 mg; 0.176 mmol) and 20 mL toluene. The flask was removed from the drybox and heated at 65 °C for 7 h. under N_2. The bright yellow solution was filtered in the air through a bed of Celite and then evaporated to dryness on a vacuum line. The resulting pale yellow residue was combined with 10 mL EtOH, collected on a fritted disk, and dried *in vacuo*. (Yield: 57.7 mg; 30%).

Anal. Calcd. for $C_{37}H_{50}CoO_{11}P_4Tc$: C, 46.66; H, 5.29%. Found: C, 46.06; H, 5.33. IR(KBr): ν 1921 (s, C≡O); 1825 (s, C≡O). ^1H NMR (C_6D_6) δ (ppm): 0.88 (t, 6 H, J = 6.6 Hz, $OCH_2C\underline{H}_3$); 1.27 (t, 6 H, J = 7.5 Hz, $OCH_2C\underline{H}_3$); 1.34 (t, 6 H, J = 7.5 Hz, $OC\underline{H}_2CH_3$); 3.45 (m, 4 H, $OC\underline{H}_2CH_3$); 4.29 (m, 8H, $OC\underline{H}_2CH_3$); 4.88 (s, 5 H, η^5-Cp); 7.15 (m, 9 H, $P(C_6\underline{H}_5)$); 7.92 (m, 6H, $P(C_6\underline{H}_5)$). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ (ppm) (125.697 MHz): 137.2 (d, J_{P-C} = 41.9 Hz, $P(C_6H_5)_3$-ipso); 134.5 (d, J_{P-C} = 10.7 Hz, $P(C_6H_5)_3$-ortho or meta); 129.3 (s, $P(C_6H_5)_3$-para); 127.8 (d, J_{P-C} = 9.2 Hz, $P(C_6H_5)_3$-ortho or meta); 89.3 (s, Cp); 61.05 (s, $O\underline{C}H_2CH_3$); 60.71 (s, $O\underline{C}H_2CH_3$); 60.13 (s, $O\underline{C}H_2CH_3$); 17.0 (s, $OCH_2\underline{C}H_3$); 16.9 (s, $OCH_2\underline{C}H_3$); 16.3 (s, $OCH_2\underline{C}H_3$). FABMS(+) *m/z*: 952 $[L_{OEt}Tc(CO)_2(PPh_3)]$; 924 $[L_{OEt}Tc(CO)(PPh_3)]$; 896 $[L_{OEt}Tc(PPh_3)]$.

Table 1. Crystal and Data Collection Parameters for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**).

Empirical Formula: $C_{43}H_{50}O_3P_2Cl_2Tc$

Crystal Parameters

a = 9.726(3) Å

b = 20.873(5) Å

c = 20.330(3) Å

β = 96.25(2)°

V = 4103(2) $Å^3$

T = 23 °C

Space Group: $P2_1/c$

Formula Weight = 844.72 amu

$Z = 4$

D_{calc} = 1.367 g/cm^3

μ_{calc} = 5.80 cm^{-1}

Size = 0.250 x 0.220 x 0.140 mm

Data Measurements Parameters

Diffractometer: Rigaku AFC6R

Radiation: MoKα (λ = 0.71069 Å)

Scan Type: ω - 2Θ

Scan Rate: 16.0 °/min (in omega) (8 rescans)

Scan Width: (1.05 + 0.35 tanΘ)°

$2\Theta_{max}$: 45.0°

No. of Reflections: Total = 5625 Unique = 5244 (R_{int} = 0.117)

Corrections: Lorentz Polarization Absorption (trans. factors: 0.90 - 1.20)

Structure Solution and Refinement

Structure Solution: Direct Methods

Refinement: Full-matrix least-squares

Function Minimized: $\Sigma w (|F_o| - |F_c|)^2$

Least Squares Weight: $4F_o^2/\sigma^2(F_o^2)$

p-factor: 0.03

No. Observations ($I>3.00\ \sigma(I)$): 3359

No. Variables: 479

Residuals: $R = 0.054$; $R_w = 0.067$

Goodness of Fit: 1.90

Max. Shift/Error in Final Cycle: 0.42

Max. Peak in Diff. Map: 0.66 $e^-/Å^3$

Min. Peak in Diff. Map: -0.78$e^-/Å^3$

Table II. Selected Intramolecular Distances for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**).

Atom 1	Atom 2	Distance (Å)
Tc	P(1)	2.439(3)
Tc	P(2)	2.458(3)
Tc	O(1)	2.152(7)
Tc	O(2)	2.135(7)
Tc	C(4)	1.84(1)
Tc	C(5)	1.87(1)
C(4)	O(3)	1.18(1)
C(5)	O(4)	1.16(1)
O(1)	C(3)	1.27(1)
O(2)	C(1)	1.28(1)
C(1)	C(2)	1.41(2)
C(1)	C(43)	1.57(2)
C(3)	C(2)	1.40(2)
C(3)	C(42)	1.54(2)

Table III. Selected Intramolecular Bond Angles for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**).

Atom 1	Atom 2	Atom 3	Angles(°)
P(1)	Tc	P(2)	178.2(1)
P(1)	Tc	O(1)	89.0(2)
P(1)	Tc	O(2)	89.2(2)
P(1)	Tc	C(4)	88.6(3)
P(1)	Tc	C(5)	89.6(4)
P(2)	Tc	O(1)	89.2(2)
P(2)	Tc	O(2)	90.5(2)
P(2)	Tc	C(4)	91.7(3)
P(2)	Tc	C(5)	89.6(4)
O(1)	Tc	O(2)	84.9(3)
O(1)	Tc	C(4)	93.8(4)
O(1)	Tc	C(5)	177.1(4)
O(2)	Tc	C(4)	177.5(4)
O(2)	Tc	C(5)	92.5(4)
C(4)	Tc	C(5)	88.8(5)

Table IV. Positional Parameters and Standard Deviations (Å^2) for $Tc(CO)_2(acac)(PPh_3)_2$ (**8**).

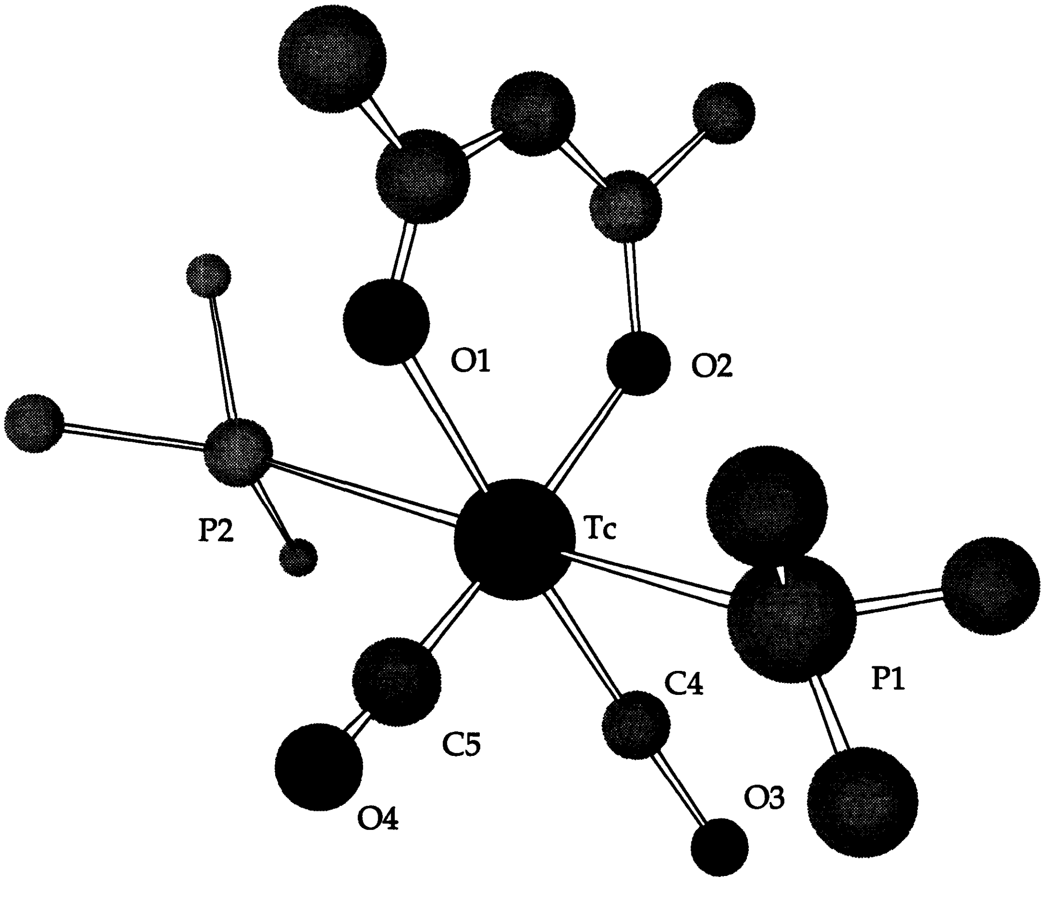
atom	x	y	z	B(eq)
Tc	0.28952(8)	0.22721(4)	0.19956(4)	2.46(4)
P(1)	0.4176(3)	0.3244(1)	0.2331(1)	2.7(1)
P(2)	0.1589(2)	0.1288(1)	0.1692(1)	2.7(1)
O(1)	0.2249(6)	0.2208(3)	0.2970(3)	3.5(3)
O(2)	0.4632(6)	0.1719(3)	0.2392(3)	3.5(3)
O(3)	0.0494(7)	0.3132(4)	0.1474(4)	5.4(4)
O(4)	0.3868(8)	0.2277(4)	0.0623(4)	5.4(4)
C(1)	0.496(1)	0.1581(5)	0.2992(6)	4.3(6)
C(2)	0.418(1)	0.1677(6)	0.3522(5)	4.8(6)
C(3)	0.290(1)	0.1954(5)	0.3474(6)	4.1(6)
C(4)	0.142(1)	0.2794(5)	0.1681(5)	3.0(5)
C(5)	0.349(1)	0.2268(5)	0.1148(5)	3.4(5)
C(6)	0.344(1)	0.3648(4)	0.3013(5)	2.8(5)

C(7)	0.247(1)	0.4138(5)	0.2871(5)	4.5(6)
C(8)	0.178(1)	0.4390(6)	0.3384(6)	5.3(7)
C(9)	0.203(1)	0.4173(7)	0.4017(7)	5.7(7)
C(10)	0.300(1)	0.3714(6)	0.4159(5)	4.8(6)
C(11)	0.369(1)	0.3435(5)	0.3659(5)	3.9(5)
C(12)	0.241(1)	0.0701(5)	0.1200(4)	3.1(5)
C(13)	0.383(1)	0.0633(5)	0.1284(5)	4.0(6)
C(14)	0.445(1)	0.0134(6)	0.0961(6)	4.7(6)
C(15)	0.366(1)	-0.0270(5)	0.0541(5)	4.7(6)
C(16)	0.226(1)	-0.0201(5)	0.0458(5)	4.2(6)
C(17)	0.164(1)	0.0265(5)	0.0787(5)	3.6(5)
C(18)	0.6028(9)	0.3148(5)	0.2608(4)	2.8(5)
C(19)	0.673(1)	0.3491(5)	0.3137(5)	3.5(5)
C(20)	0.525(1)	0.4880(6)	0.1387(7)	6.5(8)
C(21)	0.888(1)	0.3031(6)	0.2904(6)	4.7(6)
C(22)	0.821(1)	0.2703(5)	0.2378(6)	4.5(6)
C(23)	0.678(1)	0.2768(4)	0.2233(5)	3.4(5)

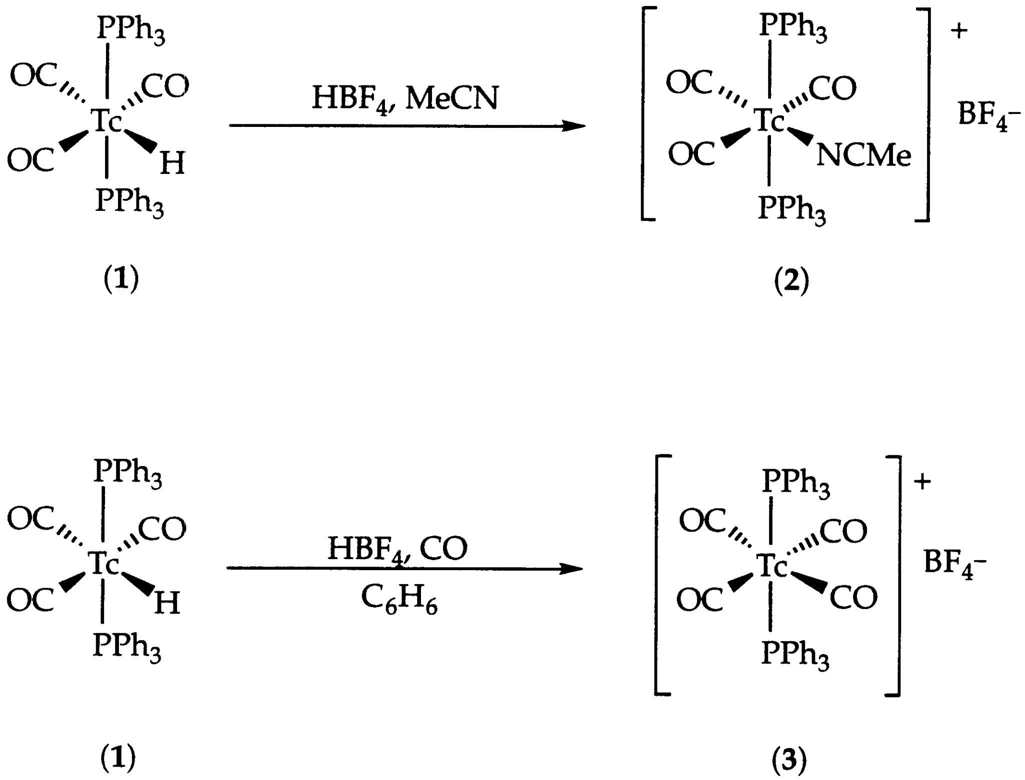
C(24)	0.816(1)	0.3418(76)	0.3289(5)	4.6(6)
C(25)	-0.002(1)	0.1437(5)	0.1155(5)	3.2(5)
C(26)	-0.131(1)	0.1280(5)	0.1325(5)	3.9(6)
C(27)	-0.251(1)	0.1458(6)	0.0911(7)	5.6(7)
C(28)	-0.237(2)	0.1785(6)	0.0331(7)	6.0(8)
C(29)	-0.109(1)	0.1941(6)	0.0156(6)	5.7(7)
C(30)	0.006(1)	0.1772(5)	0.0571(6)	4.3(6)
C(31)	0.1055(1)	0.0789(4)	0.2359(4)	2.7(5)
C(32)	0.139(1)	0.0156(5)	0.2424(5)	4.1(6)
C(33)	0.096(1)	-0.0228(5)	0.2935(6)	4.9(6)
C(34)	0.015(1)	0.0049(7)	0.3372(6)	5.8(7)
C(35)	-0.017(1)	0.0685(6)	0.3324(6)	4.7(7)
C(36)	0.027(1)	0.1069(5)	0.2822(5)	4.2(6)
C(37)	0.425(1)	0.3890(5)	0.1712(5)	3.2(5)
C(38)	0.335(1)	0.3901(6)	0.1126(6)	4.9(6)
C(39)	0.342(2)	0.4400(6)	0.0687(6)	5.8(7)
C(40)	0.436(2)	0.4882(6)	0.0803(7)	6.1(8)

C(41)	0.519(1)	0.4396(5)	0.1850(6)	5.3(6)
C(42)	0.215(1)	0.1959(6)	0.4094(6)	6.3(7)
C(43)	0.642(1)	0.1285(7)	0.3133(7)	7.4(8)
Cl(1)	0.6361(4)	0.1597(2)	0.5212(2)	10.6(3)
Cl(2)	0.8938(6)	0.0985(3)	0.5051(2)	14.4(4)
C(44)	0.787(2)	0.130(1)	0.5578(6)	10(1)

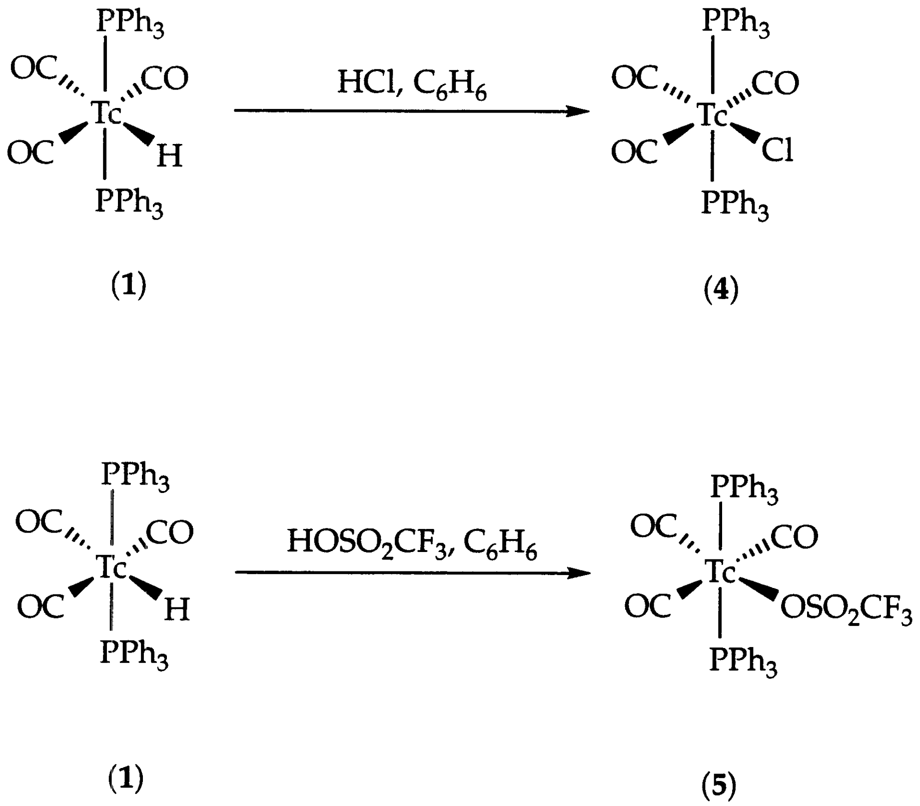
Figure 1. Chem 3D representation of **8**. The CH_2Cl_2 molecule of solvation and the phenyl rings of the PPh_3 ligands were omitted for the sake of clarity.



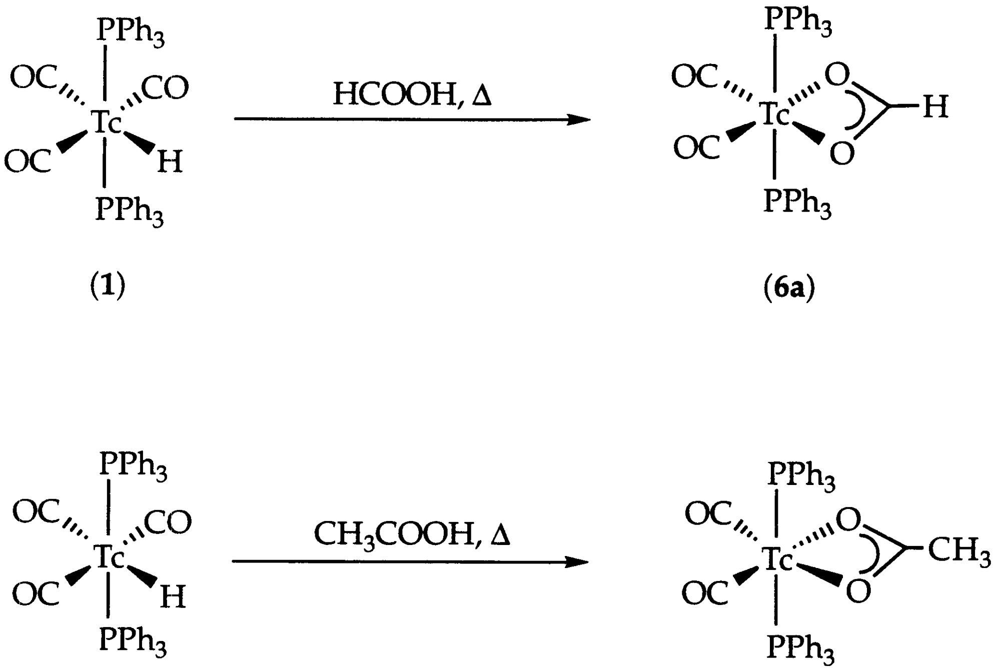
Scheme I


PPh₃
OC
CO
Tc
OC
H
PPh₃
HBF₄, MeCN
PPh₃
OC
CO
Tc
OC
NCMe
PPh₃
+
BF₄⁻
(1)
(2)
PPh₃
OC
CO
Tc
OC
H
PPh₃
HBF₄, CO
C₆H₆
PPh₃
OC
CO
Tc
OC
CO
PPh₃
+
BF₄⁻
(1)
(3)

Scheme II


PPh3
OC
CO
Tc
OC
H
PPh3
HCl, C6H6
PPh3
OC
CO
Tc
OC
Cl
PPh3
(1)
(4)
PPh3
OC
CO
Tc
OC
H
PPh3
HOSO2CF3, C6H6
PPh3
OC
CO
Tc
OC
OSO2CF3
PPh3
(1)
(5)

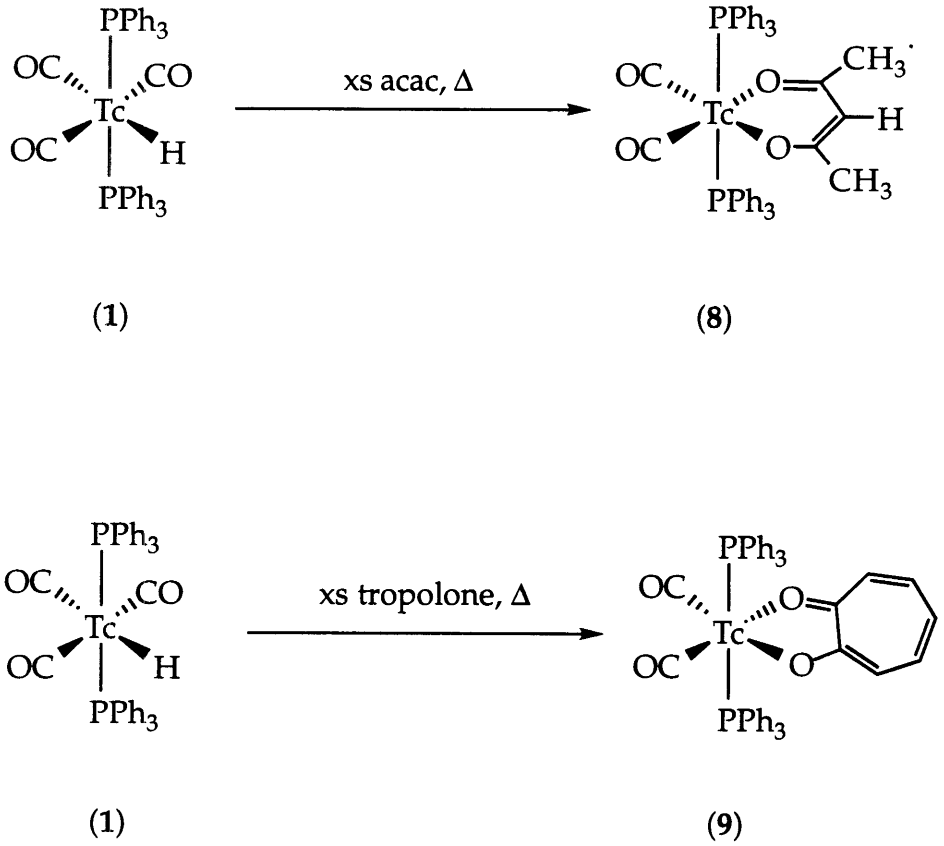
Scheme III



(**1**) (**6a**)

(**1**) (**6b**)

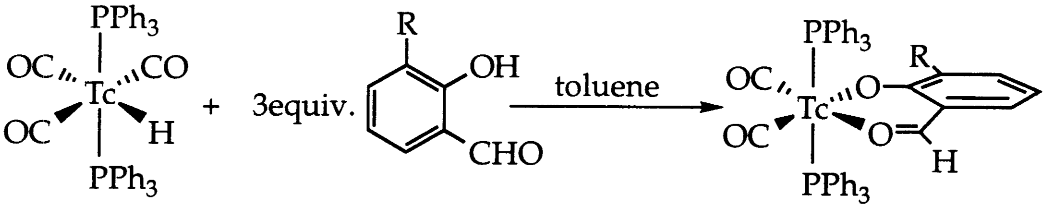
Scheme IV



(1) (8)

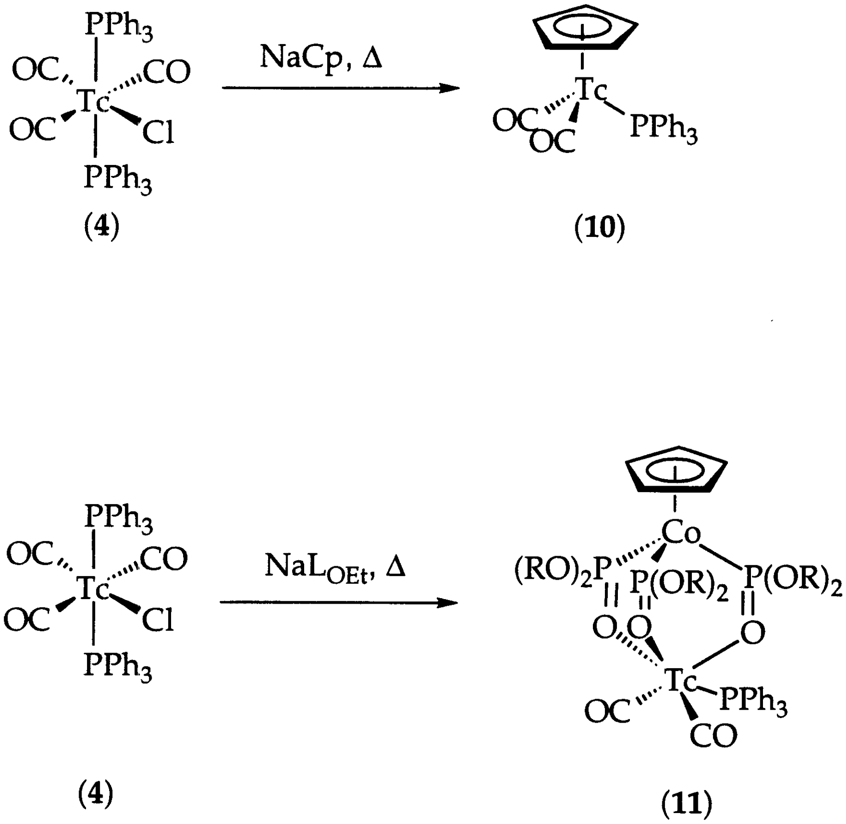
(1) (9)

Scheme V



R = OH (**9a**)
H (**9b**)

Scheme VI



(4) (10)

(4) (11)

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(18) It has been found by workers in our laboratory that analytical analyses of Tc complexes can be up to 1 carbon low. This may be due to incomplete combustion which leads to the formation of TcC. The best analytical data obtained for the reported complexes is presented. deVries, N.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989,** *19,* 3728.

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Chapter 5

Nucleophilic Attack on Coordinated Carbon Monoxide In the Cation $[Tc(CO)_4(PPh_3)_2]BF_4$

Introduction

Transition metal nucleophile-carbonyl adducts have received considerable attention because they have been shown to be intermediates in many important processes including the water-gas shift reaction, hydroformylation, the carboalkoxylation of olefins, and the carbonylation of alcohols.[1,2] For the Group VII metals Mn and Re, a wide variety acyl,[3,4] formyl,[5,6] hydroxycarbonyl,[7] and alkoxycarbonyl[8] complexes have been synthesized and characterized. Similar chemistry with Tc however has not yet been explored.

We have recently reported a simple synthesis of the cation *trans*-$[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) from the neutral Tc(I) monohydride complex $HTc(CO)_3(PPh_3)_2$.[9] The carbonyl ligands in **1** are susceptible to attack by a variety of nucleophiles. Herein we wish to report the synthesis and characterization of a number of neutral Tc(I) nucleophile-carbonyl adducts.

Results and Discussion

Treatment of *trans*-$[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) with 1 equiv. $LiBEt_3H$ gives the pale yellow Tc(I) formyl, $Tc(CO)_3(C(O)H)(PPh_3)_2$ (**2**) in 76% yield. Complex **4** is stable as a solid under inert atmosphere, however it is unstable in solution. Benzene solutions of **2** show slight decomposition to the monohydride complex $HTc(CO)_3(PPh_3)_2$[10] after 12 h. at room temperature. This reaction has been observed for several other Group VII formyl complexes.[5]

As is characteristic of an η^1-formyl ligand,[5] the carbonyl stretching frequency of the formyl group is observed at 1581 cm^{-1} in the IR spectrum of **2**. The meridional arrangement of CO ligands is supported by the presence of two strong peaks at 1951 and 1858 cm^{-1} and one higher energy peak of lower intensity at 2035 cm^{-1}.[11] In the ^1H NMR spectrum of **2** the resonance for the formyl hydrogen atom occurs at δ 14.88. The formyl carbon atom resonance is observed as a broadened doublet at δ 279 (J_{C-H} = 105 Hz) in the proton-coupled ^{13}C NMR spectrum of **2**. The broadening of this peak is believed to be caused by coupling between the quadrapolar ^{99}Tc nucleus (I = 9/2) and the carbon nuclei. This effect is commonly observed in the $^{31}P\{H\}$ NMR and $^{13}C\{H\}$ NMR spectra of ^{99}Tc complexes where the phosphorus or carbon nuclei are bound directly to the metal center.[10,12]

Addition of 1 equiv. $CH_3SO_3CF_3$ to a toluene solution of **2** gives the Fischer carbene $[Tc(CO)_3(=C(OMe)H)(PPh_3)_2]SO_3CF_3$ (**3**). Technetium complexes containing a Tc=C bond are rare. The only two examples in the literature are the recently reported vinylidene complex, $Tc(=C=CHR)Cl(dppe)_2$[13] (where R = Ph, Me, ^tBu; dppe = bis(diphenylphosphinoethane) and the dimeric complex $(CO)_9Tc_2C(OCH_3)R$[14] (where R = CH_3, C_6H_5). The resonance for the carbene hydrogen atom is observed in the ^1H NMR spectrum of **3** as a singlet at δ 11.8. The $^{13}C\{H\}$ NMR spectrum shows the signal for the carbene carbon atom as a broad singlet at δ 323. The carbonyl ligands are also broad peaks occurring at δ 203 (*cis*) and 207 (*trans*).

The reaction of $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) with excess sodium hydroxide in MeCN leads to the rapid precipitation of the hydroxycarbonyl complex $Tc(CO)_3(C(O)OH)(PPh_3)_2$ (**4**). This precipitate appears to contain only pure $Tc(CO)_3(C(O)OH)(PPh_3)_2$ (**4**). In KBr, the IR spectrum of the precipitate shows ν(C=O) at 1566 cm^{-1} and ν(C≡O) at 2052 (m), 1954 (s) and 1936 (s). No stretches corresponding to $HTc(CO)_3(PPh_3)_2$[10] were observed. Although an OH stretch could not be assigned in the IR spectrum of **4**, the OH proton was observed in the ^{1}H NMR(DMSO) spectrum as a singlet at δ 9.89. In addition to the singlet at δ 9.89 the ^{1}H NMR spectrum of **4** shows a triplet at δ -4.25 ($J_{P\text{-}H}$ = 19.7 Hz) which corresponds to the monohydride $HTc(CO)_3(PPh_3)_2$.[10] The decarboxylation of **4** in DMSO solution to give $HTc(CO)_3(PPh_3)_2$ occurs readily at room temperature to cleanly form the hydride after 6 h. Decarboxylation of the deuterium analog $Tc(CO)_3(C(O)OD)(PPh_3)_2$ has proved to be convenient method of preparation for the deuteride complex $DTc(CO)_3(PPh_3)_2$.[10]

The reaction of **1** with NaOH in alcohol solvents gives the corresponding ester complexes $Tc(CO)_3(C(O)OR)(PPh_3)_2$ (R = Me **5**; Et **6**) in 84% and 59% yield. Base is necessary for the formation of **5** and **6**, since these complexes are not formed when $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) is dissolved in alcohols.

The method employed for the preparation of complexes **5** and **6** could not be extended to arylalcohols. The analogous aryloxycarbonyl complex $Tc(CO)_3(C(O)OC_6H_4CH_3)(PPh_3)_2$ (**7**) was prepared in 35% yield by treatment of **1** with the nucleophile $K[OC_6H_4CH_3]$ in THF.

The observed IR, ^{1}H NMR, and $^{13}C\{H\}$ NMR data for complexes **5-7** are consistent with the formation of alkoxycarbonyl complexes.[2,6-8] The IR spectra of these complexes show ν(C=O) within the expected range 1580-1703.[2] Also the ^{13}C chemical shifts of the η^1-C(O)OR central carbon atom fall within the δ 158-215 range observed for other η^1-alkoxycarbonyl adducts.[2] The molecular ions for complexes **5-7** were not observed in the FAB(+) mass spectra of the complexes. In all spectra the major peak observed corresponds to the tetracarbonyl fragment, $[Tc(CO)_4(PPh_3)_2]$.

Several Re hydroxycarbonyl and alkoxycarbonyl complexes of the type $Re(CO)_3(LL)(C(O)OR)$ (where LL = 1,2-bis(diphenylphosphinoethane), 1,3-bis(diphenylphosphinopropane; R = H, D, Me, Et) have been synthesized and characterized.[7] These complexes exhibit behavior similar to that observed for the Tc complexes **4-7**. For example both the methyl and ethyl alkoxycarbonyl complexes are prepared readily from solutions of the hydroxycarbonyls and methanol or ethanol. These alkoxycarbonyl complexes are easily transesterified. Both $Re(CO)_3(dppe)(C(O)OMe)$ and complex **5** react with EtOH to give the corresponding ethyl ester complexes. The decarboxylation of the hydroxycarbonyl complex $Tc(CO)_3(C(O)OH)(PPh_3)$ (**4**) is much faster than is observed for the similar complex $Re(CO)_3(C(O)OH)(dppe)$ (where dppe = bis(diphenylphosphinoethane)).[7] This is not surprising since transition metal complexes of second row metals are known to be less robust than their third row congeners.

Reaction of **1** with NaN_3 gives the isocyanate complex $Tc(CO)_3(NCO)(PPh_3)_2$ (**8**) in 66% yield. As shown in Scheme III, this reaction is believed to occur *via* an acyl-azide intermediate which quickly loses N_2.[8,15] The intermediate nitrene undergoes a Curtius-like rearrangement to form the observed product. No evidence for the formation of an azide complex was observed. The IR spectrum of **8** gives two strong $\nu(C\equiv O)$ stretches at 2056 and 1957 cm^{-1} and one very strong peak at 2239 cm^{-1} for $\nu(NCO)$. The FAB(+) mass spectrum shows a peak at 750 *m/z* corresponding to the molecular ion $[Tc(CO)_3(NCO)(PPh_3)_2]$.

Conclusions

From the Tc(I) cation $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) we have synthesized and characterized several new Tc formyl and alkoxycarbonyl adducts. The rich chemistry of these complexes as precursors in preparative organometallic chemistry will be investigated in the future.

Experimental Section

Caution! Technetium-99 is a weak β^--emitter (E = 0.292 MeV, $t_{1/2}$ = 2.12×10^5 years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[16]

All reactions were carried out under an atmosphere of N_2(g). Reagents and solvents were used as received unless otherwise stated. Drybox solvents (toluene, THF, pentane, Et_2O) were distilled from sodium/benzophenone. The complex $[Tc(CO)_4(PPh_3)_2]BF_4$ was prepared as described by Cook *et al.*[9] A Mattson Cynus 100 FTIR instrument was used to record all infrared spectra. Only representative IR data is presented. Fast atom bombardment mass spectra (FABMS(+)) were obtained using a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV and equipped with a Ion Tech B11N FAB gun. The FAB gun produces a beam of 6-8 keV xenon neutrals. All compounds were run in a matrix of neat 3-nitrobenzyl alcohol. ^1H, ^{13}C, and ^{31}P NMR were recorded at 300.0 MHz, 75.429 MHz, and 121.421 MHz, respectively on a Varian Unity spectrometer, unless otherwise noted. Where obtained, $^{13}C\{H\}$ NMR data was obtained on ^{13}C labeled complex prepared from $[Tc(CO)_3(^{13}CO)(PPh_3)_2]BF_4$. All $^{31}P\{H\}$ NMR are referenced to an external standard of 85% phosphoric acid in $CDCl_3$. The elemental analyses were performed by Atlantic Microlab, Norcross, GA.

$Tc(CO)_3(C(O)H)(PPh_3)_2$ (2). In the drybox a solution containing $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) (97.4 mg; 0.118 mmol) and 15 mL toluene was treated with Super Hydride (0.12 mL $LiEt_3BH$ as a 1M THF solution) and allowed to stir for 30 min. The reaction mixture was then filtered through Celite and reduced to dryness. The remaining pale yellow solid was stirred for 30 min.

in 10 mL MeCN, filtered on a fritted disk, washed with 10 mL MeCN, Et_2O, and dried *in vacuo*. Yield: (59.1 mg; 76%).

Anal. Calcd. for $C_{40}H_{31}O_4P_2Tc$: C, 65.23; H, 4.24. Found: C, 64.75; H, 4.08.[17] IR (KBr): ν 2035 (m, C≡O); 1951 (s, C≡O); 1858 (s, C≡O); 1581 (s, C=O). ^1H NMR (C_6D_6) δ (ppm): 7.02 (m, 18 H, $P(C_6H_5)$); 7.78 (m, 12 H, $P(C_6H_5)$); 14.88 (s, 1 H, C(O)$\underline{H}$). ^{13}C NMR (C_6D_6) δ (ppm): 278.9 (d, $J_{C\text{-}H}$ = 105 Hz, Tc$\underline{C}$OH). $^{13}C\{H\}$ NMR (C_6D_6) δ (ppm): ($P(C_6H_5)$-ortho or meta partially obscured by C_6D_6); 130.1 (s, $P(C_6H_5)$-para); 132.99 (t, $J_{P\text{-}C}$=5.4 Hz, $P(C_6H_5)$-ortho or meta); 136.23 (t, $J_{P\text{-}C}$ = 22 Hz, $P(C_6H_5)$-ipso); 207 (br, CO *trans* to TcC(O)H); 211 (br, CO *cis* to TcC(O)H); 280 (s, $J_{P\text{-}C}$ = 105.5 Hz, Tc$\underline{C}$(O)H). $^{31}P\{H\}$ (CD_2Cl_2, 202.334 MHz) δ (ppm): ~57 (br). FABMS(+) *m/z*: 707 $[Tc(CO)_3(PPh_3)_2]$; 679 $[Tc(CO)_2(PPh_3)_2]$.

$[Tc(CO)_3(=C(OMe)H)(PPh_3)_2]SO_3CF_3$ (3). In the drybox $Tc(CO)_3(C(O)H)(PPh_3)_2$ **(2)** (120 mg; 0.163 mmol) was added to $CH_3SO_3CF_3$ (20 μL; 0.163 mmol) in 15 mL toluene at 0° C. The mixture was stirred for 3 h. during which time the pale yellow solid dissolves and a new white solid precipitates. The solid was collected by filtration washed with 10 mL Et_2O, and dried *in vacuo* overnight. Yield: (61.6 mg; 42%).

Anal. Calcd. for $C_{42}H_{34}F_3O_7P_2STc$: C, 56.01; H, 3.80; S, 3.56. Found: C, 55.55; H, 3.70; S, 3.41. IR (KBr): ν 2058 (m, C≡O); 2013 (s, C≡O); 1979 (s, C≡O); 1267 (s, SO_3CF_3). ^1H NMR (CD_2Cl_2) δ (ppm): 3.58 (s, O$\underline{CH_3}$, 3H); 7.52 (m, 30 H, $P(C_6H_5)$); 11.84 (s, 1H, Tc=C$\underline{H}$(OMe)). $^{13}C\{H\}$ NMR (C_6D_6) δ (ppm): 77.1 (s, O$\underline{C}H_3$); 129.63 (t, $J_{P\text{-}C}$ = 6.4 Hz, $P(C_6H_5)$-ortho or meta); 129.9 (s, $P(C_6H_5)$-para); 132.87 (t, $J_{P\text{-}C}$ = 5.4 Hz, $P(C_6H_5)$-ortho or meta); 134.06 (t, $J_{P\text{-}C}$ = 22.9 Hz, $P(C_6H_5)$-ipso); 203 (br, CO *cis* to Tc=C(OMe)H); 207 (br, CO *trans* to Tc=C(OMe)H); 323 (br, Tc=$\underline{C}$(OMe)H). FABMS(+) *m/z*: 723 $[Tc(CO)_2(=C(OMe)H)(PPh_3)_2]$; 695 $[Tc(CO)(=C(OMe)H)(PPh_3)_2]$.

$Tc(CO)_3(C(O)OH)(PPh_3)_2$ (4). To a vigorously stirring solution of $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) (69.8 mg, 0.085 mmol) in 5 mL MeCN was slowly added 1 equiv. NaOH (1.5 M H_2O solution) at 0° C. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 2-3 minutes. The white material which formed was filtered on a fritted disk, washed with 50 mL Et_2O and dried *in vacuo*. Yield: (30.1 mg; 51%).

Anal. Calcd. for $C_{40}H_{31}O_5P_2Tc$: C, 63.84; H, 4.15. Found: C, 63.37; H, 4.09. IR (KBr): ν 2052 (m, C≡O); 1954 (s, C≡O); 1936 (s, C≡O); 1566 (s, C=O). ^1H NMR (DMSO) δ (ppm): 7.12 (m, 12 H, $P(C_6H_5)$); 7.89 (m, 18 H, $P(C_6H_5)$); 9.79 (s, 1 H, C(O)O$\underline{H}$). Peaks corresponding to the monohydride complex $HTc(CO)_3(PPh_3)_2$ were also visible.[10] FABMS(+) *m/z*: 735 $[Tc(CO)_4(PPh_3)_2]$; 707 $[Tc(CO)_3(PPh_3)_2]$; 679 $[Tc(CO)_2(PPh_3)_2]$.

$Tc(CO)_3(C(O)OMe)(PPh_3)_2$ (5). To a solution containing $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) (74.1 mg; 0.090 mmol) dissolved in 50 mL MeOH was added 0.5 mL 1M NaOH. After stirring for 30 min., the white precipitate which had formed was collected by filtration, washed with Et_2O, and dried *in vacuo*. This complex was recrystallized from benzene/hexane mixtures stored at 0° C overnight. Yield: (54.0 mg; 84%).

Anal. Calcd. for $C_{41}H_{33}O_5P_2Tc$: C, 64.24; H, 4.34. Found: C, 63.93; H, 4.16. IR(KBr): ν 2023 (C≡O); 1957 (br, C≡O); 1623 (C=O). ^1H NMR ($CDCl_3$) δ (ppm): 2.67 (s, 3H, TcC(O)O$\underline{Me}$); 7.34 (m, br, 18 H, $P(C_6H_5)$); 7.60 (m, br, 12H, $P(C_6H_5)$). $^{13}C\{^1H\}$ NMR (C_6D_6) δ (ppm): 48.0 (s, TcC(O)O$\underline{Me}$); 126 ($P(C_6H_5)$-ortho or meta, partially obscured by C_6D_6 resonance); 129.99 (s, $J_{P\text{-}C}$ = 6.5 Hz, $P(C_6H_5)$-ortho or meta); 134.81 (s, $P(C_6H_5)$-para); 137.08 (t, $J_{P\text{-}C}$ = 21 Hz, $P(C_6H_5)$-ipso); 204 (br, CO *cis* to TcC(O)OMe); 208, (br, CO *trans* to TcC(O)OMe); 213 (br, Tc$\underline{C}$(O)OMe).

$^{31}P\{H\}$ (CD_2Cl_2, 202.334 MHz) δ (ppm): ~49 (br). FABMS(+) *m/z*: 735 $[Tc(CO)_4(PPh_3)_2]$; 707 $[Tc(CO)_3(PPh_3)_2]$; 679 $[Tc(CO)_2(PPh_3)_2]$.

$Tc(CO)_3(C(O)OEt)(PPh_3)_2$ (6). Method 1: This complex was prepared similarly to **5** with the exception of EtOH being employed as the solvent and the length of the reaction being extended to 8 h. Yield: (43.4 mg; 59%).

Method 2: To $Tc(CO)_3(C(O)OMe)(PPh_3)_2$ (**5**) (20.0 mg; 0.026 mmol) in 50 mL acetone was added an equal volume of EtOH. After stirring for 24 h. the volume of the reaction mixture was reduced to 5 mL under vacuum. A white material precipitated and was filtered onto a fritted disk, washed with Et_2O, and dried *in vacuo*. Yield: (14.2 mg; 69%).

Anal. Calcd. for $C_{42}H_{35}O_5P_2Tc$: C, 64.63; H, 4.52. Found: C, 63.92; H, 4.51. IR (KBr): ν 2028 (m, C≡O); 1955 (s, C≡O); 1916 (s, C≡O); 1615 (s, C=O). ^1H NMR (C_6D_6) δ (ppm): 0.88 (t, 3H, J = 4.4 Hz, $OCH_2C\underline{H_3}$); 3.43 (q, 2H, J = 4.1 Hz, $OC\underline{H_2}CH_3$); 7.05 (m, br, 18 H, $P(C_6H_5)$); 7.91 (m, br, 12H, $P(C_6H_5)$). $^{13}C\{H\}$ (CD_2Cl_2) δ (ppm): 14.47 (s, $OCH_2\underline{C}H_3$); 26.20 (s, $O\underline{C}H_2CH_3$); 128.38 (t, $J_{P\text{-}C}$ = 5.6 Hz, $P(C_6H_5)$-ortho or meta); 130.00 (s, $P(C_6H_5)$-para); 133.67 (t, $J_{P\text{-}C}$ = 5.4 Hz, $P(C_6H_5)$-ortho or meta); 136.82 (t, $J_{P\text{-}C}$ = 20.1 Hz, $P(C_6H_5)$-ipso); 206 (br, CO *cis* to TcC(O)OEt); 208 (br, CO *trans* to TcC(O)OEt); 212 (br, $Tc\underline{C}O(OEt)$). $^{31}P\{H\}$ (CD_2Cl_2, 202.334 MHz) δ (ppm): ~42 (br). FABMS(+) *m/z*: 735 $[Tc(CO)_4(PPh_3)_2]$; 707 $[Tc(CO)_3(PPh_3)_2]$; 679 $[Tc(CO)_2(PPh_3)_2]$.

$Tc(CO)_3(C(O)OC_6H_4CH_3)(PPh_3)_2$ (7). To a solution containing $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) (154 mg; 0.147 mmol) in 30 mL THF in the drybox was added $K[OC_6H_4CH_3]$ (54 mg; 0.369 mmol)). The reaction mixture was stirred for 30 min. and then evaporated to dryness *in vacuo*. The beige residue was extracted into 15 mL toluene and filtered through a bed of Celite. The toluene solution was layered with 30 mL hexane and stored at -40 °C overnight. The microcrystalline material which had formed was collected by filtration and dried *in vacuo*. Yield: (53.6 mg; 35%).

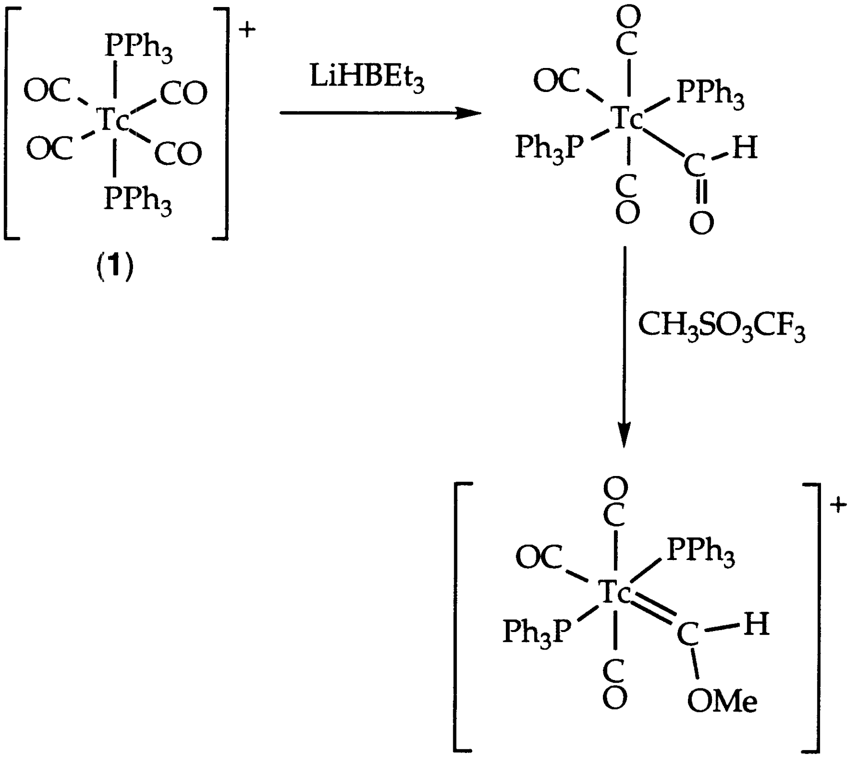
Anal. Calcd. for $C_{47}H_{37}O_5P_2Tc$: C, 66.99; H, 4.43. Found: C, 66.39; H, 4.39. IR (KBr): ν 2012 (m, C≡O); 1954 (s, C≡O); 1926 (s, C≡O); 1648 (s, C=O). ^{1}H NMR (CD_2Cl_2) δ (ppm): 2.22 (s, 3H, $C\underline{H}_3$); 6.94 (d, 2H, J = 8.6 Hz, $C_6\underline{H}_4$); 6.66 (d, 2H, J = 7.7 Hz, $C_6\underline{H}_4$); 7.43 (m, 18 H, $P(C_6H_5)$); 7.57 (m, 12 H, $P(C_6H_5)$). $^{13}C\{H\}$ (CD_2Cl_2) δ (ppm): 21.43 (s, $OC_6H_4\underline{C}H_3$); 125.98 (s, $OC_6H_4CH_3$-$C\underline{H}$); 127.35 (t, $J_{P\text{-}C}$ = 4.9 Hz, $P(C_6H_5)$-ortho or meta); 129.65 (s, $P(C_6H_5)$-para); 131.24 (t, $J_{P\text{-}C}$ = 6.9 Hz, $P(C_6H_5)$-ortho or meta); 132.47 (s, $OC_6H_4CH_3$-$C\underline{H}$); 134.09 (t, $J_{P\text{-}C}$ = 25 Hz, $P(C_6H_5)$-ipso, partially obscured); 134.14 (s, $OC_6H_4CH_3$-ipso bonded to carbon); 153.15 (s, $OC_6H_4CH_3$-ipso bonded to oxygen); 202 (br, CO *cis* to $TcC(O)OC_6H_4\underline{C}H_3$); 205 (br, CO *trans* to $TcC(O)OC_6H_4CH_3$); 214 (br, $Tc\underline{C}(O)OC_6H_4CH_3$). FABMS(+) *m/z*: 735 $[Tc(CO)_4(PPh_3)_2]$; 707 $[Tc(CO)_3(PPh_3)_2]$; 679 $[Tc(CO)_2(PPh_3)_2]$.

$Tc(CO)_3(NCO)(PPh_3)_2$ (8). To $[Tc(CO)_4(PPh_3)_2]BF_4$ (**1**) (76.6 mg; 0.093 mmol) dissolved in 30 mL MeOH was added 6.9 mg NaN_3. The reaction mixture was stirred for 25 h. and evaporated to dryness with a stream of N_2. The remaining solid residue was extracted into 3 x 15 mL portions of C_6H_6, filtered through Celite, and reduced in volume to 5 mL. The solution was then layered with 75 mL pentane and stored at -15° C overnight. The cream solid which precipitated was filtered on a fritted disk, washed with 10 mL pentane, and dried *in vacuo*. Yield: (41.9 mg; 66%).

Anal. Calcd. for $C_{40}H_{30}O_4P_2Tc$: C, 64.10; H, 4.03. Found: C, 63.69; H, 4.00. IR(KBr): ν 2239(s, NCO); 2056 (w, C≡O); 1957 (s, C≡O); 1919 (s, C≡O). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.34 (m, br, $P(C_6H_5)$); 7.60 (m, br, $P(C_6H_5)$). FABMS(+) *m/z*:

750 [$Tc(CO)_3(NCO)(PPh_3)_2$]; 721 [$Tc(CO)_2(N)(PPh_3)_2$]; 707 [$Tc(CO)_3(PPh_3)_2$]; 693 [$Tc(CO)(NCO)(PPh_3)_2$]; [$Tc(CO)_2(PPh_3)_2$].

Scheme I

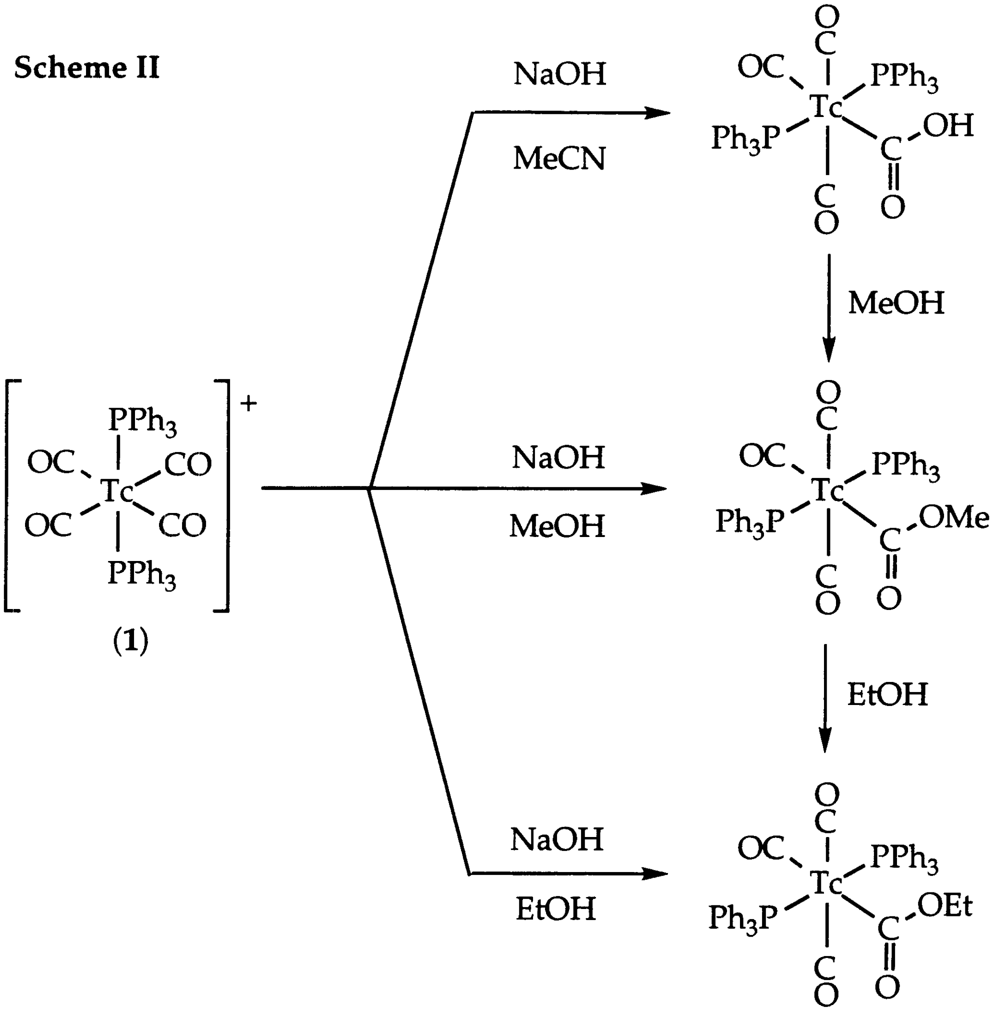


(1)

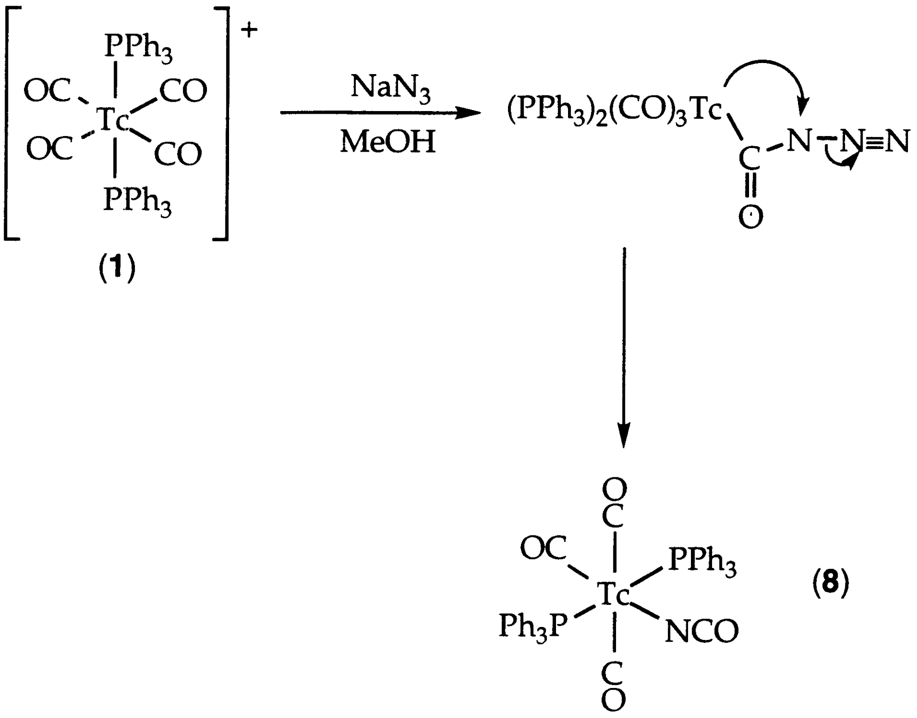
(2)

(3)

Scheme II



Scheme III


$[Tc(CO)_4(PPh_3)_2]^+$
(1)
NaN3
MeOH
$(PPh_3)_2(CO)_3Tc-C(=O)-N-N\equiv N$
(8)
OC
PPh3
Ph3P
NCO
Tc
CO

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Biographical Note

The author was born on May 7, 1969, in New York City, New York. She was raised in the Bronx, where she attended Cardinal Spellman High High School. She then moved to Cambridge where she obtained a B.S. in chemistry from the Massachusetts Institute of Technology. During her sophmore year as an undergraduate at MIT the author began doing research in the area of technetium thiol chemistry with Professor Alan Davison.

She continued in this research through her senior year and then decided to remain at MIT to obtain her doctorate with Alan Davison. During her graduate years she moved away from coordination chemistry and focused on the organometallic chemistry of technetium.

The author plans to continue her chemistry career as a postdoctoral associate in Professor M. L. H. Green's laboratories at Oxford University, Oxford, England.