Synthesis of the 16-Electron Complex TcCl(dppe)$_2$ and Its Reaction with Hydrogen To Give *trans*-Tc(H$_2$)Cl(dppe)$_2$: The First η^2-Dihydrogen Complex of Technetium

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Received August 13, 1993

It has been some time since the first confirmed report of a complex containing a side-bound dihydrogen (η^2-H_2) ligand.[1] Subsequent to this initial publication, a large number of such complexes have been discovered,[2] although relatively few of these have been structurally characterized.[3] A major goal of our investigations has been to map out the reaction coordinate for hydrogen activation by metal centers. Toward this end we have begun to examine a variety of 16-electron complexes with differing ligand combinations and formal metal charge.[4] Herein, we report the synthesis of a stable 16-electron complex of technetium and the formation of the first η^2-dihydrogen complex of technetium.[5]

Treatment of $TcCl_4(PPh_3)_2$ with an excess of zinc powder in the presence of 1,2-bis(diphenylphosphino)ethane (dppe) gives a deep green solution of TcCl(dppe)$_2$ (Scheme 1).[6] This complex, while extremely air sensitive, is completely stable under helium or argon. However, prolonged exposure of solutions of TcCl(dppe)$_2$ to nitrogen atmospheres results in conversion to the nitrogen complex, TcN_2Cl(dppe)$_2$.[7] This nitrogen complex can be converted back to TcCl(dppe)$_2$ by simply heating in toluene. This is not the case with the rhenium analog, which readily undergoes ortho-metalation in solution.[8] The NMR data for TcCl(dppe)$_2$ are consistent with a dynamic coordination geometry. For example, the methylene protons of the dppe appear as a single multiplet in the ^{1}H NMR, while only a single resonance is observed for the phosphorus atoms in the ^{31}P NMR spectrum. The spectral data are consistent with a trigonal bipyramidal type geometry undergoing rapid Berry rotation. A single-crystal X-ray analysis of TcCl(dppe)$_2$·C_7H_8 was undertaken.[9] The structure (Figure 1) is that of a distorted trigonal bipyramid, similar to that observed for ReCl(dppe)$_2$.[8]

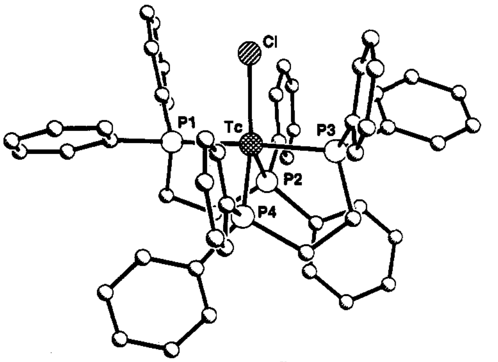
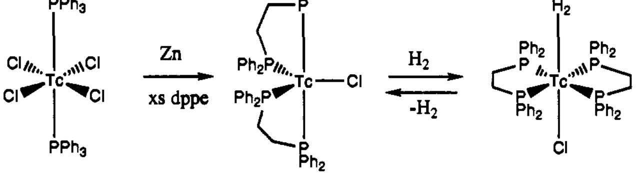


Figure 1. Drawing of TcCl(dppe)$_2$. Selected bond lengths (Å) are as follows: Tc–Cl, 2.432(2); Tc–P(1), 2.376(2); Tc–P(2), 2.240(2); Tc–P(3), 2.359(2); Tc–P(4), 2.255(2). Bond angles (deg): Cl–Tc–P(1), 92.2(1); Cl–Tc–P(2), 128.2(1); Cl–Tc–P(3), 91.2(1); Cl–Tc–P(4), 137.7(1); P(1)–Tc–P(2), 79.5(1); P(1)–Tc–P(3), 7175.2(1); P(1)–Tc–P(4), 99.6(1); P(2)–Tc–P(3), 95.7(1); P(2)–Tc–P(4), 93.9(1); P(3)–Tc–P(4), 80.1(1).

Scheme 1



Treatment of an intense green solution of TcCl(dppe)$_2$ with hydrogen gives an instant change to the yellow color of Tc(H$_2$)Cl(dppe)$_2$.[10] This reaction is completely reversible. For example, allowing the yellow solution to sit in an inert atmosphere quickly results in a return to the green color of TcCl(dppe)$_2$. If this reaction is carried out in an NMR tube it is possible to monitor these changes. Addition of 1 atm of hydrogen gas to an NMR tube containing a solution of TcCl(dppe)$_2$ instantly results in the formation of Tc(H$_2$)Cl(dppe)$_2$. Degassing the frozen solution regenerates the complex TcCl(dppe)$_2$. This process has been repeated for 10 cycles with no noticeable deterioration in the sample.

The ^{1}H NMR spectrum of Tc(H$_2$)Cl(dppe)$_2$ is consistent with an overall octahedral geometry. The methylene protons of the

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(6) TcCl(dppe)$_2$: $TcCl_4(PPh_3)_2$ (200 mg, 0.24 mmol) was suspended in benzene (20 mL) with dppe (300 mg, 0.75 mmol) and Zn (200 mg, 3.0 mmol). This solution was placed in a sealed tube and suspended in an ultrasonic cleaning bath. After 12 h the solution was deep green. The mixture was filtered and the filtrate chromatographed on silica. The intense green band was collected. Addition of hexamethyldisiloxane ($(SiMe_3)_2O$) gives the product as green crystals (198 mg, 81%). ^{31}P NMR ($C_6D_5CD_3$, 295 K): δ 100.1 (b). ^{1}H NMR ($C_6D_5CD_3$, 295 K): δ 6.7–8.05 (m, C_6H_5, 40 H), 2.23 (m, CH_2, 8 H). Anal. Calcd for $C_{52}H_{48}ClP_4Tc$: C, 67.14; H, 5.20. Found: C, 67.46; H, 4.77.

(7) TcN_2Cl(dppe)$_2$: TcCl(dppe)$_2$ (50 mg, 0.05 mmol) was dissolved in THF (5 mL) and the solution then flushed with nitrogen gas. The solution was left for 12 h, and the addition of $(SiMe_3)_2O$ gave the product as a yellow solid (35 mg, 68%). ^{1}H NMR ($C_6D_5CD_3$, 295 K): δ 6.7–8.05 (m, C_6H_5, 40 H), 2.65 (m, CH_2, 4 H), 1.98 (m, CH_2, 4 H). IR (Nujol, KBr): 1978 (ν N_2). Anal. Calcd for $C_{52}H_{48}ClN_2P_4Tc$: C, 65.17; H, 5.05; N, 2.92. Found: C, 65.56; H, 5.76; N, 2.46.

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(9) TcCl(dppe)$_2$·C_7H_8: dark green, rhombohedral, 0.55 × 0.32 × 0.60 mm; M_r = 1020.2; space group $P\bar{1}$; a = 12.920(3) Å; b = 13.115(3) Å; c = 16.091(5) Å, α = 101.09(3)°, β = 95.96(3)°, γ = 111.85(3)°; V = 2437(1) Å^3; Z = 2; d_{calc} = 1.389 g/cm^3; Enraf CAD4 diffractometer; 188 K; Mo Kα radiation (λ = 0.710 73 Å); scan method 2θ-θ; data collection range 4.0–44.0°; total number of data measured 6466; number of independent reflections 5962 (R_{int} = 1.91%); number of observed reflections 4364 ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of $R = 0.0609$ and $R_w = 0.0803$; GOF = 1.27. From final difference Fourier maps, residual electron densities of 1.28 and −2.05 e/Å^3 were present.

(10) Tc(H$_2$)Cl(dppe)$_2$: TcCl(dppe)$_2$ (50 mg, 0.05 mmol) was dissolved in THF (5 mL) and the solution then flushed with hydrogen gas. The solution instantly became pale yellow. Addition of $(SiMe_3)_2O$ precipitated the product as a yellow solid (48 mg, 97%). ^{1}H NMR ($C_6D_5CD_3$, 295 K): δ 6.7–8.05 (m, C_6H_5, 40 H), 2.52 (m, CH_2, 4 H), 1.91 (m, CH_2, 4 H), −13.3 (br, TcH_2, 2 H). Anal. Calcd for $C_{52}H_{50}ClP_4Tc$: C, 66.99; H, 5.41. Found: C, 67.04; H, 5.02.

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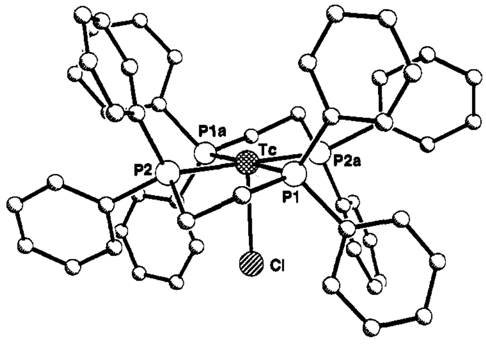

Figure 2. Drawing of $Tc(H_2)Cl(dppe)_2$. Selected bond lengths (Å) and angles (deg) are as follows: Tc–Cl, 2.629(4); Tc–P(1), 2.380(2); Tc–P(2), 2.383(2); Cl–Tc–P(1), 96.7(1); Cl–Tc–P(2), 93.3(1); P(1)–Tc–P(2), 81.1(1).

dppe ligands now appear as two separate multiplets. The H_2 ligand is identified as a broad (~230 Hz) resonance at −13.3 ppm. This signal remains broad with no apparent structure over the temperature range 180–300 K. The measurement of T_1 for dihydrogen/dihydride ligands has been used successfully as a discriminator between "classical" and "nonclassical" structures.[11] Care must be taken in the application of the T_1 criterion,[12] especially in this case, as ^{99}Tc has a spin of $^{9}/_{2}$ and metal–hydrogen dipole–dipole interactions (MHDDI) are expected to significantly affect the T_1 of metal-bound hydrogen atoms. The temperature dependence of T_1 over the range 200–300 K gives a sharp "V-shaped" plot as predicted by theory[2d,10a] and a minimum T_1 value of 20 ± 2 ms at 245 K (200 MHz). The MHDDI was accessed by determining the T_1 for the hydride ligand of *trans*-$[TcHCl(dppe)_2]BF_4$,[13] which has a $T_{1(\mathrm{min})}$ at 200 MHz of 48 ± 5 ms (at 250 K). Therefore the corrected $T_{1(\mathrm{HH})}$ for $Tc(H_2)Cl(dppe)_2$ (given by eq 1 assuming that R_{other} is insignificant compared to R_{HH} and R_{TcH})[12c] is 34 ms.

$$R_{\mathrm{obs}} = R_{\mathrm{HH}} + R_{\mathrm{TcH}} + R_{\mathrm{other}} \qquad (1)$$

This corresponds to an uncorrected intermolecular H–H distance of 1.37 Å, following the method of Hamilton and Crabtree.[11a] Alternatively, using the correction factor of 0.79 suggested by Morris et al.[11b] for systems where the η^2-H_2 rotation is relatively rapid, a H–H distance of 1.08 Å is obtained.[14]

Single-crystal X-ray diffraction of $Tc(H_2)Cl(dppe)_2{\cdot}C_7H_8$ (Figure 2) yields an octahedral structure with the technetium atom on a crystallographic inversion center.[15] The chloride ligand refines with reasonable thermal parameters when its site occupancy factor is set to $^1/_2$. Therefore another half-chloride occupies the vacant coordination site *trans* to Cl in Figure 2, but is not drawn. Thus there is disorder between the *trans*-Cl and η^2-H_2 ligands. The chloride sites are presumably also occupied half-time by the dihydrogen ligand. While electron density can be detected and refined as a half-dihydrogen ligand in the space between the technetium and half-chloride atoms, it is probably too ambitious to assign this as a dihydrogen ligand.

It should be noted that another complex with the formula $TcH_2Cl(dppe)_2$ has been reported.[16] This other complex is formed from the reduction of $TcCl_4(PPh_3)_2$ using $LiAlH_4$ in the presence of an excess of dppe. However, there is no indication that the complex obtained using this method contains a dihydrogen ligand, and this compound has spectral properties[17] completely different from those of the complex obtained in our study. It is likely that these complexes have different geometries (i.e., the hydride ligands occupy *trans* type sites with respect to the dppe ligand plane in the complex described by Kaden et al.).[17] A similar geometrical dependence has been observed for the complexes $MoH_2(CO)(L)_2$ (L = dppe gives a dihydrogen complex; L = bis(diethylphosphino)ethane gives a *distal* dihydride complex).[18] Clearly the isolation of the 16-electron complex, $TcCl(dppe)_2$, is vital in the synthesis of the dihydrogen complex.

One other interesting observation should be noted. A related complex, $TcH_3(dppe)_2$, was prepared in the course of this work.[19] This compound behaves as a classical hydride complex.[20] Clearly the ligand *trans* to the site of hydrogen coordination has a dramatic effect on the dihydrogen/dihydride reaction coordinate. $TcCl(dppe)_2$ offers an excellent opportunity to examine this *trans*-effect in detail, as the substitution of the chloride for other ligands in this complex appears to proceed without difficulty.[21]

This work is being extended to similar technetium complexes of monodentate phosphines. A particular target is $Tc(H_2)Cl(PMePh_2)_4$ as the rhenium analog is described as containing an asymmetrically bound dihydrogen ligand.[3b,22]

Acknowledgment. This work is supported by the Laboratory Directed Research and Development program and the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences. We also thank David L. Clark, Xiao-Liang Luo, and the reviewers for helpful discussions.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and a summary of X-ray diffraction data and ORTEP diagrams for $TcCl(dppe)_2$ and $Tc(H_2)Cl(dppe)_2$ (23 pages); listing of observed and calculated structure factors for $TcCl(dppe)_2$ and $Tc(H_2)Cl(dppe)_2$ (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) $TcHCl(dppe)_2BF_4$: $TcCl(dppe)_2$ (50 mg, 0.05 mmol) was dissolved in THF (5 mL). To this solution was added $HBF_4{\cdot}OEt_2$ (0.08 mmol). The solution instantly became deep purple. Addition of $(SiMe_3)_2O$ gave the product as a purple solid (52 mg, 96%). ^{1}H NMR ($C_6D_5CD_3$, 295 K): δ 6.6–8.6 (m, C_6H_5, 40 H), 2.42 (br m, CH_2, 8 H), −8.37 (q, Tc*H*, H, $^2J_{\mathrm{PH}}$ = 30 Hz). Anal. Calcd for $C_{52}H_{49}BClF_4P_4Tc$: C, 61.35; H, 4.85. Found: C, 60.52; H, 4.83.

(14) Unfortunaly the J_{HD} could not be observed in the analogous HD complex, $Tc(HD)Cl(dppe)_2$. This is likely due to the broad nature of the H_2 and HD signals (~230 Hz) in the ^{1}H NMR. Also $^3J_{\mathrm{HP}}$ coupling is not observed at any temperature.

(15) $Tc(H_2)Cl(dppe)_2{\cdot}C_7H_8$: pale yellow, rhombohedral, 0.10 × 0.17 × 0.27 mm; M_r = 1025.3; space group $C2/c$; a = 27.866(6) Å; b = 14.174(3) Å; c = 12.909(3) Å, β = 105.09(3)°, V = 4926(1) Å^3; Z = 4; d_{calc} = 1.381 g/cm^3; Enraf CAD4 diffractometer; 193 K; Mo Kα radiation (λ = 0.710 73 Å); scan method 2θ-θ; data collection range 4.0–46.0°; total number of data measured 10 444; number of independent reflections 3251 (R_{int} = 2.73%); number of observed reflections 2534 ($F > 4.0\sigma(F)$). The structure was solved by direct methods and refined by a full-matrix least-squares procedure to give final residuals of R = 0.0743 and R_w = 0.0813; GOF = 2.49. From final difference Fourier maps, residual electron densities of 1.27 and −0.52 e/Å^3 were present.

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(19) $TcH_3(dppe)_2$: $TcCl_4(PPh_3)_2$ (200 mg, 0.24 mmol) was suspended in benzene (20 mL) with dppe (300 mg, 0.75 mmol) and Na/Hg (1%, 1.0 mmol). This solution was placed in a flask under an atmosphere of hydrogen gas. The mixture was then stirred for 12 h. During this time the solution changed from green to yellow. The mixture was filtered through Celite. Methanol (20 mL) was added to the filtrate and the solution concentrated to give the product as yellow crystals (86 mg, 37%). ^{1}H NMR ($C_6D_5CD_3$, 295 K): δ 6.7–8.05 (m, C_6H_5, 40 H), 2.23 (m, CH_2, 4 H), 1.96 (m, CH_2, 4 H), −6.9 (quintet, Tc*H*, 3 H, J = 21 Hz). Anal. Calcd for $C_{52}H_{51}P_4Tc$: C, 69.56; H, 5.73. Found: C, 69.88; H, 5.92.

(20) $T_{1(\mathrm{min})}$ = 44 ± 4 ms for $TcH_3(dppe)_3$ at 240 K. This corresponds to a corrected $T_{1(\mathrm{min})}$ of 528 ms, using eq 1 and $1/R_{\mathrm{TcH}}$ = 48 ± 5 ms.

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