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Unusual ^{1}H NMR Properties of Tungsten(II) Tris(pyrazolyl)borate Hydride Complexes

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Protonation of several $[TpW(CO)_3]^-$ salts, substituted differently on the pyrazolyl rings, yields a series of $[TpW(CO)_3H]$ complexes. The hydride chemical shift lies in the normal range for such complexes (δ −2 to −3 ppm), but the one-bond $J(^{183}WH)$ value is surprisingly low (5–9 Hz). A related alkyne derivative has been prepared by reaction of $Na[BH_4]$ with $[Tp^{I}W(CO)(PhC{\equiv}CMe)(N{\equiv}CMe)][BF_4]$ to give $[Tp^{I}W(CO)(PhC{\equiv}CMe)H]$ as the net result of H^- for MeCN substitution. The hydride chemical shift is surprisingly far downfield in this complex (δ 10.8 ppm), but the one-bond $J(^{183}WH)$ value is large (115 Hz). Single-crystal X-ray structures of $[Tp^{I}W(CO)_3H]$ (monoclinic, space group $P2_1/c$, $a = 8.032$ (1) Å, $b = 13.978$ (4) Å, $c = 18.878$ (5) Å, $\beta = 98.11$ (2)°, $V = 2098$ (2) Å^3, $Z = 4$, $R = 0.039$, $R_w = 0.037$) and $[Tp^{I}W(CO)(PhC{\equiv}CMe)H]$ (triclinic, space group $P\bar{1}$, $a = 11.411$ (7) Å, $b = 12.311$ (7) Å, $c = 12.63$ (1) Å, $\alpha = 74.31$ (7)°, $\beta = 64.05$ (7)°, $\gamma = 75.55$ (5)°, $V = 1519$ (2) Å^3, $Z = 2$, $R = 0.058$, $R_w = 0.064$) are reported; the hydride ligands were not located, but the integrity of all the other ligands is reassuring evidence that these are indeed tungsten(II) hydride monomers.

Introduction

In recent years tris(pyrazolyl)borate ligands have attracted considerable attention. An important feature of these ligands is that their framework easily allows for the introduction of substituent groups on the pyrazole rings. In particular, the steric bulk of substituents at the 3-position has been shown to greatly effect the accessibility of a complexed metal atom. The tris(3-*tert*-butylpyrazolyl)borate ligand is especially sterically demanding, with an estimated cone angle of 244°.[1] The label "tetrahedral enforcer" has been used to describe it. We have attempted to synthesize a range of 7-coordinate hydride complexes with different Tp ligands in the coordination sphere.

In this paper we report protonation of variously substituted $[Tp^*W(CO)_3]^-$ salts. Protonation at the metal in the relatively unhindered cases was reported by Trofimenko in 1969.[2] We report here the unusually low tungsten–hydrogen coupling constants of the hydride complexes $Tp^*W(CO)_3H$ and compare their ^{1}H NMR properties with those of the related alkyne-substituted hydride complexes $Tp^{I}W(CO)(RC{\equiv}CR')H$. These rare examples of mononuclear group 6 d^4 alkyne hydride compounds were synthesized by reaction of $Na[BH_4]$ with $[Tp^{I}W(CO)(RC{\equiv}CR')(N{\equiv}CMe)][BF_4]$. The path of this reaction is discussed in the light of other reported reactions of hydride reagents with four-electron-donor alkyne complexes.

Experimental Section

General Methods. Manipulations involving air-sensitive reagents were performed under nitrogen with use of Schlenk techniques. Solvents were purified as follows: THF and hexane were distilled from potassium benzophenone ketyl, CH_2Cl_2 was distilled from CaH_2, and CH_3CN was distilled frorm P_2O_5. Anhydrous *N,N*-dimethylformamide (DMF, 99%+) was purchased from Aldrich. $W(CO)_3(EtCN)_3$,[3] KTp,[4] KTp^{I},[5] KTp^{II},[1] KTp^{III},[6] and KTp^{IV}[1] were prepared by literature methods. All other reagents were purchased from commercial sources and used without further purification. Infrared spectra were recorded on a Mattson Polaris FT IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-400 (400 MHz) or Bruker AC-200 (200 MHz) spectrometers. Chemical shifts were referenced to residual solvent protons. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, or Oneida Research Services, Whitesboro, NY.

Syntheses. $[NEt_4][TpW(CO)_3]$ (1).[2] A solution of $[W(CO)_6]$ (16.8 g, 50 mmol) and potassium hydrotris(pyrazolyl)borate (KTp, 9.4 g, 50 mmol) in 150 mL of DMF was heated at 100 °C until CO evolution ceased (ca. 2 h). The volume of the solution was reduced by half under vacuum. The remaining solution was added to a stirred solution of 1 M aqueous tetraethylammonium chloride (ca. 100 mL). The resulting yellow precipitate was isolated by filtration and washed with distilled water. The crude compound was recrystallized from acetonitrile–water (2:1) to give 1 (16.6 g, 57%).

$[NEt_4][Tp^{I}W(CO)_3]$ (2).[2] A solution of $[W(CO)_6]$ (16.8 g, 50 mmol) and potassium hydrotris(3,5-dimethylpyrazolyl)borate (KTp^{I}, 16.8 g, 50 mmol) in 100 mL of DMF was stirred at 90 °C. After 25 h, IR spectroscopy indicated that no $[W(CO)_6]$ remained. The solution was concentrated at 70 °C under vacuum to about half of the original volume and then poured into a stirred solution of excess $[Et_4N][Br]$ (30 g) in 300 mL of distilled water. The resulting precipitate was filtered, washed with water, and recrystallized from acetonitrile–water (2:1). The product was washed with water, cold methanol, and cold ether and dried in vacuo to give bright yellow crystalline 2 (17.1 g, 50%).

$[NEt_4][Tp^{II}W(CO)_3]$ (3). A solution of $[W(CO)_6]$ (3.78 g, 11 mmol) and potassium hydrotris(3-phenylpyrazolyl)borate (KTp^{II}, 5.15 g, 11 mmol) in 100 mL of DMF was heated to reflux. After 45 min, during which time the solution changed from yellow to orange to dark red, the solution was cooled and the solvent volume was reduced by half under vacuum. The mixture was then poured into a stirred solution of excess $[Et_4N][Br]$ (4.3 g) in 100 mL of distilled water. The resulting precipitate was filtered, washed with water, cold methanol, and cold ether, and dried in vacuo to give bright yellow crystalline 3 (3.9 g, 43%).

$[Et_4N][Tp^{III}W(CO)_3]$ (4). A solution of $[W(CO)_6]$ (5.8 g, 16 mmol) and potassium hydrotris(3-isopropylpyrazolyl)borate (KTp^{III}, 5.8 g, 15 mmol) in 120 mL of DMF was refluxed for 1 h. The solution changed from yellow to orange and finally to dark red. The solution was cooled, and the volume was reduced to

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[1] Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507.

[2] Trofimenko, S. *J. Am. Chem. Soc.* **1969**, *91*, 588.

[3] Kubas, G. J. *Inorg. Chem.* **1983**, *22*, 692.

[4] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

[5] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288.

[6] Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091.

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about 50 mL. The mixture was then poured into a stirred solution of excess [Et$_4$N][Br] (8 g) in 100 mL of distilled water. The resulting yellow precipitate was filtered, washed with water, cold methanol, and cold ether, and recrystallized from CH$_2$Cl$_2$–ether to give 4 (5.1 g, 42%).

[NEt$_4$][Tp^{IV}W(CO)$_3$] (5). Potassium hydrotris(3-*tert*-butylpyrazolyl)borate (KTp^{IV}, 4.2 g, 10 mmol) was added to a slurry of [W(CO)$_3$(EtCN)$_3$] (5.0 g, 10 mmol) in 200 mL of THF at 25 °C. After the mixture was stirred for 15 min, the solvent volume was reduced to ca. 40 mL under vacuum; a dark brown liquid remained. An aqueous solution of excess [Et$_4$N][Br] (5.5 g) was added, and a dark orange solid precipitated. After filtration the residue was washed with water, cold methanol (which removes a brown impurity), and cold ether and recrystallized from CH$_2$Cl$_2$–ether to give bright yellow **5** (3.1 g, 40%). Anal. Calcd for C$_{32}$H$_{54}$BN$_7$O$_3$W: C, 49.31; H, 6.93; N, 12.58. Found: C, 49.40; H, 7.04; N, 12.69.

[TpW(CO)$_3$H] (6).[2] [NEt$_4$][TpW(CO)$_3$] (1; 1.0 g, 1.6 mmol) was dissolved in 50 mL of acetonitrile. One milliliter of concentrated HCl was added dropwise to the solution, and a bright yellow precipitate formed. The precipitate was filtered under N$_2$ and washed with cold acetonitrile (2 × 25 mL). Drying in vacuo gave yellow **6**. Anal. Calcd for C$_{12}$H$_{11}$BN$_6$O$_3$W: C, 29.88; H, 2.30; N, 17.44. Found: C, 30.15; H, 2.65; N, 17.59.

[Tp^{I}W(CO)$_3$H] (7).[2] In a procedure analogous to that outlined above, **2** (1.0 g, 1.4 mmol) gave yellow **7** (0.7 g, 86%). Anal. Calcd for C$_{18}$H$_{23}$BN$_6$O$_3$W: C, 38.10; H, 4.16; N, 14.46. Found: C, 38.10; H, 4.10; N, 14.80.

[Tp^{II}W(CO)$_3$H] (8). In a procedure analogous to that outlined above, **3** (0.16 g, 0.19 mmol) gave pale yellow **8** (0.10 g, 74%). Anal. Calcd for C$_{30}$H$_{23}$BN$_6$O$_3$W: C, 50.72; H, 3.24; N, 11.83. Found: C, 50.03; H, 3.42; N, 11.65.

[Tp^{III}W(CO)$_3$H] (9). In a procedure analogous to that outlined above, **4** (0.15 g, 0.20 mmol) gave pale yellow **9** (0.105 g, 85%). Anal. Calcd for C$_{21}$H$_{29}$BN$_6$O$_3$W: C, 41.46; H, 4.77; N, 13.82. Found: C, 41.57; H, 4.98; N, 14.21.

[Tp^{I}W(CO)(RC≡CMe)H] (R = Ph (10), Me (11)). In a representative synthesis, to a blue THF solution of [Tp^{I}W(CO)(PhC≡CMe)(N≡CMe)][BF$_4$] (0.5 g, 0.66 mmol) was added 2 equiv of Na[BH$_4$] (0.05 g). The solution changed to wine purple after it was stirred at room temperature for 1 h. The solution was filtered, the solvent was removed, the residue was dissolved in toluene, and this solution was then chromatographed on alumina with toluene as the eluent. A wine purple band was collected, the solvent was removed, and the residue was recrystallized from CH$_2$Cl$_2$–hexanes to yield wine purple crystals of **10** (0.21 g, 50%). [Tp^{I}W(CO)(PhC≡CMe)H] (**10**): ^{13}C NMR (CD$_2$Cl$_2$) δ 244.0 ($^{1}J_{WC}$ = 139 Hz, $^{2}J_{HC}$ = 5 Hz, *C*O), 215.0 ($^{1}J_{WC}$ = 59 Hz, ≡*C*Ph), 210.3 ($^{1}J_{WC}$ = 11 Hz, $^{2}J_{HC}$ = 7 Hz, ≡*C*CH$_3$), 153.8, 153.1, 149.6, 145.3, 145.2, 144.8 (1:1:1:1:1:1, Tp^{I} *C*CH$_3$), 138.3, 129.2, 128.8, 128.4 (Ph), 107.1, 106.9, 106.7 (1:1:1, Tp^{I} *C*H), 21.8 (q, $^{1}J_{HC}$ = 129 Hz, ≡CCH$_3$), 17.1, 16.7, 16.1, 12.9, 12.6, (1:1:1:2:1, Tp^{I} C*C*H$_3$. Anal. Calcd for C$_{25}$H$_{31}$BN$_6$OW: C, 47.95; H, 4.95; N, 13.43. Found: C, 48.04; H, 4.67; N, 13.44. [Tp^{I}W(CO)(MeC≡CMe)H] (**11**): ^{13}C NMR (CD$_2$Cl$_2$) δ 244.4 ($^{1}J_{WC}$ = 139 Hz, $^{2}J_{WC}$ = 5 Hz, *C*O), 217.2 ($^{1}J_{WC}$ = 60 Hz, ≡*C*CH$_3$), 208.1 ($^{1}J_{WC}$ = 13 Hz, CH$_3$*C*≡), 153.2, 153.0, 149.8, 145.2, 145.1, 145.0 (1:1:1:1:1:1, Tp^{I}*C*CH$_3$), 107.1, 106.9, 106.6 (1:1:1, Tp^{I}*C*H), 20.7, 19.8, 17.0, 16.9, 15.9, 12.9, 12.8, 12.6 (1:1:1:1:1:1:1:1, Tp^{I} C*C*H$_3$ and *C*H$_3$C≡C*C*H$_3$). Anal. Calcd for C$_{20}$H$_{29}$BN$_6$OW: C, 42.58; H, 5.15; N, 14.90. Found: C, 42.48; H, 5.14; N, 14.61.

X-ray Data Collection and Structure Solution and Refinement. Tp^{I}W(CO)$_3$H (7). A yellow plate of dimensions 0.60 × 0.30 × 0.15 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[7] Twenty-five centered reflections found in the region 14.0° < θ < 17.0° and refined by least-squares calculations indicated a monoclinic cell. The cell parameters are listed in Table I.

Diffraction data were collected in the quadrant ±*h*,+*k*,+*l* under the conditions specified in Table I. Three reflections chosen as intensity standards were monitored every 3 h and showed no significant (<1.5%) decay. The crystal was checked for orientation every 300 reflections and was recentered if necessary. ψ scans with nine reflections having 80° < χ < 90° were collected, and an empirical absorption correction was applied (the corrections ranged from 0.7390 to 0.9995). Only data with $I > 3\sigma(I)$ were used in the structure solution and refinement.[8] The data were corrected for Lorentz–polarization effects during the final stages of data reduction.

Table I. Crystallographic Data

	Tp^{I}W(CO)$_3$H	Tp^{I}W(CO)(PhC≡CMe)H
mol formula	C$_{18}$H$_{23}$BN$_6$O$_3$W	C$_{28}$H$_{29}$BN$_6$OW
fw	566.08	660.23
cryst dimens, mm	0.60 × 0.30 × 0.15	0.20 × 0.20 × 0.20
space group	$P2_1/c$	$P\bar{1}$
cell dimens		
a, Å	8.032 (1)	11.411 (7)
b, Å	13.978 (4)	12.311 (7)
c, Å	18.878 (5)	12.634 (13)
α, deg		74.31 (7)
β, deg	98.11 (2)	64.05 (7)
γ, deg		75.55 (5)
V, Å^3	2098 (2)	1519 (2)
Z, molecules/cell	4	2
d(calcd), g/cm^3	1.79	1.44
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.709 30)
monochromator	Zr filter	graphite
linear abs coeff, cm^{-1}	56.5	39.1
scan type	$\omega/0.83\theta$	$\theta/2\theta$
bkgd	25% of full scan width on both sides	
θ limits, deg	$2 < \theta < 25$	
2θ limit, deg		50
quadrant(s) collected	±*h*,+*k*,+*l*	±*h*,+*k*,±*l*
total no. of rflns	3694	5307
no. of data with $I \geq 3\sigma(I)$	2478	
no. of data with $I \geq 2.5\sigma(I)$		3643
R, %	3.9	5.8
R_w, %	3.7	6.4
GOF	2.17	2.24
no. of params	262	353
largest param shift	0.02	0.50

Solution of the structure was straightforward from application of the heavy-atom method. Space group $P2_1/c$ was confirmed, and the position of the tungsten atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations.

Least-squares refinement[9] of the 29 non-hydrogen atoms, with all 29 varied anisotropically, produced unweighted and weighted residuals of 4.3% and 4.5%, respectively.[10] Hydrogen atom positions were calculated by using a C–H distance of 0.95 Å and an isotropic thermal parameter of 6.0 Å^2. Location of the hydrogen was difficult, and no effort to include the hydride was pursued. Final refinement resulted in residuals of R = 3.9% and R_w = 3.7%.[11] The final difference Fourier map had three peaks with

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[7] Programs used during solution and refinement were from the Enraf-Nonius structure determination package.

[8] $I = S(C + RB)$ and $\sigma(I) = [2S^2(C + R^2B) + (\rho I)^2]^{1/2}$, where S = scan rate, C = total integrated peak count, R = ratio of scan count time to background count time, B = total background count time, and ρ = 0.01 (correction factor).

[9] The function minimized was $\sum w(|F_o| - |F_c|)^2$.

[10] $R_{\mathrm{unweighted}} = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_{\mathrm{weighted}} = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

[11] Scattering factors were taken from the following: Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, J. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2.

intensities of 0.76, 0.76, and 0.66 e/Å^3 located near tungsten. The remaining peaks were less than 0.38 e/Å^3.

$Tp^IW(CO)(PhC{\equiv}CMe)H$ (10). A wine purple cube of dimensions 0.20 × 0.20 × 0.20 mm was selected, mounted on a glass wand, and coated with epoxy. Diffraction data were collected on an Enraf-Nonius CAD-4 automated diffractometer.[7] Eighteen centered reflections found in the region $30.0° < 2\theta < 35.0°$ and refined by least-squares calculations indicated a triclinic cell. The cell parameters are listed in Table I.

Diffraction data were collected in the hemisphere $\pm h,+k,\pm l$ under the conditions specified in Table I. Only data with $I > 2.5\sigma(I)$ were used in structure solution and refinement.[8] The data were corrected for Lorentz–polarization effects during the final stages of data reduction. The crystal was checked for orientation every 200 reflections and was recentered if necessary.

Solution of the structure was straightforward from application of the heavy-atom method. Space group $P\bar{1}$ was confirmed, and the position of the tungsten atom was deduced from the three-dimensional Patterson function. The positions of the remaining non-hydrogen atoms were determined through subsequent Fourier and difference Fourier calculations. The atoms marked THF seem to be a disordered THF of solvation. The highest peaks in the difference synthesis are in this region, indicating rotational disorder, which accounts for our inability to locate the hydrogens or to determine which atom is oxygen in this solvent molecule.

The 37 non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 1.08 Å, and an isotropic thermal parameter was calculated from the anisotropic values for the atoms to which they were connected. The final residuals for 353 variables refined against 3643 data with $I > 2.5\sigma(I)$ were $R = 5.8\%$ and $R_w = 6.4\%$.[11] The final difference Fourier map had no peak greater than 1.25 e/Å^3.

Results and Discussion

The anionic complexes $[NEt_4][Tp^*W(CO)_3]$ (Tp^* = Tp, hydrotris(pyrazolyl)borate (1), Tp^I, hydrotris(3,5-dimethylpyrazolyl)borate (2), Tp^{II}, hydrotris(3-phenylpyrazolyl)borate (3), Tp^{III}, hydrotris(3-isopropylpyrazolyl)borate (4), Tp^{IV}, hydrotris(3-*tert*-butylpyrazolyl)borate (5) (see Figure 1)) were prepared by a modification of the routes used by Trofimenko[1,2,6] for the analogous molybdenum complexes. Thermolysis of the appropriate KTp^* reagent with $W(CO)_6$ in DMF solution generated $K[Tp^*W(CO)_3]$.[2] Cation exchange with $[Et_4N][Br]$ then produced the more air stable $[Et_4N][Tp^*W(CO)_3]$ salts. More forcing conditions are required for the production of the tungsten complexes than for the molybdenum analogues. Indeed, it was found that, in the case of the most sterically demanding Tp^* ligand, the complex $K[Tp^{IV}W(CO)_3]$ (5) could not be cleanly generated from the reaction of KTp^{IV} and $W(CO)_6$ in refluxing DMF.

Complexes 1–4 were isolated as yellow powders that could be briefly handled in air. ^1H NMR spectroscopy shows that the three pyrazole rings of each Tp^* ligand are equivalent. The infrared spectra of these complexes in CH_3CN solution exhibit one $\nu(CO)$ absorption band in the range 1877–1887 cm^{-1} and one in the range 1740–1756 cm^{-1}; the lower energy band is broad and significantly more intense than the higher energy absorption in all cases. Tp^* complexes have generally been observed to exhibit $\nu(CO)$ frequencies 10–20 cm^{-1} lower than those of corresponding Cp derivatives. EHMO calculations by Curtis and coworkers support the proposal that Tp is a better electron donor than Cp.[12] Complex 5 was synthesized independently, by means of substitution of the labile propionitrile ligands of $W(CO)_3(EtCN)_3$ upon reaction with KTp^{IV} in THF solution at 25 °C. IR and microanalytical data are consistent with a $Tp^{IV}W(CO)_3^-$ formulation. The ^1H NMR spectrum, however, does not show the expected three equivalent pyrazole rings. Instead, two sets of 2:1 resonances are observed for the pyrazole and pyrazole substituent protons. We tentatively propose that either dechelation of one arm with acetonitrile entering the coordination sphere or pyrazole ring rearrangement has occurred. Reversal of one and two rings would give both $\{HB(3\text{-}^tBupz)_2(5\text{-}^tBupz)\}W(CO)_3^-$ and $\{HB(3\text{-}^tBupz)(5\text{-}^tBupz)_2\}W(CO)_3^-$. Precedent for the reversal of one ring exists, as Trofimenko[6] has synthesized the complexes $Co\{HB(3\text{-}^iPrpz)_2(5\text{-}^iPrpz)\}_2$ and $Co\{HB(3\text{-}^iPr\text{-}4\text{-}Brpz)_2(5\text{-}^iPr\text{-}4\text{-}Brpz)\}_2$ from reaction of $CoCl_2$ with $TlHB(3\text{-}^iPrpz)_3$ and $TlHB(3\text{-}^iPr\text{-}4\text{-}Brpz)_3$, respectively. The in situ synthesis of the molybdenum analogue of 5 en route to the complex $Tp^{IV}Mo(CO)_2(NO)$ has been described. No ^1H NMR data, however, were reported for either complex.[1]

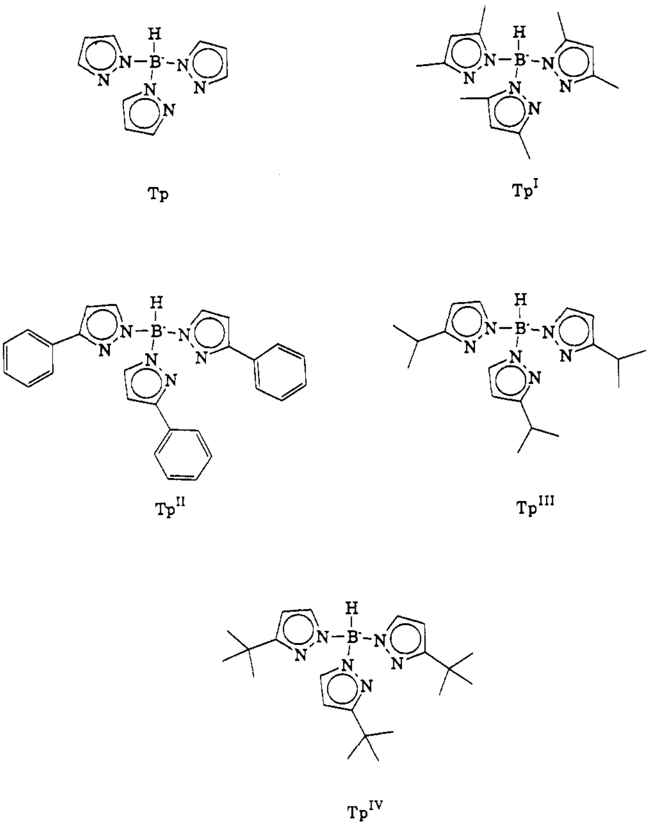

Figure 1.

The hydride complexes $Tp^*W(CO)_3H$ (Tp^* = Tp (6), Tp^I (7), Tp^{II} (8), Tp^{III} (9)) are formed by protonation of MeCN solutions of the anionic complexes with aqueous HCl. The products precipitate from solution and are isolated as mildly air-sensitive yellow and cream powders. Although we had hoped that with the more hindered Tp^* ligands a possible alternative might be protonation at a carbonyl oxygen, there was no evidence for the production of a hydroxycarbyne species. Relatively few 7-coordinate Tp complexes have been synthesized compared to the number of Cp analogues. It appears that Tp ligands are able to polarize metal orbitals more effectively into an octahedral array than the delocalized Cp anions. The observations of three infrared $\nu(CO)$ bands for these $Tp^*W(CO)_3H$ complexes suggests that a 4:3 geometry, similar to that observed for $TpMo(CO)_3Br$,[12] is adopted by $Tp^*W(CO)_3H$, with the hydrogen atom and the carbon atoms of the carbonyl ligands lying approximately at the corners of a square. Two $\nu(CO)$ absorptions (a_1 + e) would be expected for a structure with the hydride capping the triangular $(CO)_3$ face to retain C_{3v} symmetry in a 3:3:1

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[12] Curtis, M. D.; Shiu, K.-B. *Inorg. Chem.* **1985**, *24*, 1213.

Table II. Complete Atomic Coordinates for $Tp^IW(CO)_3H$ (7)

atom	*x*	*y*	*z*
W	0.43891 (5)	0.26721 (3)	0.36044 (2)
O(1)	0.643 (1)	0.1373 (6)	0.2682 (4)
O(2)	0.605 (1)	0.4248 (5)	0.2787 (4)
O(3)	0.145 (1)	0.3377 (6)	0.2483 (5)
N(1)	0.351 (1)	0.3595 (5)	0.4433 (4)
N(2)	0.352 (1)	0.3249 (5)	0.5114 (4)
N(3)	0.3122 (9)	0.1528 (5)	0.4198 (4)
N(4)	0.348 (1)	0.1479 (5)	0.4929 (4)
N(5)	0.6480 (9)	0.2517 (5)	0.4494 (4)
N(6)	0.6211 (9)	0.2352 (5)	0.5180 (4)
C(1)	0.565 (1)	0.1846 (7)	0.3033 (5)
C(2)	0.546 (1)	0.3690 (7)	0.3120 (6)
C(3)	0.253 (1)	0.3097 (8)	0.2915 (6)
C(4)	0.285 (1)	0.3901 (7)	0.5520 (5)
C(5)	0.241 (1)	0.4647 (7)	0.5100 (6)
C(6)	0.285 (1)	0.4478 (7)	0.4435 (6)
C(7)	0.266 (2)	0.3746 (8)	0.6287 (6)
C(8)	0.262 (2)	0.5104 (8)	0.3793 (7)
C(9)	0.274 (1)	0.0671 (7)	0.5147 (6)
C(10)	0.191 (1)	0.0236 (7)	0.4553 (6)
C(11)	0.213 (1)	0.0786 (7)	0.3960 (6)
C(12)	0.291 (2)	0.0386 (8)	0.5904 (7)
C(13)	0.148 (1)	0.0611 (8)	0.3198 (7)
C(14)	0.766 (1)	0.2297 (7)	0.5623 (5)
C(15)	0.894 (1)	0.2420 (7)	0.5214 (6)
C(16)	0.822 (1)	0.2557 (6)	0.4513 (6)
C(17)	0.780 (1)	0.2121 (8)	0.6401 (6)
C(18)	0.909 (1)	0.2763 (8)	0.3869 (6)
B	0.441 (1)	0.2303 (9)	0.5333 (6)

geometry. This is also compatible with the geometry proposed for $CpW(CO)_3H$, although only two of the three expected ν(CO) absorptions were observed. Variable-temperature ^1H NMR measurements with $CpW(CO)_3H$ suggested that a 4:3 structure was the lowest energy configuration and was adopted at low temperature. At room temperature the complex underwent rapid carbonyl exchange, possibly via a 3:3:1 transition state or intermediate.[13]

The ^1H NMR spectra of **6–9** show the pyrazolyl rings to be equivalent, suggesting that these 7-coordinate hydride complexes are fluxional. This correlates with Curtis and Shiu's studies in which the complexes $TpMo(CO)_3X$ (X = H, Br, I) were observed to be fluxional in the temperature range −80 to +30 °C.[12] The most unusual feature of the ^1H NMR spectra is the surprisingly small one-bond $J(^{183}WH)$ coupling constants of 9, 6, 7, and 4 Hz, respectively, for **6–9**. The hydride chemical shifts (δ −2.2 to −3.0) are all in the range observed for related hydrides, but the nearest $^1J(^{183}WH)$ value we are aware of is 4–7 times larger than the value we observe (37 Hz in $CpW(CO)_3H$).[13-15] It is generally assumed that for other one-bond spin–spin coupling constants involving hydrogen the Fermi contact term is dominant.[16] This can be correlated with the amount of s character in the bond. Legzdins[17] has suggested that similar factors may govern one-bond W–H couplings. Thus, the most important contributor to the magnitude of $^1J(^{183}WH)$ should be the amount of s-electron density contributed by tungsten to the W–H linkage, since the hydride can only contribute s-electron character. In other words the unusually low value of $^1J(^{183}WH)$ for **6–9** should reflect low valence s-electron density on tungsten and a long W–H bond.

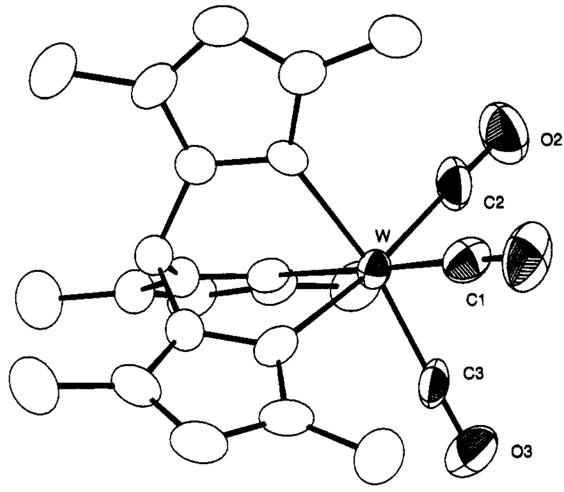

Figure 2. ORTEP plot of $Tp^IW(CO)_3H$ (7).

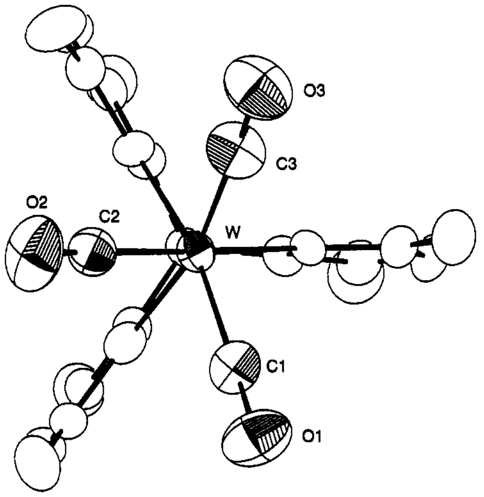

Figure 3. ORTEP plot of $Tp^IW(CO)_3H$ (7) viewed along the tungsten–boron axis.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $Tp^IW(CO)_3H$ (7)

W–N(1)	2.216 (6)	W–C(3)	1.930 (9)
W–N(3)	2.274 (6)	O(1)–C(1)	1.176 (8)
W–N(5)	2.211 (6)	O(2)–C(2)	1.148 (8)
W–C(1)	1.956 (8)	O(3)–C(3)	1.173 (9)
W–C(2)	1.954 (8)		
N(1)–W–N(3)	81.5 (2)	C(1)–W–C(2)	82.9 (3)
N(1)–W–N(5)	78.7 (2)	C(1)–W–C(3)	102.8 (4)
N(1)–W–C(1)	166.5 (3)	C(2)–W–C(3)	78.9 (4)
N(3)–W–N(5)	84.3 (2)	W–C(1)–O(1)	178.0 (7)
N(3)–W–C(2)	177.9 (3)	W–C(2)–O(2)	174.7 (8)
N(5)–W–C(3)	166.9 (3)	W–C(3)–O(3)	177.2 (8)

In the hope of testing this hypothesis and in order to determine the solid-state structure of $Tp^IW(CO)_3H$ (**7**), a single-crystal X-ray diffraction study was performed. ORTEP drawings of complex **7** are shown in Figures 2 and 3. Data collection parameters are shown in Table I. Atomic coordinates are listed in Table II and selected bond distances and angles in Table III. The hydride ligand was not located. As a result it is difficult to make a definite distinction between a 4:3 piano-stool or a capped-octahedral description of the structure. The geometry of the $LW(CO)_3$ unit, however, is similar to that observed for the 7-coordinate complexes $TpMo(CO)_3Br$,[12] $[LW(CO)_3H]^+$, and $[LW(CO)_3Br]^+$ (L = 1,4,7-triazacyclononane).[18] This

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observation lends support to the presence of a hydride in the complex. The three C–W–C bond angles are different, so a 1:3:3 geometry with C_{3v} symmetry is not present. As observed for $[LW(CO)_3H]^+$, $[LW(CO)_3Br]^+$, and particularly $TpMo(CO)_3Br$, two angles are substantially less than 90° (C(1)–W–C(2) = 82.9 (3)° and C(2)–W–C(3) = 78.9 (4)°) while the other is substantially more (C(1)–W–C(3) = 102.8 (4)°). Presumably the hydride ligand lies between the two CO ligands with the larger angle. One W–N distance (W–N(3) = 2.274 (6) Å) is significantly longer than the other two (W–N(1) = 2.216 (6) Å and W–N(5) = 2.211 (6) Å). Curtis has noted that in molybdenum tris(pyrazolyl)borate complexes longer Mo–N bonds were observed when the nitrogen donor atom was directly trans to CO.[12] Indeed, the longest Mo–N bond here lies within 3° of linearity with CO(2), while the shorter Mo–N distances (2.216 (6) and 2.211 (6) Å) have trans CO angles near 167°.

Related alkyne-substituted hydride complexes $[Tp'W(CO)(RC{\equiv}CMe)H]$ (R = Ph (**10**), Me (**11**)) can be prepared by treating cationic $[Tp'W(CO)(RC{\equiv}CMe)(N{\equiv}CMe)][BF_4]$ reagents with $Na[BH_4]$. The reaction formally involves substitution of acetonitrile by hydride. It is interesting to note, however, that the choice of hydride reagent is important, since low-temperature treatment of $[Tp'W(CO)(PhC{\equiv}CMe)(N{\equiv}CMe)][BF_4]$ with $Li[BEt_3H]$ results in hydride addition to the coordinated acetonitrile ligand to give an azavinylidene complex.[19] This observation illustrates the delicate balance that exists in this and related systems. Several instances where hydride attack on four-electron-donor alkynes results in η^2-vinyl production have been reported.[20-21] Indeed, in some cases, nucleophilic additions have yielded η^3-allyl and carbyne ligands.[22-24] In such cases reaction mechanisms involving initial η^2-vinyl formation have been proposed. Finally, Green and co-workers demonstrated that hydride could deprotonate the alkyne complex $[CpMoL_2(PhC{\equiv}CCH_2Ph)][BF_4]$ (L = $P(OMe)_3$) at C_β to produce the stable allenyl complex $CpMoL_2(\eta^2\text{-}PhC{=}C{=}CHPh)$.[25] Evidence to distinguish between initial attack at metal or carbon with hydride reagents has proved difficult to obtain. When R^- nucleophiles are used, however, it is clear that two distinct pathways are available and that alkyl migration from metal to carbon is not facile. For example, Green and co-workers found that reaction of $[CpMoL_2(PhC{\equiv}CPh)][BF_4]$ (L = $P(OMe)_3$) with $LiCuMe_2$ gave both the η^2-vinyl complex $[CpMoL_2(\eta^2\text{-}CPh{=}CMePh)]$ and an alkyne methyl product, $[CpMoL(PhC{\equiv}CPh)Me]$. Addition of $P(OMe)_3$ to the latter under a variety of conditions failed to produce the η^2-vinyl complex.[20] Of course, hydrogen migrations generally have lower activation energies than alkyl migrations. In light of these observations, it is reasonable to suggest that initial metal hydride formation is not a required precursor to η^2-vinyl or azavinylidene products in these systems. Direct hydride attack at carbon is viable. Azavinylidene production from $[Tp'W(CO)(PhC{\equiv}CMe)(N{\equiv}CMe)]^+$ may arise as a consequence of the more bulky $Li[BEt_3H]$ reagent being impeded from delivering hydride to the sterically congested tungsten center.

Table IV. Complete Atomic Coordinates for $Tp'W(CO)(PhC{\equiv}CMe)H$ (10)

	x	*y*	*z*
W(1)	0.06767 (5)	0.32733 (5)	0.23399 (6)
N(31)	0.2507 (9)	0.3481 (9)	0.2452 (9)
N(15)	0.0642 (9)	0.2772 (8)	0.4945 (9)
C(2)	0.0469 (10)	0.3331 (9)	0.0807 (11)
N(35)	0.2917 (9)	0.2788 (9)	0.3326 (10)
N(11)	−0.0055 (10)	0.3352 (8)	0.4300 (9)
N(25)	0.1756 (10)	0.1096 (8)	0.3849 (10)
O(1)	−0.2202 (9)	0.3200 (9)	0.2822 (10)
C(4)	0.1726 (12)	0.3301 (10)	0.0574 (12)
N(21)	0.1179 (9)	0.1448 (8)	0.3073 (9)
C(5)	0.2949 (12)	0.3239 (10)	−0.0504 (12)
C(32)	0.3360 (11)	0.4250 (10)	0.1841 (12)
C(1)	−0.1111 (14)	0.3219 (11)	0.2662 (13)
C(12)	−0.1101 (12)	0.3943 (11)	0.5008 (12)
C(22)	0.1048 (13)	0.0499 (11)	0.2826 (13)
C(34)	0.3992 (11)	0.3154 (12)	0.3230 (13)
C(24)	0.1986 (13)	−0.0060 (11)	0.4113 (14)
C(13)	−0.1058 (14)	0.3763 (12)	0.6102 (14)
C(36)	0.3188 (13)	0.5158 (11)	0.0891 (12)
C(33)	0.4297 (12)	0.4038 (11)	0.2295 (12)
B(1)	0.1980 (15)	0.2006 (13)	0.4366 (15)
C(23)	0.1554 (14)	−0.0428 (11)	0.3451 (14)
C(14)	0.0035 (13)	0.3010 (11)	0.6042 (12)
C(6)	0.4088 (14)	0.2615 (13)	−0.0382 (13)
C(10)	0.2965 (14)	0.3780 (12)	−0.1593 (13)
C(26)	0.0502 (18)	0.0540 (13)	0.1952 (18)
C(37)	0.4631 (14)	0.2552 (15)	0.4128 (14)
C(8)	0.5277 (15)	0.3024 (15)	−0.2457 (15)
C(16)	−0.2132 (14)	0.4735 (12)	0.4623 (15)
C(27)	0.2554 (16)	−0.0694 (12)	0.4997 (17)
C(7)	0.5255 (15)	0.2520 (15)	−0.1389 (15)
C(3)	−0.0382 (15)	0.3403 (14)	0.0166 (14)
C(17)	0.0662 (16)	0.2523 (14)	0.6930 (14)
C(9)	0.4139 (18)	0.3684 (15)	−0.2562 (14)

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for $Tp'W(CO)(PhC{\equiv}CMe)H$ (10)

W(1)–N(31)	2.235 (10)	W(1)–N(21)	2.220 (10)
W(1)–C(2)	2.033 (13)	W(1)–C(1)	1.913 (14)
W(1)–N(11)	2.262 (11)	C(2)–C(4)	1.325 (16)
W(1)–C(4)	2.013 (13)	O(1)–C(1)	1.176 (17)
N(31)–W(1)–C(2)	125.6 (4)	N(11)–W(1)–C(4)	166.1 (5)
N(31)–W(1)–N(21)	84.4 (4)	N(11)–W(1)–N(21)	79.9 (4)
N(31)–W(1)–C(1)	164.3 (5)	C(4)–W(1)–C(1)	107.3 (6)
C(2)–W(1)–N(11)	154.9 (4)	C(4)–C(2)–C(3)	139.6 (13)
C(2)–W(1)–C(4)	38.2 (5)	C(2)–C(4)–C(5)	134.0 (13)
C(2)–W(1)–C(1)	69.1 (5)	W(1)–C(1)–O(1)	177.8 (12)

The infrared spectra of complexes **10** and **11** show single terminal ν(CO) absorptions at 1877 and 1865 cm^{-1}, respectively. Unique resonances for each pyrazole ring of the Tp' ligands in the NMR spectra of **10** and **11** indicate an unsymmetrical environment for the Tp' ligands, consistent with chirality at the metal center due to a distinct ligand trans to each nitrogen.

The ^{13}C NMR chemical shifts of the alkyne carbons are observed in the range 217–208 ppm, compatible with a four-electron-donor description invoking donation from both $\pi_\parallel$ and $\pi_\perp$. Observation of two distinct $\equiv C{-}CH_3$ environments in the spectrum of **11** suggests a static alkyne orientation in solution at room temperature.

Perhaps the most intriguing feature of the ^1H NMR spectra is the fact that the hydride resonances are observed suprisingly far downfield (δ 10.8 (**10**) and δ 9.8 (**11**)) with large one-bond $J(^{183}WH)$ coupling constants (ca. 115 Hz). Although hydride signals are most commonly found upfield of Me_4Si, this is not always the case. For example, Chisholm and co-workers[26] reported that the static, ter-

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Table VI. IR and ^1H NMR Data for the Complexes

	IR/cm^{-1}	^1H NMR δ/ppm
$[NEt_4][TpW(CO)_3]$ (1)[a]	1883, 1750	7.76 (s, br, 3 H, Tp CH), 7.67 (s, br, 3 H, Tp CH), 6.13 (m, 3 H, Tp CH), 3.1 [q, 8 H, $N(CH_2CH_3)_4$], 1.15 [m, 12 H, $N(CH_2CH_3)_4$]
$[NEt_4][Tp^IW(CO)_3]$ (2)[a]	1877, 1741[b]	5.75 (s, 3 H, Tp^I CH), 3.14 [q, 8 H, $N(CH_2CH_3)_4$], 2.44 (s, 9 H, Tp^I CH_3), 2.17 (s, 9 H, Tp^I CH_3), 1.2 [m, 12 H, $N(CH_2CH_3)_4$]
$[NEt_4][Tp^{II}W(CO)_3]$ (3)[a]	1887, 1756	7.79 [d, J(HH) = 2 Hz, 3 H, Tp^{II} CH], 7.64–7.27 (m, 15 H, Ph), 6.26 [d, J(HH) = 2 Hz, 3 H, Tp^{II} CH], 3.14 [q, 8 H, $N(CH_2CH_3)_4$], 1.18 [m, 12 H, $N(CH_2CH_3)_4$]
$[NEt_4][Tp^{III}W(CO)_3]$ (4)[a]	1882, 1746	7.54 [d, J(HH) = 2 Hz, 3 H, Tp^{III} CH], 6.06 (d, 3 H, Tp^{III} CH), 4.08 [m, 3 H, Tp^{III} $CCH(CH_3)_2$], 3.15 [q, 8 H, $N(CH_2CH_3)_4$], 1.20 [m, 30 H, $N(CH_2CH_3)_4$ and Tp^{III} $CCH(CH_3)_2$]
$[NEt_4][Tp^{IV}W(CO)_3]$ (5)[a]	1903, 1770	3.14 [q, 8 H, $N(CH_2CH_3)_4$], 1.19 [m, 12 H, $N(CH_2CH_3)_4$]; isomer A, 7.60, 7.50, 6.22, 5.93 [d, J(HH) = 2 Hz, 1:2:1:2, Tp^{IV} CH], 1.55, 1.24 (s, 9:18, Tp^{IV} CCH_3); isomer B, 7.54, 7.29, 6.16, 5.88 [d, J(HH) = 2 Hz, 1:2:1:2, Tp^{IV} CH], 1.45, 1.36 (s, 18:9, Tp^{IV} CCH_3)
$[TpW(CO)_3H]$ (6)[c]	1997, 1908, 1883	7.9 (s, 3 H, Tp CH), 7.6 (s, 3 H, Tp CH), 6.2 (s, 3 H, Tp CH), −2.45 [s, $J(^{183}WH)$ = 9 Hz, 1 H, W–H]
$[Tp^IW(CO)_3H]$ (7)[c]	1993, 1904, 1867	5.89 (s, 3 H, Tp^I CH), 2.57 (s, 9 H, Tp^I CH_3), 2.33 (s, 9 H, Tp^I CH_3), −2.42 [s, $J(^{183}WH)$ = 6 Hz, 1 H, W–H]
$[Tp^{II}W(CO)_3H]$ (8)[c]	1988, 1893, 1875	7.78 [d, J(HH) = 2 Hz, 3 H, Tp^{II} CH], 7.4–7.3 (m, 15 H, Tp^{II} Ph), 6.31 (d, 3 H, Tp^{II} CH), −2.98 [s, $J(^{183}WH)$ = 7 Hz, 1 H, W–H]
$[Tp^{III}W(CO)_3H]$ (9)[c]	1997, 1908, 1872	7.59 [d, J(HH) = 2 Hz, 3 H, Tp^{III} CH], 6.16 (d, 3 H, Tp^{III} CH), 3.85 [sept, J(HH) = 7 Hz, 3 H, Tp^{III} $CCH(CH_3)_2$], 1.32 [d, 18 H, Tp^{III} $CCH(CH_3)_2$], −2.26 [s, $J(^{183}WH)$ = 4 Hz, 1 H, W–H]
$[Tp^IW(CO)(MeC{\equiv}CMe)H]$ (11)[d]	1865	9.80 [s, $J(^{183}WH)$ = 116 Hz, 1 H, W–H], 6.05, 5.78, 5.76 (1:1:1, Tp^I CH), 3.12, 2.80 (3:3, $CH_3C{\equiv}CCH_3$), 2.65, 2.49, 2.41, 2.29, 2.18, 1.52 (3:3:3:3:3:3, Tp^I CCH_3)

[a] Conditions: IR, CH_3CN; NMR, CD_3CN, 25 °C. [b] Cf. ref 2: IR (CH_3CN) 1881, 1744 cm^{-1}. [c] Conditions: IR, CH_2Cl_2; NMR, CD_2Cl_2, 25 °C. [d] Conditions: IR KBr; NMR, CD_2Cl_2, 25 °C.

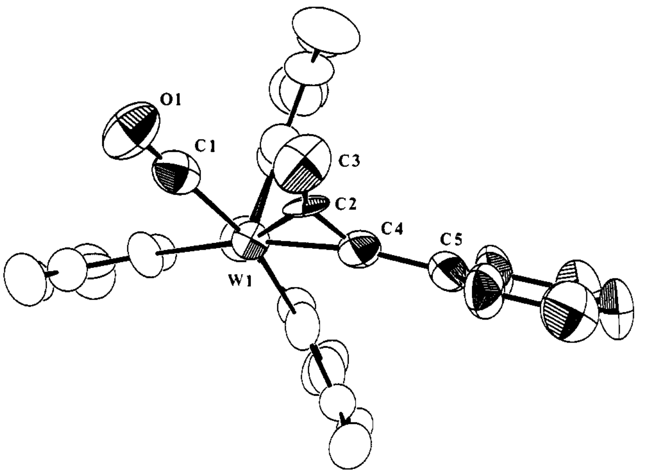

Figure 4. ORTEP plot of $Tp^IW(CO)(PhC{\equiv}CMe)H$ (**10**).

minal W-H group in the complex $W_2(\mu\text{-}C_4Me_4)(\mu\text{-}CPh)(O^iPr)_4H$ exhibits a ^1H NMR resonance at 20.4 ppm. It has generally proved difficult to rationalize the chemical shifts of individual hydride complexes.

The structure of the complex $Tp^IW(CO)(PhC{\equiv}CMe)H$ (**10**) was determined by single-crystal X-ray diffraction. An ORTEP drawing of **10** is shown in Figure 4. Data collection parameters are shown in Table I. Atomic coordinates are listed in Table IV, and selected bond distances and angles are listed in Table V.

In a vertical projection the alkyne and carbonyl ligands lie between two pyrazole rings. The hydride ligand was not located. The angles between adjacent pyrazole planes are 132.2 (3), 120.0 (3), and 107.7 (3)°, accommodating the alkyne, the carbonyl, and presumably the hydride ligands, respectively. In general the structural features of **10** appear similar to those of $CpML(RC{\equiv}CR)X$ derivatives. The consistency of four-electron-donor M–C bond distances has been noted, and complex **10** proves no exception to this observation.[27] The phenyl substituent of the alkyne ligand lies up toward the Tp^I ligand. The W–C(alkyne) bond lengths lie well within the 2.03 ± 0.03 Å range observed for the majority of other Mo(II) and W(II) four-electron-donor alkyne complexes. The C(2)–C(4) alkyne bond length (1.325 (16) Å) and the $C{\equiv}C{-}R$ bond angles (134.0 (13) and 139.6 (13)°) are also compatible with those of similar compounds. As with all previously reported group 6 metal d^4 $CpM(CO)(RC{\equiv}CR)X$ derivatives, the alkyne ligand lies cis to the CO and parallel to the M–CO axis. This orientation optimizes the π-acid and π-donor interactions of the alkyne with the tungsten $d\pi$ orbitals, while the CO can interact with both filled $d\pi$ orbitals.

The royal blue cationic $[Tp^IW(CO)(RC{\equiv}CMe)(N{\equiv}CMe)][BF_4]$ complexes can be cleanly regenerated by HBF_4 protonation of **10** or **11** in acetonitrile solution. In contrast, acidification of $Tp^*W(CO)_3H$ complexes in acetonitrile fails to yield clean tungsten(II) carbonyl products.

Summary and Conclusions

As part of his seminal contribution to the field of poly(pyrazolyl)borate chemistry, Trofimenko was the first to synthesize anionic tris(pyrazolyl)borate group 6 metal tricarbonyl complexes. We have attempted to supplement this work, specifically focussing on the ^1H NMR spectral and solid-state structural properties of the 7-coordinate hydride complexes $Tp^*W(CO)_3H$. We observed unusually small $^1J(^{183}WH)$ values in the ^1H NMR spectra of these complexes. A single-crystal X-ray diffraction study of the complex $Tp^IW(CO)_3H$ indicated that a 3:3:1 geometry with C_{3v} symmetry is not adopted in the solid state. The structure is best described as either a 4:3 piano stool or a capped trigonal prism.

Reaction of $[Tp^IW(CO)(PhC{\equiv}CMe)(N{\equiv}CMe)][BF_4]$ with $Na[BH_4]$ at room temperature yields the related

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hydride complex $[Tp^{I}W(CO)(PhC{\equiv}CMe)H]$. This contrasts sharply with the low-temperature reaction with $Li[BHEt_3]$, where azavinylidene formation is observed. The structure of this rare example of a group 6 d^4 alkyne hydride complex was confirmed by X-ray diffraction. In contrast to the $Tp^{*}W(CO)_3H$ complexes, the $^1J(^{183}WH)$ coupling constants for the alkyne derivatives are quite large, while the ^1H NMR chemical shifts for the hydride ligands are unusually low. A difference in reactivity is evident as well. Protonation of $Tp^{I}W(CO)(RC{\equiv}CMe)H$ yields tungsten(II) products that retain the $Tp^{I}W(CO)(RC{\equiv}CMe)$ unit, while $Tp^{*}W(CO)_3H$ complexes resist protonation and loss of H_2 does not occur.

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Supplementary Material Available: Tables of anisotropic temperature factors, complete bond distances and angles, and calculated hydrogen positions for 7 and 10, as well as an ORTEP drawing of 7 and a PLUTO drawing of 10 with the complete atomic numbering schemes (10 pages); listings of observed and calculated structure factors for 7 and 10 (35 pages). Ordering information is given on any current masthead page.

Formation of Iron Carbonyl Complexes of Reactive Polyenes from Dihalides Involves the Free Polyene

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Iron carbonyl complexes of reactive polyenes are commonly prepared by reaction of dihalides with iron carbonyl reagents. In the case of *o*-xylylene, reaction of iron carbonyl reagents with 1,2-bis(halomethyl)benzenes generally forms tricarbonyl(5-8-η^4-*o*-xylylene)iron, but in poor yields. This results from formation of free *o*-xylylene, which predominantly eludes trapping by the iron carbonyl and forms dimers and oligomers. Formation of free *o*-xylylene is also supported by trapping with norbornene to form the Diels–Alder adduct at the expense of iron complex. Results from the dibromobenzocyclobutene and -cyclopentene systems support the analogous formation of free benzocyclobutadiene and 2*H*-indene upon reaction with iron carbonyls. Significant improvements in yield of the *o*-xylylene complex result when the reaction is run by using disodium tetracarbonylferrate under heterogeneous conditions or by using $Fe_2(CO)_8^{2-}$ in solution.

Stabilization of reactive polyenes through coordination to transition metals has been a paradigm of organometallic chemistry at least since the report of tricarbonyl(cyclobutadiene)iron in 1965.[1] Because of the reactivity of the free polyenes, derivatives such as dihalides have often been used as precursors to the transition-metal complexes, reaction with the iron carbonyl reagent resulting (somehow) in both dehalogenation and complexation. Yields in such reactions are highly variable, but there is little information in the literature on the reason(s) for the variability, which presumably involve the mechanism of the reaction. We here report some relevant results for the *o*-xylylene system and also for the related 2*H*-indene and benzocyclobutadiene systems.

Table I. Reported Yields of 2 from Reaction of 3 with Iron Carbonyls

reagent	solvent	temp, °C	yield of 2, %	ref
$Fe_2(CO)_9$	ether	35	6	4a
$Fe_2(CO)_9$	THF	22	4	8
$Fe(CO)_5$, Me_3NO	benzene	0–80	4	4b
$Na_2Fe(CO)_4$	?	?	35	9
$(R_4N)_2Fe(CO)_4$[a]	toluene/water	20	25	10
$Na_2Fe(CO)_4$[b]	THF	30	34	11

[a] Generated in situ from NaOH and $Fe(CO)_5$ under phase-transfer conditions, using $Bu_4N^+HSO_4^-$. [b] This paper also reported isolation, in 25% yield, of tetracarbonyl-2-ferraindane, convertible into 2 by refluxing at 80 °C or photolysis. This tetracarbonyl is a plausible intermediate in formation of 2, but we, like all previous workers, have seen no sign of it in any of our reactions.

Organic derivatives of *o*-xylylene (1) (also called *o*-quinodimethane; Chemical Abstracts name 5,6-dimethylene-1,3-cyclohexadiene) have enjoyed extensive use in organic synthesis[2,3] because of their high reactivity as Diels–Alder dienes. They have been generated for synthetic purposes by several means,[2] but notably absent from the commonly used precursors to *o*-xylylenes are transition-metal complexes. The tricarbonyliron complex of *o*-xylylene (2) has been known since 1967,[4] and many other complexes of *o*-xylylenes with iron[5] and with other tran-

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(1) Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131–3. Many subsequent uses of this reaction are cited by J. M. Landesberg in: Koerner von Gustorf, E. A.; Grevels, F.-W.; Fischler, I.; Eds., *The Organic Chemistry of Iron*; Academic Press: New York, 1978; Vol. I, pp 627–51.

(2) Reviews of *o*-xylylene chemistry: (a) Charlton, J. L.; Alauddin, M. M. *Tetrahedron* **1987**, *43*, 2873–89. (b) Wiersum, U. E. *Aldrichimica Acta* **1981**, *14*, 53–8. (c) Oppolzer, W. *Synthesis* **1978**, 793–802. (d) Physical studies of 1 are conveniently summarized by R. Schulz and A. Schweig in: Liebman, J. F.; Greenberg, A. *Structure and Reactivity*; VCH Publishers: Weinheim, Germany, 1988; pp 300–304. (e) The NMR spectrum of 1 in solution has recently been observed by an ingenious flow experiment: Trahanovsky, W. S.; Chou, C.-H.; Fischer, D. R.; Gerstein, B. C. *J. Am. Chem. Soc.* **1988**, *110*, 6579–81.

(3) Some recent synthetic applications of *o*-xylylene chemistry include: Nemoto, H.; Fujita, S.; Nagai, M.; Fukumoto, K.; Kametani, T. *J. Am. Chem. Soc.* **1988**, *110*, 2931–8. Jung, M. E.; Brown, R. W.; Hagenah, J. A.; Strouse, C. E. *Tetrahedron Lett.* **1984**, *25*, 3659–62. Ito, Y.; Amino, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1983**, *105*, 1586–90. Mann, J.; Piper, S. E. *J. Chem. Soc., Chem. Commun.* **1982**, 430–2.

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