Seven-Coordinate Tungsten(II) Hydridotris(3,5-dimethylpyrazolyl)borate Tricarbonyl Phosphine Complexes with a Capped Octahedral Geometry

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A series of cationic tungsten(II) hydridotris(3,5-dimethylpyrazolyl)borate phosphine complexes of the type $[Tp'W(CO)_3L][PF_6]$ ($L = PMe_3$, PEt_3, PPh_3, PMe_2Ph) have been synthesized by oxidation of the $Tp'W(CO)_3$ radical with ferrocenium followed by addition of phosphine. These new complexes have been characterized by IR, ^1H and ^{13}C NMR, and elemental analyses. In addition, single-crystal X-ray diffractometry was used to structurally characterize two of the complexes, $[Tp'W(CO)_3PMe_3][PF_6]$ and $[Tp'W(CO)_3PMe_2Ph][PF_6]$. Crystals of the former are of the orthorhombic space group *Pnma*, $Z = 4$, with unit cell dimensions of $a = 15.491$ (3), $b = 11.641$ (2), and $c = 16.783$ (2) Å. Refinement of 233 variables led to $R = 2.9\%$ and $R_w = 3.7\%$ over 1975 reflections. The latter crystallized in the orthorhombic space group *Pmnb*, $Z = 4$, with unit cell dimensions $a = 10.852$ (1), $b = 12.604$ (3), and $c = 24.323$ (9) Å. Refinement of 230 variables led to $R = 4.8\%$ and $R_w = 5.1\%$ over 1452 reflections.

Introduction

Seven-coordination dominates the chemistry of d^4 complexes of molybdenum and tungsten.[1] In the absence of one or more strong π-donor ligands, the applicability of the 18-electron rule to metal carbonyl derivatives promotes $L_5M(CO)_2$ and $L_6M(CO)$ formulations for molybdenum(II) and tungsten(II) monomers. Capped octahedral geometries are commonly found for d^4 monomers containing carbonyl ligands in the coordination sphere.[1f] Two nice examples of capped octahedral geometries are $[WBr_3(CO)_4]^-$ [1i] and $[WBr_2(CO)_4]_2$.[1j] Examples of the capped octahedral geometry in complexes containing a tridentate ligand are much less common. The energy surfaces connecting different 7-coordinate geometries are often soft, and fluxional processes are common in solution.[2]

Quantitative assessments of the degree of distortion from standard reference structures have been proposed, and extension of the dihedral angle method of Muetterties and Guggenberger[3] to inequivalent ligand systems by Kouba and Wreford[4] has systematized geometric analysis. Of the three idealized geometries considered by Kouba and Wreford in their brief but lucid analytical discussion (pentagonal bipyramid, D_{5h}; capped octahedron, C_{3v}; capped trigonal prism, C_{2v}), the capped octahedron was identified as the least common experimental structure. Such a geometry is attractive as an intermediate along isomerization reaction coordinates for fluxional molecules,[5] and unambiguous examples of C_{3v} ground states help to fill the gap in the geometric progression from D_{5h} through C_{3v} to C_{2v} descriptions.

Molybdenum and tungsten complexes of hydridotris(pyrazolyl)borate (Tp) and hydridotris(3,5-dimethylpyrazolyl)borate (Tp′) (Chart I) display some similarities to their cyclopentadienyl analogs.[6] But in contrast to the numerous 7-coordinate structures in the literature for cyclopentadienyl derivatives of general formula $CpML_4$,[7] few simple 7-coordinate complexes have been structurally characterized for the Tp and Tp′ systems. For example, although 7-coordinate $CpMo(CO)_3R$[8] compounds have been known for many years, the Tp and Tp′ analogs are not accessible, and rather exist as the η^2-acyl isomers $Tp(CO)_2Mo(\eta^2\text{-}C(O)R)$.[9] Seven-coordinate group VI complexes containing both a Tp ligand and carbonyl ligands include $TpW(CO)_3H$,[10] $TpW(CO)_2(CS)I$,[11] and $TpMo(CO)_3X$ ($X = Br$, I).[12] In the Tp′ system $Tp'M(CO)_3H$,[10] $Tp'W(CO)_3I$,[13] and $Tp'W(CO)_2(S_2CNEt_2)$[14] have been synthesized.

The 7-coordinate Cp complexes $CpM(CO)_2LX$ ($X = Cl$, Br, I; $L = PR_3$, CO; $M = Mo$, W) have been shown by single-crystal X-ray structure determinations[15] to adopt a 4:3 geometry in the solid state. ^{13}C NMR,[16] ^1H NMR, and IR[17] spectra are compatible with retention of the 4:3 structure in solution at room

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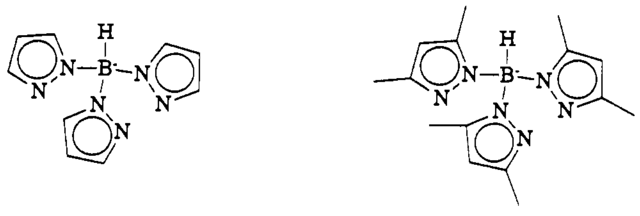
Chart I



Tp Tp′

temperature. For the tricarbonyl molecules, two carbonyl resonances are seen in the ^{13}C NMR spectra in a 2:1 ratio, consistent with a complex having C_s symmetry. The IR spectra of these complexes display three absorption bands in the carbonyl region both in the solid state and in solution, also consistent with C_s symmetry, where three normal modes (2a′ + a″) are anticipated for carbonyl stretching vibrations.

The previously reported 7-coordinate Tp and Tp′ complexes which have been structurally characterized ($TpMo(CO)_3Br$[12a] and $Tp'W(CO)_3H$[18]) can be described as adopting a 4:3 piano stool geometry in the solid state as well as in solution. Curtis and Shiu have shown by ^{1}H NMR spectroscopy that $TpMo(CO)_3X$ (X = H, Br, I) exhibits fluxional behavior in solution. They proposed that the complexes pass through a 3:3:1 capped octahedral intermediate with X as the capping atom.[12a] An EHMO calculation in the same report indicated that the 3:3:1 geometry with X as the capping atom should lie only 4.6 kcal/mol above the 4:3 geometry as opposed to the value of 24 kcal/mol reported for the analogous Cp system.[5] $Tp'W(CO)_3I$ has also been shown to be fluxional at room temperature on the NMR time scale.[13] The above Tp and Tp′ complexes all show three IR bands both in solution and in the solid state, which is characteristic of the 4:3 piano stool geometry. An X-ray structure of $TpMo(CO)_3Br$[12a] confirmed the 4:3 geometry with the three nitrogens for the Tp ligand defining the plane with three donor atoms.

The role of group VI d^4 metal centers in our research program with Tp′ ligands led us to attempt the synthesis of additional examples of 7-coordinate group VI Tp′ complexes. We now report the synthesis of new 7-coordinate complexes of the type $[Tp'W(CO)_3L]^+$ (L = PMe_3, PMe_2Ph, PEt_3, PPh_3). The PMe_3 and PMe_2Ph derivatives adopt a beautifully symmetrical simple capped octahedral structure in the solid state and appear to maintain this geometry in solution according to IR and ^{1}H and ^{13}C NMR spectra. Spectroscopic data suggest that the PEt_3 derivative follows the C_{3v} pattern, but the spectral properties for the PPh_3 derivative indicate a unique structure in this series of phosphine complexes. Perhaps the PPh_3 derivative adopts the more common piano stool geometry.

Experimental Section

Materials and Procedure. All manipulations were performed under an atmosphere of prepurified N_2 by utilizing standard Schlenk techniques. $[Et_4N][Tp'W(CO)_3]$[10] and ferrocenium hexafluorophosphate ($FcPF_6$)[19] were prepared according to literature procedures. Phosphines were used as received. CH_2Cl_2 was distilled from P_2O_5. THF, diethyl ether (Et_2O), and hexane were distilled from sodium benzophenone ketyl. Acetonitrile was distilled from CaH_2 prior to use.

Infrared spectra were recorded on a Mattson Polaris spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 400-MHz FT spectrometer. Elemental analyses were performed by Atlantic Microlab Inc.

Syntheses. $Tp'W(CO)_3^{\bullet}$ (1). In a synthesis similar to that for the molybdenum analog described by Shiu and co-workers,[20] $[Et_4N][Tp'W(CO)_3]$ (2.23 g, 3.22 mmol) was stirred as a slurry in acetonitrile. $FcPF_6$ (1.07 g, 3.22 mmol) was added, and the mixture was stirred for 30 min. The solution was filtered, and the remaining orange solid was washed several times with acetonitrile and then Et_2O to leave an orange powder (1). Yield: 80%. IR (CH_2Cl_2): ν_{CO} 1983, 1854 (b) cm^{-1}. IR (KBr): ν_{CO} 1979, 1839 (b) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ (ppm) 39.6 (s, 9 H, Tp′ C*H*$_3$), 4.6 (s, 9 H, Tp′ (C*H*$_3$), 2.5 (s, 3 H, Tp′ *H*). Anal. Calcd for $WBC_{18}H_{22}N_6O_3$: C, 38.27; H, 3.92; N, 14.87. Found: C, 36.87;[21] H, 3.98; N, 14.91.

$[Tp'W(CO)_3(PMe_3)][PF_6]$ (2). Solid **1** (1.0 mmol, 0.56 g) was dissolved in CH_2Cl_2 (25 mL). Solid $FcPF_6$ (1.0 mmol, 0.33 g) was stirred into the solution. After 2 min, an excess of PMe_3 was slowly added dropwise and an orange-brown solution formed. Solvent was evaporated under vacuum to leave a brown powder, which was washed with Et_2O until the supernatant was clear. The resultant orange-brown powder was recrystallized by slow diffusion of Et_2O into a concentrated CH_2Cl_2 solution to yield yellow-orange X-ray-quality crystals. Yield: 74%. IR (CH_2Cl_2): ν_{CO} 2040 (vw), 1943 (vs) cm^{-1}. IR (KBr): ν_{CO} 2036 (vw), 1933 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ (ppm) 2.30 (s, 9 H, Tp′ C*H*$_3$), 2.44 (s, 9 H, Tp′ C*H*$_3$), 2.49 (d, $^2J_{P-H}$ = 10.6 Hz, 9 H, PC*H*$_3$), 6.09 (s, 3 H, Tp′ *H*). ^{13}C NMR (CD_2Cl_2): δ (ppm) 13.0, 16.2 (s, Tp′ *C*H$_3$), 21.7 (d, $^1J_{P-C}$ = 41 Hz, P*C*H$_3$), 108.9 (s, Tp′ *C*H), 142.3, 152.5 (s, Tp′ *C*Me), 224.6 (d, $^2J_{P-C}$ = 34 Hz, $^1J_{W-C}$ = 135 Hz, *C*O). Anal. Calcd for $WBC_{21}O_3N_6H_{31}P_2F_6$: C, 32.08; H, 3.98; N, 10.69. Found: C, 31.90; H, 4.03; N, 10.49.

$[Tp'W(CO)_3(PMe_2Ph)][PF_6]$ (3). Solid **1** was dissolved in CH_2Cl_2 (25 mL). Solid $FcPF_6$ was stirred into the solution under N_2. After 2 min, excess PMe_2Ph was added dropwise. The color of the mixture changed from green-brown to orange. The product was precipitated as an orange solid by addition of Et_2O, and it was isolated by filtration. The product was recrystallized twice from CH_2Cl_2/Et_2O, the second recrystallization yielding X-ray-quality crystals. Yield: 68%. IR (CH_2Cl_2): 2041 (vw), 1951 (vs), 1939 (vs) cm^{-1}. IR (KBr): ν_{CO} 2043 (w), 1961 (s), 1915 (vs). ^{1}H NMR (CD_2Cl_2): δ (ppm) 2.01, 2.41 (s, 9 H, Tp′ C*H*$_3$), 2.80 (d, $^2J_{P-H}$ = 10.3 Hz, 6 H, PC*H*$_3$), 6.04 (s, 3 H, Tp′ *H*), 7.4–7.8 (m, 5 H, P*Ph*). ^{13}C NMR (CD_2Cl_2): δ (ppm) 13.0, 15.5 (s, Tp′ *C*H$_3$), 21.2 (d, $^1J_{P-C}$ = 42 Hz, P*C*H$_3$), 108.9 (s, Tp′ *C*H), 129–135 (P*Ph*), 148.3 and 152.6 (s, Tp′ *C*CH$_3$), 226.1 (d, $^2J_{P-C}$ = 33 Hz, *C*O). Anal. Calcd for $WBN_6C_{26}H_{33}O_3P_2F_6$: C, 36.78; H, 3.92; N, 9.90. Found: C, 36.24; H, 3.94; N, 9.44.

$[Tp'W(CO)_3PPh_3][PF_6]$ (4). Solid **1** (0.56 g, 1.0 mmol) was dissolved in CH_2Cl_2 (25 mL). One equivalent of $FcPF_6$ (0.33 g, 1.0 mmol) was added, and the mixture was allowed to stir for 2 min. A slight excess of PPh_3 (0.27 g, 1.1 mmol) was then added to the mixture, which turned from a green-brown mixture to a clear orange-brown solution. Removal of some of the solvent under vacuum followed by addition of Et_2O yielded an orange solid. The solid was rapidly recrystallized twice with CH_2Cl_2/Et_2O to produce an orange crystalline material. Yield: 60%. IR (CH_2Cl_2): ν_{CO} 2049 (s), 1966 (vs), 1916 (m). IR (KBr): ν_{CO} 2055 (s), 1961 (vs), 1911 (vs). Anal. Calcd for $WBN_6C_{36}H_{37}O_3P_2F_6$: C, 44.47; H, 3.89; N, 8.51. Found: C, 44.25; H, 3.84; N, 8.64.

$[Tp'W(CO)_3(PEt_3)][PF_6]$ (5). Solid **1** (0.22 g, 0.39 mmol) was dissolved in CH_2Cl_2. $FcPF_6$ (0.13 g, 0.39 mmol) was added, and the reaction mixture was stirred for 2 min, followed by a dropwise addition of PEt_3, which caused a color change from green-brown to orange. The solvent was evaporated under vacuum, leaving an orange oil, which was washed with Et_2O until the supernatant was clear. The resultant orange solid was recrystallized from CH_2Cl_2/Et_2O and then acetone/Et_2O, to leave a yellow crystalline product. Yield: 80%. IR (CH_2Cl_2): ν_{CO} 2036, 1944 (vs) cm^{-1}. IR (KBr): ν_{CO} 1918 (vs) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ (ppm) 6.09 (s, 3 H, Tp′ *H*), 2.81 (quintet, $^2J_{P-H}$ = $^3J_{H-H}$ = 8 Hz, 6 H, PC*H*$_2$CH$_3$), 2.43 and 2.35 (s, 9 H, Tp′ C*H*$_3$), 1.45 (d of t, $^3J_{P-H}$ = 17.3 Hz, $^3J_{H-H}$ = 8 Hz, 9 H, PCH$_2$C*H*$_3$). ^{13}C NMR (CD_2Cl_2): δ (ppm) 227.2 (d, $^2J_{P-C}$ = 32 Hz, *C*O), 152.7 and 148.3 (s, Tp′ *C*CH$_3$), 109.1 (s, Tp′ *C*H), 26.3 (d, $^1J_{P-C}$ = 33 Hz, P*C*H$_2$CH$_3$), 16.4 and 13.1 (s, Tp′ *C*H$_3$), 9.9 (d, $^2J_{P-C}$ = 7 Hz, PCH$_2$*C*H$_3$). Anal. Calcd for $WBP_2H_{37}C_{24}N_6F_6O_3$: C, 34.65; H, 4.52; N, 10.17. Found: C, 34.72; H, 4.49; N, 10.08.

X-ray Diffraction Data Collection for $[Tp'W(CO)_3(PMe_3)][PF_6]$ (2) and $[Tp'W(CO)_3(PMe_2Ph)][PF_6]$ (3). Crystals of **2** and **3** were each

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[21] Elemental analysis was attempted several times, and the carbon content was always too low while the nitrogen and hydrogen contents were within the accepted range. We attribute this to the formation of tungsten carbide during the combustion process.

Table I. Crystallographic Data Collection Parameters

	$[Tp'W(CO)_3PMe_3][PF_6]$	$[Tp'W(CO)_3PMe_2Ph][PF_6]$
chem formula	$WC_{21}H_{31}BF_6N_6O_3P_2$	$WC_{26}H_{33}BF_6N_6O_3P_2$
fw	786.10	848.16
space group	Pnma	Pmnb
a, Å	15.491 (3)	10.852 (1)
b, Å	11.641 (2)	12.604 (3)
c, Å	16.783 (2)	24.434 (9)
Z	4	4
V, Å^3	3026.4 (9)	3327.0 (1)
density calcd, g/cm^3	1.725	1.693
λ, Å	0.709 30	0.709 30
μ, cm^{-1}	40.7	37.1
transm coeff	0.399–0.455	0.763–0.999
R^a	0.029	0.048
$R_w{}^b$	0.037	0.051

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum(w(|F_o| - |F_c|)^2)/\sum w(F_o{}^2)]^{1/2}$.

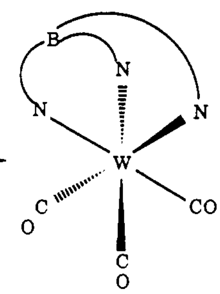
grown at room temperature from CH_2Cl_2/Et_2O solutions. An orange block of the former of dimensions 0.20 × 0.20 × 0.40 mm and an orange block of **3** of dimensions 0.40 × 0.20 × 0.10 mm were selected and mounted on separate glass wands coated with epoxy. All single-crystal X-ray diffraction data were collected at room temperature on a Rigaku AFC6S automated diffractometer. Twenty-five centered reflections found in the region $33.0° < 2\theta < 40.0°$ for **2** and refined by least-squares calculations indicated an orthorhombic cell. For **3**, 25 centered reflections found in the region $25.0° < 2\theta < 35.0°$ and refined by least-squares calculations also indicated an orthorhombic cell. Details of the crystal data are reported in Table I. Diffraction data were collected in the octant $+h,+k,-l$ for **2** and $+h,+k,+l$ for **3** under the conditions specified in Table I. Only data with $I > 2.5\sigma(I)$ were used in the structure solutions and refinements. For **2**, 1975 out of 2791 unique reflections collected were used; for **3**, 1452 out of the 2309 unique reflections collected were used. In both cases, an absorption correction was made. The data were corrected for Lorentz–polarization effects in the final stages of data reduction.

Space group *Pnma* was confirmed for **2**, and the position of the tungsten was deduced from the three-dimensional Patterson function. For **3**, space group *Pmnb* was confirmed and the position of the tungsten 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 using NRCVAX.[22] The asymmetric unit in each structure consists of only half of the molecule with a crystallographic mirror plane relating the halves. The PF_6 anion is disordered in both structures. In **2**, the fluorines were modeled using two sets of six fluorines, each with 50% occupancy. The resulting thermal parameters are not reliable. The PF_6 anion in **3** was represented by a phosphorus atom surrounded by 14 fluorines with occupancies of $^6/_{14}$. There is no obvious fit to octahedra, but examination of pictures indicates rotational disorder about the 3-fold axis.

The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated by using a C–H distance of 0.96 Å and given an isotropic thermal parameter 0.1 greater than that of the associated atom. Final least-squares refinement of **2** resulted in the residuals R = 2.9% and R_w = 3.7%. The final difference Fourier map had no peak greater than 1.68 e/Å^3. For **3**, final least-squares refinement resulted in the residuals R = 4.8% and R_w = 5.1%. The final difference map had no peak greater than 1.13 e/Å^3.

Results and Discussion

I. Synthesis. Oxidation of the anionic tungsten(0) tricarbonyl reagent $Tp'W(CO)_3{}^-$ by ferrocenium generates a neutral 17-electron radical tungsten(I) product (**1**) in relatively high yield (80%) (eq 1). This bright orange complex was purified by washing with CH_3CN and Et_2O to remove ferrocene, the other redox product formed in the reaction, from the desired tungsten complex. As was the case for the Mo product,[20] the $Tp'W(CO)_3$ radical is surprisingly heat-stable. The tungsten product from most preparations slowly decomposes in air to form $Tp'W(CO)_3H$, but on one occasion the radical ignited upon exposure to moist air. The radical has proved to be resistant to ligand substitution; no reaction occurs with triethylphosphine, even in refluxing toluene.

$[Et_4N][Tp'W(CO)_3] \xrightarrow{[Fc][PF_6]}$  (1)

1

The 7-coordinate phosphine complexes (**2**–**5**) were prepared in good yields (60–80%) by further oxidizing the $Tp'W(CO)_3$ radical with ferrocenium. Presumably a cationic 16-electron tungsten(II) intermediate $Tp'W(CO)_3{}^+$ is generated, which may have solvent coordinated in accord with 18-electron-rule guidelines. Although no intermediate has been isolated, a species with carbonyl absorptions at 2117 and 2054 cm^{-1} was observed by IR spectroscopy in the CH_2Cl_2 reaction solution. Addition of phosphine then led to the formation of the 7-coordinate cationic complexes $Tp'W(CO)_3L^+$ (Scheme I).

II. X-ray Crystal Structures of $[Tp'W(CO)_3(PMe_3)][PF_6]$ (2) and $[Tp'W(CO)_3(PMe_2Ph)][PF_6]$ (3). The striking molecular structures of **2** and **3** are shown in Figures 1–4.[23] The coordination sphere of tungsten for both of these complexes can be accurately described as a 3:3:1 capped octahedron. The molecular symmetry is C_{3v} for **2**, including the PMe_3 ligand, and C_s for **3** due to the PMe_2Ph ligand. The Tp′ ligand occupies three coordination sites in a *fac* orientation. The three CO ligands have been pushed up substantially in comparison to the ideal octahedral geometry, with the phosphine ligand decorating the face defined by the three carbonyl ligands. Atomic positional parameters are listed in Tables II (**2**) and III (**3**). Selected intramolecular bond distances and angles are listed in Tables IV and V for **2** and **3**, respectively.

The nicely symmetric 3:3:1 geometry is intuitively attractive for 7-coordinate $Tp'W(CO)_3L$ compounds, but previously reported structures for the neutral complexes $Tp'W(CO)_3H$[18] and $TpMo(CO)_3Br$[12] instead revealed ground-state geometries resembling a 4:3 structure of C_s symmetry. Furthermore, the structures for the related cyclopentadienyl derivative and $(\eta^5\text{-}C_5Ph_4H)Mo(CO)_2(L_2\text{-}P,P')$[24] also correspond to a 4:3 geometry. It is in fact rare for 7-coordination complexes with a tridentate ligand to adopt the 3:3:1 capped octahedral ground-state geometry in the solid state.

The W–CO and W–Tp′ distances and the N–W–N bond angles are all comparable to those of previously reported Tp′–W complexes. The W–P bond distances (**2**, 2.537 (2) Å; **3**, 2.545 (6) Å) are also in the expected range of 2.5–2.6 Å.

Given the unambiguous assignment of the 3:3:1 structural description to both **2** and **3**, it is noteworthy that the δ' angles defined to quantify the degree of distortion[4] are calculated to be δ'_1 = 19.2°, δ'_2 = 17.9°, and δ'_3 = 17.9° for **2** and δ'_1 = 18.9°, δ'_2 = 15.4°, and δ'_3 = 13.5° for **3** where δ'_1 is the angle between the planes defined by C(1)–N(21)–C(1a) and C(1)–P–C(1a), δ'_2 is the angle between the planes defined by C(1)–C(2)–N(11) and C(1)–C(2)–P, and δ'_3 is the angle between the planes defined by C(2)–P–C(1a) and C(2)–C(1a)–N(11a) for the trimethylphosphine complex and δ'_1 is the angle between the planes

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(22) Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

(23) Johnson, C. K. A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1977.

(24) Mao, F.; Philbin, C. E.; Weakley, J. R.; Tyler, D. R. *Organometallics* **1990**, *9*, 1510.

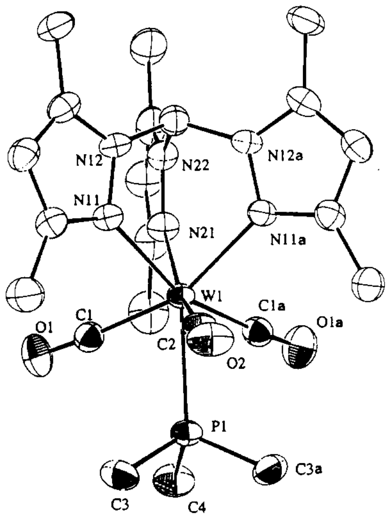


Figure 1. ORTEP diagram of $Tp'W(CO)_3PMe_3^+$.

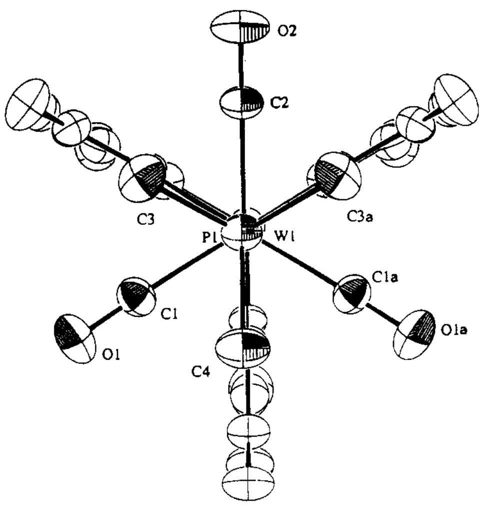
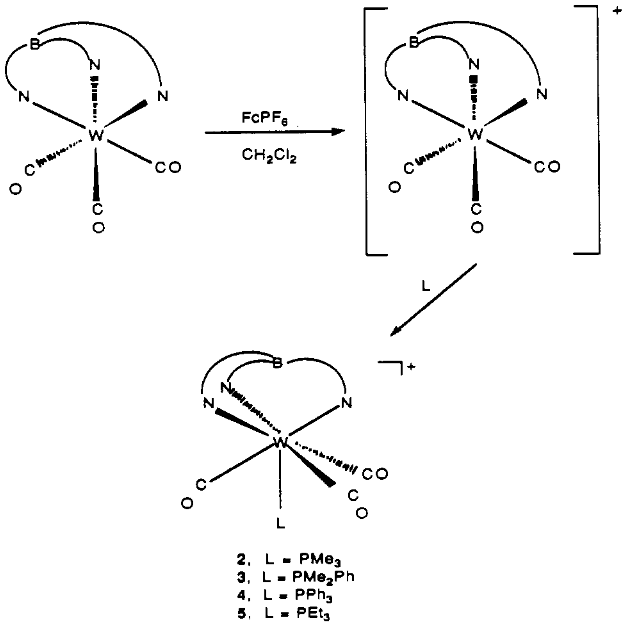


Figure 2. ORTEP diagram of $Tp'W(CO)_3PMe_3^+$ viewed down the C_3 axis (P–W–B).

Scheme I



defined by P–C(1)–C(2a) and C(1)–C(2a)–N(11a), δ'_2 is the angle between the planes defined by P–C(2)–C(2a) and C(2)–C(2a)–N(21), and δ'_3 is the angle between the planes defined by C(1)–C(2)–P and C(1)–C(2)–N(11) for the dimethylphenylphosphine complex after normalization of the metal–ligand bond lengths. These can be compared to the idealized values of 24.2° for δ'_1, δ'_2, and δ'_3 in a C_{3v} reference structure. Indeed the deviation is small, particularly when one recalls that idealized δ_i values of 54.4, 54.4, and −72.8° characterize the D_{5h} structure and 41.5, 0, and 0° are appropriate for a C_{2v} capped trigonal prism.[4]

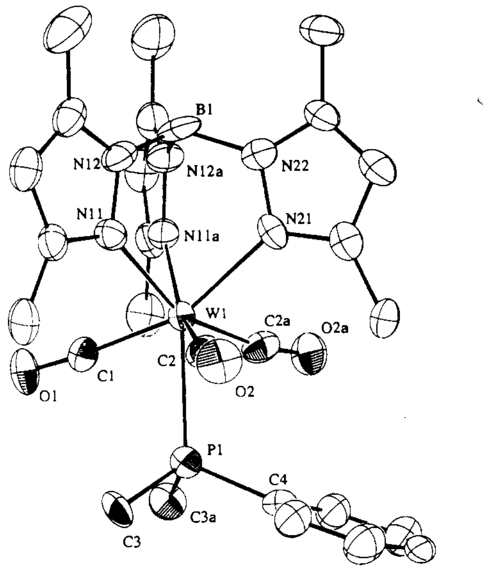


Figure 3. ORTEP diagram of $Tp'W(CO)_3PMe_2Ph^+$.

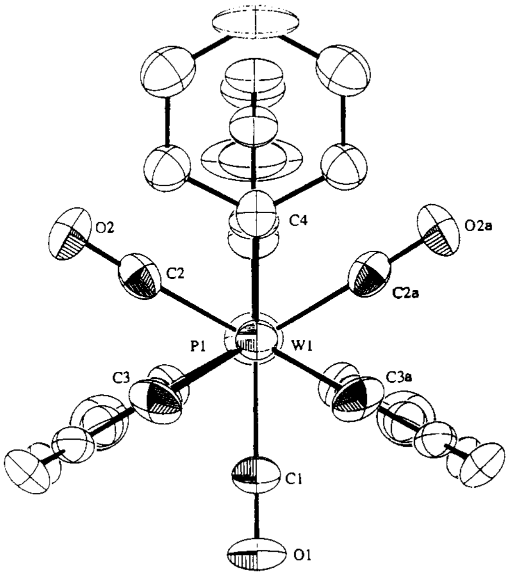


Figure 4. ORTEP diagram of $Tp'W(CO)_3PMe_2Ph^+$ viewed down the P–W–B axis.

III. Spectral Properties. Spectral data for the complexes are listed in Table VI. Figure 5 shows solution IR spectra of the carbonyl stretching region for the $Tp'W(CO)_3$ radical (**1**), $Tp'W(CO)_3^-$, the dimethylphenylphosphine complex (**3**), the triethylphosphine complex (**5**), the triphenylphosphine complex (**4**), and $Tp'W(CO)_3H$. The radical (**1**), the anion, and three of the 7-coordinate complexes (**2**, **3**, and **5**) display solution IR spectra (CH_2Cl_2) with only two carbonyl bands. (The lower energy band is slightly split in the PMe_2Ph case.) The solution infrared spectra of these three phosphine complexes are appropriate for a 3:3:1 structure of C_{3v} symmetry with two carbonyl stretching normal modes ($a_1 + e$). This observation contrasts with structures found for $CpMo(CO)_3PEt_3$,[25] $Tp'W(CO)_3H$,[18] $TpMo(CO)_3Br$,[12] Tp'W-

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[25] Sünkel, K.; Ernst, H.; Beck, W. *Z. Naturforsch.* **1981**, *36B*, 474.

Table II. Atomic Positional and Thermal Parameters for $[TP'W(CO)_3PMe_3][PF_6]$

	x	*y*	*z*	B_{iso}, Å^2
W(1)	0.55068 (1)	0.25	0.67561 (2)	3.14 (2)
C(1)	0.4759 (4)	0.1105 (6)	0.6758 (3)	4.5 (2)
O(1)	0.4339 (3)	0.0309 (5)	0.6694 (3)	7.1 (3)
C(2)	0.6258 (5)	0.25	0.7715 (5)	4.0 (4)
O(2)	0.6727 (4)	0.25	0.8248 (4)	6.1 (3)
P(1)	0.460 (1)	0.25	0.8013 (1)	3.98 (9)
C(3)	0.4754 (4)	0.3726 (6)	0.8656 (4)	5.4 (3)
C(4)	0.3432 (6)	0.25	0.7845 (6)	6.3 (5)
B(1)	0.6689 (7)	0.25	0.5136 (5)	4.5 (4)
N(11)	0.6481 (3)	0.1239 (4)	0.6340 (2)	3.9 (2)
N(12)	0.6883 (3)	0.1420 (4)	0.5622 (2)	4.0 (2)
C(13)	0.7420 (4)	0.0536 (5)	0.5467 (3)	4.7 (3)
C(14)	0.7373 (4)	−0.0211 (5)	0.6094 (4)	5.0 (3)
C(15)	0.6783 (4)	0.0234 (5)	0.6624 (3)	4.4 (3)
C(16)	0.7946 (4)	0.0452 (6)	0.4714 (4)	6.2 (3)
C(17)	0.6501 (4)	−0.0288 (6)	0.7392 (4)	6.2 (3)
N(21)	0.5108 (4)	0.25	0.5481 (4)	4.1 (3)
N(22)	0.5734 (4)	0.25	0.4905 (4)	4.0 (3)
C(23)	0.5361 (8)	0.25	0.4175 (6)	5.9 (5)
C(24)	0.4479 (7)	0.25	0.4290 (6)	6.1 (5)
C(25)	0.4328 (6)	0.25	0.5108 (6)	5.4 (5)
C(26)	0.5904 (9)	0.25	0.3429 (6)	6.7 (6)
C(27)	0.3477 (7)	0.25	0.5516 (7)	6.9 (6)

Table III. Atomic Positional and Thermal Parameters for $[Tp'W(CO)_3PMe_2Ph][PF_6]$

	x	*y*	*z*	B_{iso}, Å^2
W(1)	0.75	0.30247 (7)	0.13191 (3)	3.04 (4)
C(1)	0.75	0.294 (2)	0.2135 (8)	4 (1)
O(1)	0.75	0.295 (2)	0.2605 (5)	6.1 (9)
C(2)	0.598 (2)	0.237 (1)	0.1019 (6)	4.3 (7)
O(2)	0.507 (1)	0.2127 (9)	0.0797 (4)	5.7 (6)
P(1)	0.75	0.1076 (5)	0.1592 (2)	3.8 (3)
C(3)	0.621 (1)	0.068 (1)	0.2003 (6)	5.1 (8)
C(4)	0.75	0.016 (2)	0.0993 (9)	4 (1)
C(5)	0.637 (1)	−0.014 (1)	0.0770 (6)	4.8 (8)
C(6)	0.639 (2)	−0.075 (1)	0.0307 (7)	5.9 (9)
C(7)	0.75	−0.102 (2)	0.0063 (9)	7 (2)
B(1)	0.75	0.550 (2)	0.095 (1)	6 (2)
N(11)	0.615 (1)	0.4291 (8)	0.1479 (4)	3.7 (6)
N(12)	0.632 (1)	0.5289 (9)	0.1280 (5)	4.4 (6)
C(13)	0.540 (2)	0.593 (1)	0.1426 (6)	4.7 (8)
C(14)	0.462 (1)	0.536 (1)	0.1728 (6)	4.8 (8)
C(15)	0.506 (1)	0.434 (1)	0.1752 (6)	4.0 (7)
C(16)	0.534 (2)	0.707 (1)	0.1250 (8)	8 (1)
C(17)	0.448 (2)	0.341 (1)	0.2033 (6)	5.7 (9)
N(21)	0.75	0.375 (1)	0.0483 (6)	5 (1)
N(22)	0.75	0.483 (1)	0.0419 (8)	5 (1)
C(23)	0.75	0.507 (2)	−0.012 (1)	6 (2)
C(24)	0.75	0.415 (2)	−0.0415 (9)	7 (2)
C(25)	0.75	0.332 (2)	−0.004 (1)	5 (1)
C(26)	0.75	0.619 (2)	−0.030 (1)	12 (3)
C(27)	0.75	0.215 (2)	−0.0157 (8)	5 (1)

Table IV. Selected Bond Distances (Å) and Angles (deg) for $[Tp'W(CO)_3PMe_3][PF_6]$ (**2**)

W–C(1)	1.995 (6)	C(1)–O(1)	1.137 (8)
W–C(2)	1.986 (8)	C(2)–O(2)	1.152 (1)
W–P(1)	2.537 (2)	P(1)–C(3)	1.806 (7)
W–N(11)	2.219 (4)	P(1)–C(4)	1.826 (9)
W–N(21)	2.228 (6)		
C(1)–W–C(1a)	109.0 (3)	P(1)–W–N(11)	129.8 (1)
C(1)–W–C(2)	109.8 (2)	P(1)–W–N(21)	130.2 (2)
C(1)–W–P(1)	71.1 (2)	N(11)–W–N(11a)	82.9 (2)
C(1)–W–N(11)	81.8 (2)	N(11)–W–N(21)	83.3 (2)
C(1)–W–N(11a)	159.2 (2)	W–C(1)–O(1)	174.5 (5)
C(1)–W–N(21)	80.8 (2)	W–C(2)–O(2)	176.7 (6)
C(2)–W–P(1)	69.6 (2)	W–P(1)–C(3)	115.0 (2)
C(2)–W–N(11)	81.8 (2)	W–P(1)–C(4)	114.9 (3)
C(2)–W–N(21)	160.3 (3)		

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Tp'W(CO)_3PMe_2Ph][PF_6]$ (**3**)

W–C(1)	1.99 (2)	C(1)–O(1)	1.14 (2)
W–C(2)	1.98 (2)	C(2)–O(2)	1.17 (2)
W–P(1)	2.55 (6)	P(1)–C(3)	1.79 (1)
W–N(11)	2.20 (1)	P(1)–C(4)	1.86 (2)
W–N(21)	2.23 (2)		
C(1)–W–C(2)	110.1 (5)	P(1)–W–N(21)	129.4 (5)
C(1)–W–P(1)	71.6 (7)	N(11)–W–N(11a)	83.6 (4)
C(1)–W–N(11)	82.2 (6)	N(11)–W–N(21)	82.2 (4)
C(1)–W–N(21)	159.0 (8)	W–C(1)–O(1)	175.8 (2)
C(2)–W–C(2a)	112.7 (6)	W–C(2)–O(2)	169.9 (1)
C(2)–W–P(1)	72.3 (4)	W–P(1)–C(3)	114.3 (5)
C(2)–W–N(11)	79.1 (5)	W–P(1)–C(4)	113.4 (7)
C(2)–W–N(11a)	156.9 (5)	C(3)–P(1)–C(3a)	103.1 (8)
C(2)–W–N(21)	80.4 (5)	C(3)–P(1)–C(4)	105.3 (6)
P(1)–W–N(11)	130.8 (3)		

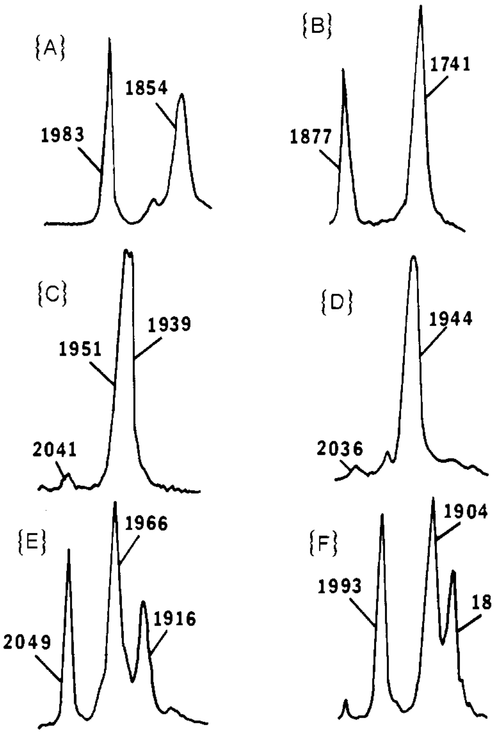

Figure 5. Solution infrared spectra for selected complexes: (A) $Tp'W(CO)_3$; (B) $Tp'W(CO)_3^-$; (C) $Tp'W(CO)_3PMe_2Ph^+$; (D) $Tp'W(CO)_3PEt_3^+$; (E) $Tp'W(CO)_3PPh_3^+$; (F) $Tp'W(CO)_3H$.

$(CO)_3I$,[13] and $CpM(CO)_3X$ (M = W, W, Mo; X = Cl, Br, I),[17] which show three carbonyl bands consistent with a ground-state geometry of lower symmetry such as a 4:3 structure of C_s symmetry with three normal modes (2a′ + a″) for CO stretching. The intensity of the symmetric stretch for **2**, **3**, and **5** is very weak compared to the strong asymmetric absorption. The low intensity for the higher energy band is due to the very small change in the dipole moment of these complexes during the vibration.

Solid-state IR spectra of these complexes are similar to the solution spectra with the exception that the asymmetric band is slightly split for PMe_3, broadened and shifted to lower energy for PEt_3, and split into two distinct bands for PMe_2Ph. It should be noted that the symmetric stretch is so weak that it was not observable in the solid-state IR spectrum for the PEt_3 complex. The broadening or splitting of the lower energy asymmetric stretch in the solid-state IR spectra of **2**, **3**, and **5** may be attributed to solid-state effects splitting the doubly degenerate asymmetric stretch. It should be noted that the PMe_2Ph derivative's degenerate e absorption band is split to a much greater extent than the comparable band in the phosphine derivatives which contain a molecular C_3 axis. Note also that the intensities of the split absorption differ dramatically from intensities in spectra of 4:3 structures such as $Tp'W(CO)_3H$ or the triphenylphosphine derivative.

The triphenylphosphine complex shows an IR spectrum markedly different from those of the other three phosphine

Table VI. Selected IR and NMR Data

complex	IR (CH_2Cl_2) ν_{CO}, cm^{-1}	IR (KBr) ν_{CO}, cm^{-1}	^1H NMR δ, ppm	^{13}C NMR (CO) δ, ppm ($^2J_{P-C}$, Hz)
$Tp'W(CO)_3$	1983, 1854	1979, 1839	Tp′ H: 2.5 Tp′ CH_3: 4.6, 39.6	
$Tp'W(CO)_3PMe_3^+$	2040, 1943	2036, 1933	Tp′ H: 6.09 Tp′ CH_3: 2.44, 2.30	224.6 (34.4)
$Tp'W(CO)_3PMe_2Ph^+$	2041, 1951, 1939	2043, 1961, 1915	Tp′ H: 6.04 Tp′ CH_3: 2.41, 2.01	226.1 (33.1)
$Tp'W(CO)_3PPh_3^+$	2049, 1966, 1916	2055, 1961, 1911		
$Tp'W(CO)_3PEt_3^+$	2036, 1944	1918	Tp′ H: 6.09 Tp′ CH_3: 2.43, 2.35	227.2 (32.0)

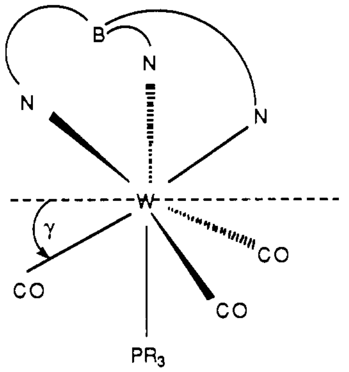

Figure 6. Definition of the angle γ.

complexes. The PPh_3 adduct shows three carbonyl bands in both solution and the solid state with intensities similar to those for $Tp'W(CO)_3H$. This would suggest a 4:3 ground state structure of C_s symmetry in both solution and the solid state similar to that of $Tp'W(CO)_3H$. The change in geometry as a function of phosphine ligand probably has steric origins. In order to adopt a 3:3:1 structure, the bulky triphenylphosphine would have to push the three carbonyls too close to the Tp′ ligand, and the result is evidently adoption of the 4:3 geometry.

An intense absorption near 840 cm^{-1} for each of the solid-state phosphine complexes is assigned to the t_{1u} P–F stretch of the PF_6 anion. An absorption near 1542 cm^{-1} in both the solution and solid-state spectra for each of the complexes is characteristic of the Tp′ ligand.

A ^1H NMR spectrum of **1** showed three proton signals, as expected for Tp′ attached to a molecule with C_{3v} symmetry. This paramagnetic complex shows resonances for the Tp′ *Me* groups that have been shifted downfield considerably (δ = 39.6 and 4.6 ppm) from where they normally appear for diamagnetic complexes (δ = 1–3 ppm). The Tp′ *H* signal has been shifted upfield (δ = 2.5 ppm) from its value for diamagnetic complexes (near δ = 6 ppm).

The ^1H and ^{13}C NMR spectra for **2, 3,** and **5** are also consistent with the 3:3:1 structure of C_{3v} symmetry. This is apparent by the single signal for the Tp′ *H* in the ^1H NMR spectra and the two signals for the Tp′ *Me* groups in both the ^1H and ^{13}C spectra, indicative of equivalent environments for the three pyrazole rings. A single ^{13}C carbonyl resonance, split into a doublet due to phosphorus coupling, is also observed for each of these complexes, indicating that the three carbonyls are magnetically equivalent. The PMe_2Ph derivative could conceivably show a 2:1 pattern for the Tp′ *H* and the Tp′ *Me* signals in its ^1H NMR spectrum, as well as two signals for the carbonyl carbons in its ^{13}C NMR spectrum, due to loss of axial C_3 symmetry because of the phosphine substituents, but rapid rotation about the W–P bond creates an apparent C_{3v} symmetry on the NMR time scale, as expected. Dissociation of the triphenylphosphine complex prohibited us from obtaining meaningful NMR spectra for **4**.

γ-Angle Calculation. The average P–W–C angles obtained from the X-ray structures for **2** and **3** are 70.58 and 72.07°, respectively. The γ-angles (defined in Figure 6) are therefore 19.4 and 17.9° for the two compounds. This would mean that the CO ligands are pushed significantly up toward the Tp′ ligand, which has a formal cone angle of 225°. These features are evident in the ORTEP plots.

Table VII. γ-Angles (deg) As Defined by Figure 6

complex	calcd from IR intensities	found in the solid-state structure
$Tp'W(CO)_3^-$	29	
$Tp'W(CO)_3^•$	35	
$Tp'W(CO)_3PMe_3^+$	10	19.4
$Tp'W(CO)_3PMe_2Ph^+$	21	17.9
$Tp'W(CO)_3PEt_3^+$	~0	
octahedral angle	35	

Theoretical calculations of the γ-angle were done by the method described by Burdett (eq 2).[26] The intensities were obtained by

$$\tan^2 \gamma = I_s/I_a \qquad (2)$$

taking an infrared spectrum and cutting out the peaks for the symmetric (I_s) and asymmetric (I_a) carbonyl stretches. The peaks were weighed, and the γ-angles were calculated.

A γ-angle of 35° is calculated for **1** by this method, compatible with the idealized octahedral γ-angle. Table VII lists the γ-angles calculated from the infrared data and also the γ-angles found in the two X-ray structures. The PMe_2Ph complex has a stronger symmetric absorption than the PR_3 derivatives, possibly due to the loss of overall C_{3v} symmetry. While the agreement is far from quantitative, the qualitative value of structural information derived from relative infrared intensities for the tricarbonyl derivatives reported here is underscored by these calculations.

Summary

Formation of the 17-electron radical $Tp'W(CO)_3$ and a series of 7-coordinate cationic tricarbonyl phosphine complexes has been achieved. Spectral data indicate that three of these phosphine complexes, the PMe_3, PEt_3, and PMe_2Ph derivatives, adopt a 3:3:1 capped octahedral geometry both in solution and in the solid state. In addition, single-crystal X-ray analysis has confirmed this aesthetically pleasing geometry for the PMe_3 and PMe_2Ph derivatives. For steric reasons, the PPh_3 complex prefers the more common 4:3 piano stool geometry. This study again shows that the pyrazolylborate ligand, while similar to the Cp ligand in many ways, creates a new and unique chemistry to explore.

Acknowledgment. We thank the U.S. Department of Energy, Basic Energy Sciences, for generous support of this research (Contract 85ER13430).

Supplementary Material Available: Tables of anisotropic temperature factors and complete bond distances and angles and labeled structural diagrams for **2** and **3** (8 pages). Ordering information is given on any current masthead page.

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[26] Burdett, J. K. *Inorg. Chem.* **1981**, *20*, 2607.