Contribution from Los Alamos National Laboratory, Los Alamos, New Mexico 87545,
and Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Protonation of W(CO)₃(PCy₃)₂

Lori Stepan Van Der Sluys, Kimberly A. Kubat-Martin, Gregory J. Kubas, and Kenneth G. Caulton*

Received June 27, 1990

Protonation of $W(CO)_3(PCy_3)_2$ with equimolar $HBF_4·OEt_2$ in toluene produces $WH(BF_4)(CO)_3(PCy_3)_2$. This was characterized by spectroscopic methods and single-crystal X-ray diffraction as a seven-coordinate *molecule* with η^1-coordinated BF_4^-. The location of the hydride, in the WFP_2CO plane and in the cis position relative to one P and CO, makes the phosphines inequivalent. This inequivalence is evident in both the ^{31}P and ^1H NMR spectra, but the onset of hydride fluxionality is detected already at 25 °C. The low-temperature ^{19}F NMR spectrum and also the comparison of the spectral data of this molecule to that of the analogous products from HO_3SCF_3, $H_2C(SO_2CF_3)_2$, and $HCl·Et_2O$ indicate that the conjugate base of the acid employed for protonation remains coordinated in aromatic solvents. Reactivity studies of $W(CO)_3P_2$ with BF_4^- are consistent with the idea that the overall protonation reaction of 16-electron $W(CO)_3(PCy_3)_2$ is initiated by proton transfer, not by coordination of a lone pair of the conjugate base (e.g., BF_4^- or OEt_2).

Introduction

$W(CO)_3(PCy_3)_2$ is an apparent 16-electron complex which is in fact an 18-electron species due to an agostic C–H → W interaction of a cyclohexyl hydrogen.[1] Nevertheless, this agostic interaction is weak enough to allow replacement by Lewis bases that are sufficiently slender to enter the rather sterically hindered coordination sphere.[1,2] We explore here the rather peculiar question of whether this latent 16-electron complex and one bearing three electron-withdrawing carbonyl groups can react with a strong Brønsted acid.

Another statement of this problem is that 16-electron hydride compounds devoid of π-donor ligands (e.g., Cl, OR, ...) are rare.[3] Thus, is it possible to produce a 16-electron hydride cation by protonation of $W(CO)_3(PCy_3)_2$?

Experimental Section

General Procedures. All manipulations were carried out under a prepurified atmosphere of Ar or He by using standard Schlenk and drybox techniques. Solvents were dried and deoxygenated by using conventional procedures. $W(CO)_3(PCy_3)_2$ was prepared as described in the literature.[1] $W(^{13}CO)_3(PCy_3)_2$ was prepared in the same manner starting from $W(^{13}CO)_6$, which was prepared as described in the literature.[4] $HBF_4·Et_2O$ (85%), HO_3SCF_3, and 1.0 M $HCl·Et_2O$ were obtained commercially, used without further purification, and kept under Ar or N₂. $H_2C(SO_2CF_3)_2$ was obtained from A. R. Siedle at 3M Central Research Laboratories. ^1H NMR spectra were recorded on an IBM AF-250 MHz spectrometer and referenced to toluene-d_8 at 6.98 ppm or C_6D_6 at 7.15 ppm. ^{31}P NMR spectra were recorded on an IBM AF-250-MHz spectrometer at 101 MHz and referenced externally to 85% H_3PO_4 at 0 ppm. ^{19}F NMR spectra were recorded on an IBM AF-250-MHz spectrometer at 235 MHz and referenced externally to $CFCl_3$ at 0 ppm. ^{13}C NMR spectra were recorded on an IBM AF-250 spectrometer at 62 MHz and referenced to toluene-d_8 at 137.5 ppm. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer or a Digilab FTS-40 spectrophotometer and referenced to polystyrene at 1601 cm⁻¹.

W(H)(BF₄)(CO)₃(PCy₃)₂. $W(CO)_3(PCy_3)_2$ (0.030 g, 0.036 mmol) was dissolved in 1 mL of toluene-d_8, and $HBF_4·Et_2O$ (1.9 μL, 0.0027 g, 0.031 mmol) was added via syringe. A color change from purple to yellow occurred within 1 h; upon addition of 4 equiv of acid (7.7 μL, 0.146 mmol), the color change was immediate, and precipitation of the yellow microcrystalline product occurred after ~1 h.

^1H NMR (25 °C, toluene-d_8): δ –5.83 (m, W*H*), 1.33 (m), 1.63 (m), 1.75 (m), 2.51 (m). ^1H NMR (55 °C, toluene-d_8): δ –5.83 (t, W*H*). ^1H NMR (–9 °C, toluene-d_8): δ –5.78 (dd, J_{PH} = 17.0, 67.8 Hz). $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8): δ 35.5 (br AB pattern). $^{31}P\{^1H\}$ NMR (–35 °C, toluene-d_8): δ 33.28 (AB pattern). ^{19}F NMR (25 °C, toluene-d_8): δ –147.1 (s). ^{19}F NMR (–43 °C, toluene): δ –147.0 (d, J = 96 Hz), –257.8 (br). $^{13}C\{^1H\}$ NMR (25 °C, toluene-d_8, ^{13}C-labeled CO ligands): δ 209.6 (m), 208.1 (br s), 65.9 (s), 35.0 (br), 30.3 (br s), 28.0 (m), 26.7 (m), 25.6 (s). IR (25 °C, toluene, cm⁻¹): ν(WH) = 2002 (s), ν(CO) = 1906 (br), 1889 (br), 1872 (br). IR (25 °C, C_6D_6, cm⁻¹): ν(WH) = 2013 (s), ν(CO) = 1907 (br), 1887 (br), 1852 (br). IR (25 °C, Nujol, cm⁻¹): ν(WH) = 2000 (s) ν(C) = 1893 (br).

Table I. Crystallographic Data for WH(BF₄)(CO)₃(PCy₃)₂

chem formula: $C_{39}H_{67}BF_4O_3P_2W$	space group: $C2/c$
fw = 915.75	$T = -70$ °C
$a = 24.360$ (5) Å	$\lambda = 0.709\,30$ Å
$b = 15.641$ (2) Å	$\rho_{calc} = 1.47$ gm cm⁻³
$c = 22.214$ (4) Å	$\mu = 29.7$ cm⁻¹
$\beta = 101.15$ (2)°	transm coeff = 0.55–0.60
$V = 8304.4$ Å³	$R(F_o) = 0.065$
$Z = 8$	$R_w(F_o) = 0.071$

$W(CO)_4(PCy_3)_2$ is a thermodynamic "sink" in this reaction system due to release of CO on decomposition. It is sometimes evident in the precipitate formed initially and increases after long reaction times. $^{31}P\{^1H\}$ NMR (25 °C, toluene-d_8): δ 31.5 (s). ^{13}C NMR (25 °C, toluene-d_8): δ 208.9 (t, J_{PC} = 6 Hz, J_{WC} = 128 Hz). IR (25 °C, C_6D_6, cm⁻¹): ν(CO) = 1920 (w), 1870 (s).

Protonation of $WH_2(CO)_3(PCy_3)_2$ also yields $W(H)(BF_4)(CO)_3(PCy_3)_2$, but via a detectable intermediate, which is apparently $WH_3(CO)_3(PCy_3)_2BF_4$.

Crystal Structure Determination. A suitable crystal was grown from a concentrated toluene-d_8 NMR sample, examined under degassed Fluorolube, mounted on a fiber in silicone grease, and kept in a N₂ cold stream on the goniometer. Unit cell parameters were derived from a least-squares analysis of 25 reflections (graphite-monochromated Mo Kα radiation λ = 0.709 26 Å, range 17° < θ < 26.5°) automatically centered on an Enraf Nonius CAD-4 diffractometer. The intensities and orientation of the standard reflections were monitored every 2 h of X-ray exposure time and every 200 reflections, respectively. The standard reflections showed no significant intensity fluctuations; reorientation was not required. Further details of data collection for $WH(BF_4)(CO)_3(PCy_3)_2$ are contained in Table I. Intensity data were corrected for Lorentz and polarization factors. The W and P atoms were located via Patterson methods; the rest of the structure was solved by difference Fourier methods. Several of the cyclohexyl groups show some carbon disorder, as does the carbonyl ligand containing C3. Site occupancy refinements on the oxygen atoms of this disordered CO ligand converged to population values of 0.7 (1) for O3 and 0.2 (1) for O4. Although the C–O distances involving C3 are unreasonably long, we still formulate this ligand as a disordered carbonyl because substitution of other atoms (such as B, N, or F) in these positions results in atoms with unreasonable isotropic thermal parameters. In addition, IR and ^{13}C NMR data support the presence of a third carbonyl ligand in the structure. It was not possible to resolve two separated carbon atoms for this disordered carbonyl. The structure was refined with full-matrix least-squares methods using appropriate neutral scattering factors and anomalous scattering terms.[5] The Los Alamos crystal structure codes were used for all calculations.[6] The function minimized was $R = \sum w^2(F_o - F_c)^2$, and weights

(1) (a) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, 61. (b) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294.
(2) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallic* **1988**, *7*, 2429.
(3) Strauss, S. H.; Diamond, S. E.; Mares, F.; Shriver, D. F. *Inorg. Chem.* **1978**, *17*, 3064.
(4) (a) Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068. (b) Darensbourg, D. J.; Darensbourg, M. Y.; Gray, R. L.; Simmons, D.; Arndt, L. W. *Inorg. Chem.* **1986**, *25*, 880.
(5) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. Cromer, D. T. *Ibid.*, Table 2.3.1.

*To whom correspondence should be addressed at Indiana University.

Table II. Fractional Coordinates and Isotropic Thermal Parameters for WH(BF₄)(CO)₃(PCy₃)₂

| atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
W1	0.1088 (1)	0.1621 (1)	0.1061 (1)	3.51	P1	0.062 (4)	0.2953 (6)	0.0506 (4)	3.5
P2	0.1785 (4)	0.0492 (6)	0.1608 (4)	3.5	C1	0.0728 (13)	0.1752 (25)	0.1779 (14)	4.4 (8)
O1	0.0474 (10)	0.1809 (16)	0.2171 (10)	6.5 (7)	C2	0.1425 (11)	0.1502 (23)	0.0331 (13)	2.9 (7)
O2	0.1588 (8)	0.1417 (14)	-0.0139 (9)	4.7 (5)	C3	0.0544 (26)	0.0876 (47)	0.0789 (23)	16.4
O3	0.0366 (20)	0.0049 (32)	0.0627 (18)	10.5 (20)	O4	0.9920 (43)	0.0667 (58)	0.0509 (37)	4.9 (39)
B1	0.1881 (23)	0.3013 (33)	0.2041 (25)	5.7 (14)	F1	0.1725 (8)	0.2499 (13)	0.1492 (9)	4.7 (5)
F2	0.2017 (12)	0.2576 (19)	0.2536 (14)	11.5 (9)	F3	0.2338 (10)	0.3480 (18)	0.1973 (9)	9.1 (6)
F4	0.1449 (12)	0.3617 (18)	0.2089 (11)	11.2 (8)	C4	0.0024 (10)	0.3424 (22)	0.0793 (10)	2.0 (5)
C5	0.0194 (12)	0.3842 (19)	0.1431 (13)	2.7 (7)	C6	-0.0325 (15)	0.4279 (23)	0.1616 (15)	5.2 (9)
C7	-0.0789 (13)	0.3609 (22)	0.1585 (14)	4.9 (9)	C8	-0.0980 (13)	0.3147 (21)	0.0950 (14)	4.7 (9)
C9	-0.0425 (14)	0.2732 (22)	0.0747 (15)	4.8 (9)	C10	0.0404 (12)	0.2804 (19)	-0.0345 (13)	2.8 (7)
C11	0.0161 (12)	0.1898 (19)	-0.0538 (13)	3.6 (8)	C12	0.0079 (11)	0.1880 (17)	-0.1256 (12)	2.6 (7)
C13	-0.0340 (14)	0.2535 (22)	-0.1560 (14)	4.2 (8)	C14	-0.0131 (13)	0.3367 (29)	-0.1340 (15)	6.0 (8)
C15	-0.0035 (11)	0.3491 (23)	-0.0638 (12)	3.1 (7)	C16	0.1135 (11)	0.3857 (16)	0.0575 (11)	1.4 (6)
C17	0.1650 (11)	0.3614 (8)	0.0287 (12)	2.9 (7)	C18	0.2106 (14)	0.4280 (23)	0.0500 (15)	4.9 (9)
C19	0.1898 (14)	0.5190 (23)	0.0300 (15)	4.6 (9)	C20	0.1357 (12)	0.5411 (24)	0.0559 (16)	5.4 (10)
C21	0.0886 (14)	0.4728 (21)	0.299 (14)	4.2 (8)	C22	0.1626 (12)	0.0048 (20)	0.2331 (13)	2.9 (7)
C23	0.1021 (13)	-0.0335 (20)	0.2209 (14)	3.9 (8)	C24	0.0937 (14)	-0.0772 (23)	0.2826 (16)	5.3 (9)
C25	0.0988 (15)	-0.0068 (24)	0.3311 (15)	5.2 (9)	C26	0.1572 (16)	0.0287 (24)	0.3470 (16)	6.2 (10)
C27	0.1723 (13)	0.0718 (21)	0.2838 (15)	3.9 (8)	C28	0.2515 (12)	0.0923 (19)	0.1829 (13)	2.6 (7)
C29	0.2950 (16)	0.0347 (24)	0.2195 (16)	6.1 (10)	C30	0.3481 (16)	0.0817 (24)	0.2431 (17)	5.7 (10)
C31	0.3668 (15)	0.1292 (23)	0.1908 (17)	6.0 (10)	C32	0.3265 (12)	0.1873 (19)	0.1523 (13)	3.5 (8)
C33	0.2709 (13)	0.1376 (21)	0.1266 (14)	4.5 (9)	C34	0.1862 (15)	-0.0508 (25)	0.1134 (17)	5.5 (9)
C35	0.1431 (27)	-0.0583 (42)	0.0571 (30)	15.9 (23)	C36	0.1683 (17)	-0.1266 (27)	0.0165 (18)	7.0 (11)
C37	0.1965 (22)	-0.2105 (34)	0.0506 (26)	9.6 (16)	C38	0.2170 (39)	-0.1946 (59)	0.0985 (42)	22.7 (41)
C39	0.2097 (16)	-0.1240 (25)	0.1490 (17)	6.4 (11)					
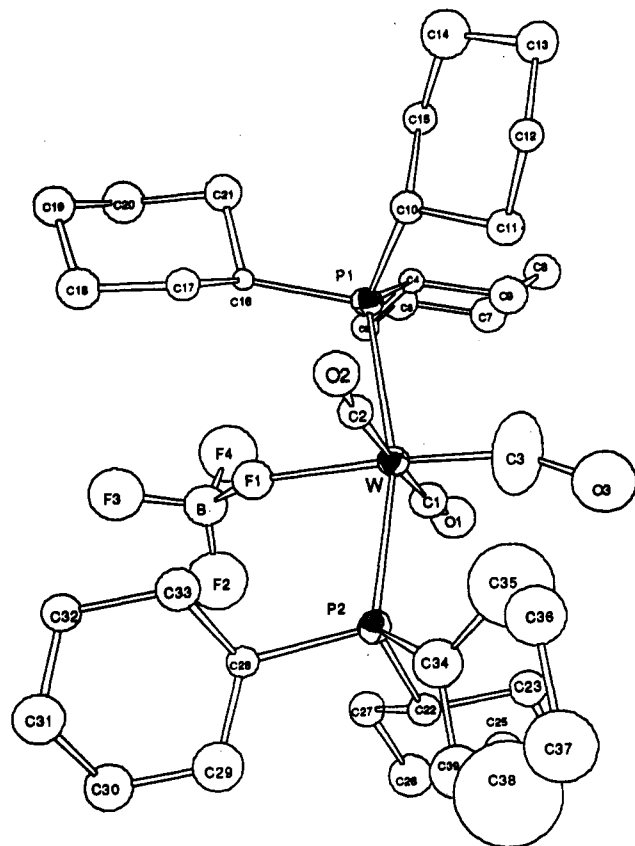
Figure 1. ORTEP drawing of WH(BF₄)(CO)₃(PCy₃)₂, showing atom labeling. The hydride ligand (not located by X-ray diffraction) is proposed to lie between each P and C3, and only one of the two disordered oxygens O3 is portrayed.

were calculated as $w^2 = 4F^2/\sigma^2(I)$, where $\sigma(I) = \sigma_c(I) + (0.030I)^2$; $\sigma_c(I)$ is the error based on counting statistics. Refinements for all atoms included atom positions, the scale factor, and a secondary extinction parameter.[7] The small number of data prevented anisotropic refinement

(6) Larson, A. C. *American Crystallographic Association Program and Abstracts*; American Crystallographic Association: Storrs, CT, 1977; Series 2, Vol. 5, No. 2, p 67.

(7) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558. Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.

Table III. Selected Distances and Angles for WH(BF₄)(CO)₃(PCy₃)₂

Distances (Å)			
W-P1	2.568 (9)	P1-C4	1.86 (2)
W-P2	2.586 (9)	P1-C10	1.88 (3)
W-F1	2.15 (2)	P1-C16	1.87 (3)
W-C1	1.97 (3)	P2-C22	1.86 (3)
W-C2	1.96 (3)	P2-C28	1.87 (3)
W-C3	1.78 (6)	P2-C34	1.92 (4)
C1-O1	1.16 (3)	B-F1	1.45 (5)
C2-O2	1.19 (3)	B-F2	1.28 (5)
C3-O3	1.39 (6)	B-F3	1.36 (5)
C3-O4	1.56 (10)	B-F4	1.43 (5)

Angles (deg)			
P1-W1-P2	165.4 (3)	W1-F1-B1	141 (2)
C1-W1-C2	178 (1)	F1-B1-F2	114 (4)
C1-W1-C3	85 (2)	F1-B1-F3	106 (4)
C2-W1-C3	93 (2)	F1-B1-F4	111 (4)
C1-W1-F1	88 (1)	F2-B1-F3	107 (4)
C2-W1-F1	92 (1)	F2-B1-F4	111 (4)
C3-W1-F1	173 (2)	F3-B1-F4	106 (4)
F1-W1-P1	85 (1)	W1-C1-O1	174 (3)
F1-W1-P2	83 (1)	W1-C2-O2	175 (2)
C1-W1-P1	95 (1)	W1-C3-O3	151 (6)
C1-W1-P2	93 (1)	W1-C3-O4	151 (6)
C2-W1-P1	84 (1)		
C2-W1-P2	89 (1)		
C3-W1-P1	98 (2)		
C3-W1-P2	95 (2)		
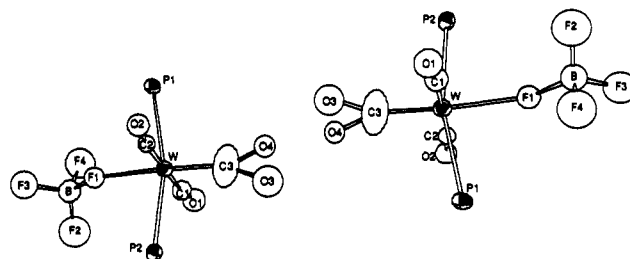
Figure 2. ORTEP drawing of the relationship of two BF₄P₂WC₃O₃ units related by a center of symmetry.

of all of the atoms. A final difference Fourier map for this structure indicated no peaks larger than 1.2 e/Å³; the smaller observed peaks were not in chemically reasonable positions. Results are presented in Tables II and III and Figures 1 and 2. A table of anisotropic thermal parameters and a listing of observed and calculated structure factor amplitudes

are given as supplementary material.

Two adjacent $WH(BF_4)(CO)_3(PCy_3)_2$ molecules are related by a crystallographic center of symmetry. The disordered W(H)(CO) portion of each molecule points toward its partner (Figure 2), across the center of symmetry. We have considered the possibility that this is due to intermolecular hydrogen bonding (W–H to carbonyl oxygens) but find the distances and the geometry of these groups to be unsuitable.

Reaction of $W(CO)_3(PCy_3)_2$ with HO_3SCF_3. $W(CO)_3(PCy_3)_2$ (0.036 g, 0.044 mmol) was dissolved in 1 mL of toluene-d_8 and immersed in an ice bath, and HO_3SCF_3 (4.0 μL, 0.0068 g, 0.045 mmol) was added via syringe. A color change from purple to yellow-brown occurred immediately; upon overnight standing, a brown oil separated. The product was much more soluble than the HBF_4 analogue, and solid products were not obtained. Upon 1 week of standing in solution, ligand redistribution occurred to form yellow crystals of $W(CO)_4(PCy_3)_2$, which we have structurally characterized by X-ray diffraction.

^{1}H NMR (25 °C, toluene-d_8): δ –5.71 (m, WH), 1.31 (m), 1.62 (m), 1.79 (m), 2.07 (m), 2.51 (m). ^{1}H NMR (42 °C, toluene-d_8): δ –5.68 (t, J_{PH} = 37.4 Hz). ^{1}H NMR (–46 °C, toluene-d_8): δ –5.71 (dd, J_{PH} = 57.0, 16.8 Hz). ^{31}P{^{1}H} NMR (25 °C, toluene-d_8): δ 28.7 (br, s). ^{31}P{^{1}H} NMR (–23 °C, toluene-d_8): δ 35.35 (d, J_{PP} = 114 Hz), 32.07 (d, J_{PP} = 114 Hz). ^{13}C NMR (25 °C, toluene-d_8, ^{13}C-labeled CO ligands): δ 217.6 (br s), 207.5 (br s), 30.5 (br), 27.8 (s), 26.7 (s), 25.4 (s). IR (25 °C, C_6D_6, cm^{-1}): ν(WH) = 2013 (s), ν(CO) = 1905 (br), 1878 (br), 1856 (br).

Reaction of $W(CO)_3(PCy_3)_2$ with $HCl\cdot Et_2O$. $W(CO)_3(PCy_3)_2$ (0.018 g, 0.022 mmol) was dissolved in 1 mL of toluene-d_8 and immersed in an ice bath, and $HCl\cdot Et_2O$ (20.0 μL, 0.0070 g, 0.020 mmol) was added via syringe. A color change from purple to gray occurred within a few minutes; upon overnight standing, the color became yellow-brown.

^{1}H NMR (25 °C, toluene-d_8): δ –5.20 (m, WH), 1.25 (m), 1.58 (m), 1.70 (m), 1.90 (m), 2.20 (m), 2.55 (m). ^{31}P{^{1}H} NMR (25 °C, toluene-d_8): δ 21.0 (br). IR (25 °C, C_6D_6, cm^{-1}): ν(WH) = 1998 (s), ν(CO) = 1907 (sh), 1885 (br), 1856 (br).

Reaction of $W(CO)_3(PCy_3)_2$ with $H_2C(SO_2CF_3)_2$. $W(CO)_3(PCy_3)_2$ (0.032 g, 0.039 mmol) was dissolved in 1 mL of toluene-d_8 and immersed in an ice bath, and solid $H_2C(SO_2CF_3)_2$ (0.015 g, 0.054 mmol) was added. A color change from purple to yellow-brown slowly occurred within 1 h. The product was much more soluble than the HBF_4 analogue, and solid products were not obtained.

^{1}H NMR (25 °C, toluene-d_8): δ –5.38 (m, WH), 1.1 (m), 1.2 (m), 1.6 (m), 1.7 (m), 2.1 (m), 3.71 (s, $HC(SO_2CF_3)_2$). ^{31}P{^{1}H} NMR (25 °C, toluene-d_8): δ 28.5 (br). IR (25 °C, C_6D_6, cm^{-1}): ν(WH) = 2021 (s), ν(CO) = 1932 (br), 1860 (sh), 1852 (br).

$W(CO)_3(PCy_3)_2 + [^nBu_4N]BF_4$. $[^nBu_4N]BF_4$ (0.020 g, 0.061 mmol) was dissolved in 1 mL of toluene-d_8, and $W(CO)_3(PCy_3)_2$ (0.032 g, 0.039 mmol) was added. No change was observed in either the color of the solution or the ^{31}P{^{1}H} NMR spectrum of the mixture after 1 h.

$W(CO)_3(PCy_3)_2 + [^nBu_4N]BF_4 + Et_2O$. $[^nBu_4N]BF_4$ (0.020 g, 0.061 mmol) was dissolved in a solution of 1 mL of toluene-d_8 containing 0.05 mL of Et_2O, and $W(CO)_3(PCy_3)_2$ (0.032 g, 0.039 mmol) was added. No change was observed in either the color of the solution or the ^{31}P{^{1}H} NMR spectrum of the mixture after 1 h.

Results

Synthesis and Characterization. Reaction of purple $W(CO)_3(PCy_3)_2$ with equimolar $HBF_4\cdot OEt_2$ in toluene (at –78 or +25 °C) slowly produces a color change to yellow. The major product is a hydride compound. At high initial concentrations of $W(CO)_3(PCy_3)_2$, the toluene-soluble product precipitates as a yellow solid. The color change and precipitate occur more rapidly if the reaction is carried out with a 4:1 H$^+$:W ratio. The ^{1}H and ^{31}P NMR spectra of this yellow solid, redissolved in fresh toluene-d_8, show broad lines characteristic of a dynamic process. Thus, the ^{31}P{^{1}H} NMR spectrum shows an AB pattern but with each line with a full width at half-maximum of 100 Hz. As the temperature is raised to 328 K, the AB pattern collapses into the base line, but the compound decomposes irreversibly (340 K with evolution of H_2 and precipitation of a dark solid) before the fast-exchange regime can be reached. The ^{31}P{^{1}H} NMR spectrum at 238 K is an AB pattern with sharp lines. The ^{1}H NMR spectrum of the hydride peak (–5.8 ppm) at 25 °C is an unconventional triplet, where the outside lines are sharp but the inner one is broad. At 328 K, the hydride pattern is nearly a binomial triplet, and at 264 K, the hydride is an ABX pattern showing coupling to the phosphines of 17.0 and 67.8 Hz. The infrared spectrum of the yellow product in toluene shows peaks at 2002, 1906, 1889, and 1872 cm^{-1}.

Altogether these observations show the presence of two phosphine ligands, carbonyls and hydride(s), and at least one BF_4^-. The solubility would suggest a molecular species with coordinated BF_4^-,[8] but the lack of coupling of fluorine in any other spin-active nucleus in the molecule is then unexplained.

Solid-State Structure. The structure of material obtained directly from the toluene reaction mixture was determined by X-ray diffraction. This revealed two trans PCy_3 groups, two trans carbonyls, and a η^1-coordinated BF_4^- (Figures 1 and 2). Trans to BF_4^- in difference Fourier maps were at least three peaks of electron density, which we attribute to crystallographic disorder. Compounds containing the $W(PR_3)_2$ (R = cyclohexyl, cyclopentyl, or ^iPr) unit or the trans-$(H_2)M(CO)$ unit have a consistent tendency to disorder,[1,9] and we interpret the V-shaped three-peak unit trans to F to be one carbonyl ligand disordered over two sites, each with unequal O–W–P angles.

Because of this disorder, there was no evidence for the location of the hydride ligand. While the carbon positions are too close to refine independently, the oxygens can be resolved. The composite carbon peak has a W–C distance short enough to rule out any alternative assignment of this ligand as formyl, CO_2, CO_2H, COH(carbyne), $C(OH)_2$ (carbene), F(partial occupancy), or OR_2(ether). The ^{13}C{^{1}H} NMR spectrum also supports the assignment of this disordered group as CO in that one sees two peaks in the carbonyl region in an intensity ratio of 1:2 at 25 °C.

What then is the reason for the 2-fold off-axis disorder of this carbonyl? Since the single BF_4^- ligand ensures that the molecule contains *one* hydride ligand, we propose that it is the hydride ligand which forces the CO off the position directly trans to F by occupying the larger P–W–C sector.
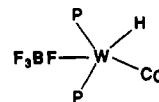
We rule out the situation where the hydrogen is on a triangular CCP face of the octahedron. If true, this would make the angles F1–W–C1 and –C2 different, as well as the angles F1–W–P1 and –P2 different, which they are not. The formula of the protonation product of $W(CO)_3(PCy_3)_2$ is thus $W(H)(BF_4)(CO)_3(PCy_3)_2$, and it is molecular, consistent with its solubility in toluene. The off-axis location of the unique CO *and* the *hydride* are also essential to understanding that the phosphine ligands are inequivalent, as detected by both ^{1}H (splitting pattern) and ^{31}P NMR spectroscopy.

It is noteworthy that the site of protonation, the edge of an octahedron, is the site of one of the filled t_{2g} orbitals (see below). Moreover, this structure puts both strong ligands (H$^-$ and CO) trans to the weak ligand, BF_4^-. The resulting structure of $W(H)(BF_4)(CO)_3(PCy_3)_2$ is then surprising only with regard to its high barrier to rearrangement. Generally, one expects high coordination numbers and also hydride ligands to contribute to stereochemical nonrigidity.

Solution-Phase Behavior. In view of our initial question of whether protonation of $W(CO)_3(PCy_3)_2$ can produce the unsaturated hydride $WH(CO)_3(PCy_3)_2^+$, it is important to establish whether the solid-state structure of $WH(BF_4)(CO)_3(PCy_3)_2$ is retained in "noncoordinating" (e.g., aromatic) solvents. The W–F bond length in the solid state is not particularly long (cf. the W–CH$_3$ distance[10] of 2.31 (2) Å in $WCH_3(CO)_5^-$).

(8) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.
(9) (a) $W(H_2)(CO)_3(P^iPr_3)_2$: Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) $Mo(H_2)(CO)(dppe)_2$: Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339. (c) $W(H_2)(CO)_3(PCy_3)_2$, $W(H_2)(CO)_3(PCyp_3)_2$, $Mo(H_2)(CO)_3(PCy_3)_2$: Kubat-Martin, K. A.; Kubas, G. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Wasserman, H. J.; Ryan, R. R. *Acta Crystallogr., Sect. C*, in press.
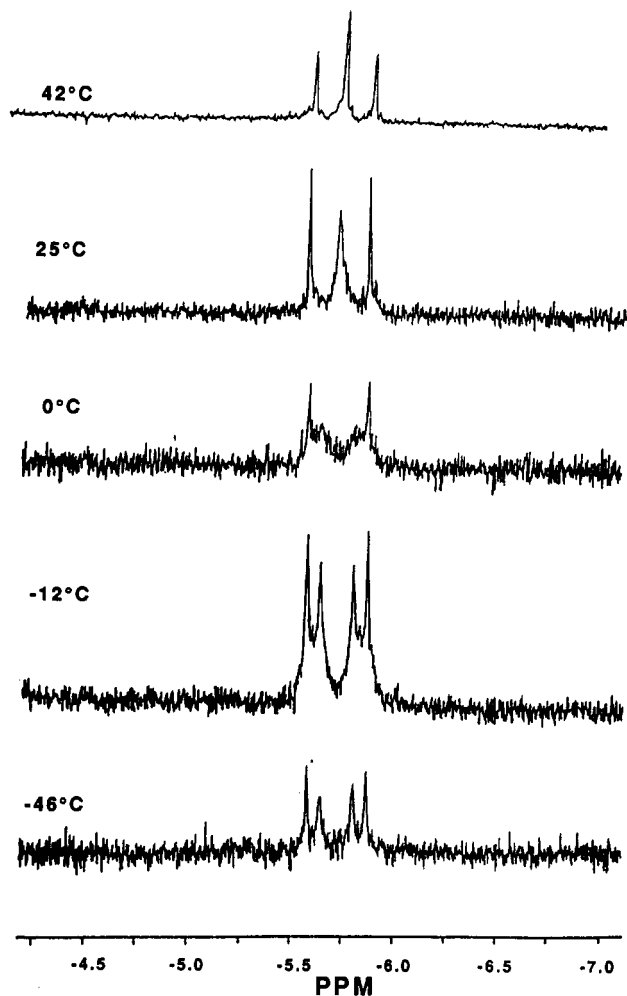
Figure 3. ¹H NMR spectra in the hydride region of W(H)(OTf)-(CO)₃(PCy₃)₂ in toluene-d_8.

WAVENUMBERS (cm⁻¹)

Figure 4. IR spectra in C_6D_6 solution of W(H)(BF₄)(CO)₃(PCy₃)₂ (—), of W(H)(OTf)(CO)₃(PCy₃)₂ (- - -), and of a 1:1 mixture of the two complexes (— · —).

Evidence for the question of retention of the BF₄⁻ ligand of WH(BF₄)(CO)₃(PCy₃)₂ in aromatic solvents comes from the protonation of W(CO)₃(PCy₃)₂ with HO₃SCF₃ in toluene-d_8. The reaction proceeds to an *analogous* product, but the ¹H NMR hydride triplet at 25 °C has a chemical shift 0.12 ppm different from that of WH(BF₄)(CO)₃(PCy₃)₂ (Figure 3). Moreover, the pattern observed in the HO₃SCF₃ case is closer to a binomial triplet than that in the HBF₄ case (the broad center line has greater amplitude compared to the sharp outer lines), and the temperature (315 K) at which the hydride pattern becomes a triplet is lower than in the fluoroborate case (328 K). Since the triflate complex is at a different point in the coalescence process, $\Delta\delta$ and/or ΔG^* are/is different for X = BF₄⁻ and O₃SCF₃, indicating that these are distinct molecules and not both free WH(CO)₃(PCy₃)₂⁺. Finally, the ³¹P{¹H} NMR spectrum of the product from HO₃SCF₃ is a broad singlet at 25 °C centered 6.8 ppm *away* from that of WH(BF₄)(CO)₃(PCy₃)₂. The low-temperature ³¹P{¹H} NMR spectrum reveals an AB pattern at 220 K.

Protonation of W(CO)₃(PCy₃)₂ with HCl·Et₂O resulted in a similar color change to yellow and similar NMR spectra. The ¹H NMR spectrum at 25 °C in toluene-d_8 consisted of a hydride "triplet" at −5.20 ppm (now 0.63 ppm different from that in the fluoroborate case), and the corresponding ³¹P{¹H} NMR spectrum consisted of a broad resonance at 21.0 ppm.

Use of the carbon acid H₂C(SO₂CF₃)₂ again resulted in a similar color change and similar spectra; however the hydride pattern of this product came at −5.38 ppm (in toluene) or 0.4 ppm different from that of the BF₄⁻ analogue. The corresponding
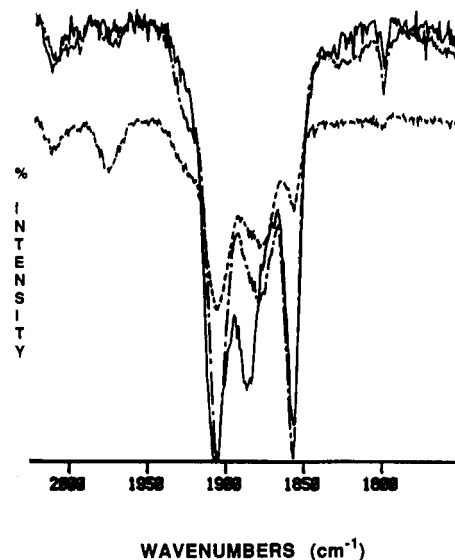
(10) Darensbourg, D. J.; Bauch, C. G.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 977.

³¹P{¹H} NMR resonance is a very broad line at 28.5 ppm (in toluene).

The ¹³C{¹H} NMR spectra of CO ligands of WH-(X)(¹³CO)₃(PCy₃)₂ in toluene also establish that X is coordinated, since spectral parameters depend on the identity of X. These values (ppm) for X = BF₄(O₃SCF₃) are 209.6 (217.6) (1 C) and 208.1 (207.5) (2 C). As for W(CO)₃(PCy₃)₂, unresolved C–C coupling obscures coupling of carbon to other nuclei in the molecule. In these chemical shifts, the carbonyl group trans to X is much more sensitive to the identity of X than are the values of the two carbonyls cis to X. Moreover, these chemical shifts, being upfield from those of W(CO)₃(PCy₃)₂, are consistent with the idea of metal oxidation by HX. For comparison, the carbonyl groups of W(CO)₃(PCy₃)₂ are stereochemically rigid. The ¹³C NMR spectrum of 99% ¹³CO-labeled material shows signals at 223.7 ppm (1 P, J_{CW} = 210 Hz) and 216.3 ppm (2 P, J_{CW} = 128 Hz, J_{PC} = 6 Hz). Unresolved C–C coupling makes these signals broader than those of *trans*-W(CO)₄(PCy₃)₂.

Finally, the solubility of all of these products in aromatic solvents is inconsistent with true separated-ion behavior, [WH-(CO)₃(PCy₃)₂]X. Moreover, separated-ion behavior would give *identical* CO stretching frequencies for the materials when X⁻ is varied. The infrared spectrum of WH(BF₄)(CO)₃(PCy₃)₂ in C_6D_6 shows a four-band pattern in the region 2050–1750 cm⁻¹. The product from HO₃SCF₃ also shows three bands, but with different relative intensities from those of the BF₄⁻ compound. Moreover, one of the three bands differs in frequency by 5 cm⁻¹ in these two compounds. In addition, the infrared spectrum of a 1:1 mixture of WH(BF₄)(CO)₃(PCy₃)₂ and WH(O₃SCF₃)-(CO)₃(PCy₃)₂ shows bands and relative intensities consistent with a mixture of the two different spectra of the individual components (Figure 4). The two species are thus *distinct*, even by internal comparison. Finally, the product from HCl has perceptably different spectra from either of the above, suggesting that we are dealing with three different molecular species WH(X)(CO)₃-(PCy₃)₂. By this "fast" technique (i.e., one which is not confused by dynamic processes), coordinated X⁻ is present in the major (>95%) species in toluene.

The infrared frequencies themselves can be used as probes of metal oxidation state. Comparison of the frequencies for WH-(BF₄)(CO)₃(PCy₃)₂, 1907 (s), 1887 (m), and 1852 (s) cm⁻¹, to those for W(CO)₃(PCy₃)₂L (L = N₂,[1] H₂O,[1] H₂,[1] or L absent[1]) shows the latter to be lower, consistent with a higher metal oxidation state in WH(BF₄)(CO)₃(PCy₃)₂. On the other hand, the dihydride W(H)₂(CO)₃(PⁱPr₃)₂ has higher frequency bands (1993, 1913, 1867, and 1828 cm⁻¹ in hexane) similar to those of WH-(BF₄)(CO)₃(PCy₃)₂. We feel that the dihydride (which is de-

tectable but is in equilibrium with the dihydrogen isomer[11]) is the best comparison compound.

The ^{19}F NMR spectrum of $WH(BF_4)(CO)_3(PCy_3)_2$ in toluene shows only one signal at 25 °C. The chemical shift (-147.1 ppm) is very close to the literature[12] value (-147.0 ppm) for BF_4^-. The ^{19}F chemical shift of $N(^nBu)_4BF_4$ is -149.1 ppm in toluene at 25 °C. Since site exchange of free and coordinated F in η^1-BF_4 has been observed,[8,13] variable-temperature studies are required for $WH(BF_4)(CO)_3(PCy_3)_2$. The ^{19}F NMR spectrum at 230 K in toluene shows a sharp doublet ($J = 96$ Hz) at -147.0 ppm and a broad line of unresolved multiplicity at -257.8 ppm, which we assign to three terminal and one μ_2-fluoride, respectively. The breadth of the latter probably originates in coupling to the hydride and/or two inequivalent phosphorus nuclei.

Discussion

The picture which emerges is that $WH(BF_4)(CO)_3(PCy_3)_2$ is a molecular species both in the solid state and in solution. The CO stretching frequencies are most consistent with an oxidation state greater than that in $W(CO)_3L(PCy_3)_2$; these frequencies agree quite well with those of the dihydride $W(H)_2(CO)_3(P^iPr_3)_2$. Most important, the ^{31}P NMR spectrum of the dihydride shows the phosphines to be inequivalent,[11] a structural feature that it thus shares with the hydride/BF_4 complex. Note, however, that $J_{PP'}$ is 43 Hz in $W(H)_2(CO)_3(P^iPr_3)_2$, while it is 115 and 101 Hz in $WHX(CO)_3(PCy_3)_2$ where X = triflate and BF_4^-. In broad strokes, then, these two compounds show a consistent structural pattern.

The *thermodynamically* preferred site for the proton, in the yz plane (z toward F and y along the P–W–P axis), is also consistent with the spatial orientation of the most energetically accessible of the (nondegenerate) t_{2g}-derived orbitals of a *trans,-mer*-$W(CO)_3(PCy_3)_2(BF_4)^-$ ion.
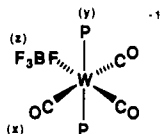
The order of increasing stability of the filled d orbitals is yz (least stabilized) $< xy < xz$ (most stable); this follows because these are stabilized by one, two, and three carbonyl π^* orbitals, respectively.
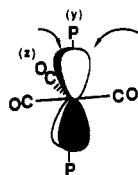
Being the least delocalized onto carbonyl ligands, the yz orbital is also the most (metal-) localized orbital. This same ordering pertains in $W(CO)_3(PCy_3)_2$ and thus permits the mechanistic prediction that protonation will occur in the plane of the two

phosphorus nuclei and the unique CO (i.e., cis to phosphorus); one of these two is the actual location of the hydrogen in the *final* product. Attack by H^+ in the yz plane thus represents attack at the HOMO (i.e., frontier control).

This work represents the first demonstration of protonation of a 16-electron d^6 species. It established that the electron-rich character of W(0) is sufficient to permit protonation of what is, at least in a latent sense (given the agostic structure), a Lewis acid. There is, of course, the question of whether the reaction of $W(CO)_3(PCy_3)_2$ is actually initiated by proton transfer or whether BF_4^- coordination occurs first. This is relevant because HBF_4·OEt_2 is probably the oxonium compound $[HOEt_2]BF_4$,[14] which in toluene is an intimate ion pair (via H···F hydrogen bonding). Thus, the initial interaction could be formation of a W–F–B bridge, followed by proton transfer to the now-saturated W(0) center. If correct, this would represent a unique example where precoordination of the intact acid via the conjugate base is then *followed* by proton transfer. This represents a synergic activation of both the reagent acid *and* the proton acceptor (tungsten) *by* the proton acceptor and is clearly a feature that would be unique to protonation of a Lewis acid (16-electron complex).

To test the viability of such a mechanism, we sought a mimic of $HOEt_2BF_4$. For this purpose, we selected the species Bu_4NBF_4. This compound is toluene-soluble to the extent that both ^1H and ^{19}F NMR spectra can be obtained. Such solubility suggests ion pairing in toluene. Both the purple color and the $^{31}P\{^1H\}$ NMR spectrum of $W(CO)_3P_2$ are unchanged upon addition of NBu_4BF_4 in toluene. Thinking that the Et_2O present in the reaction with $HOEt_2BF_4$ might promote coordination of BF_4^-, we added 0.05 mL of Et_2O to the above sample. The $^{31}P\{^1H\}$ spectrum remained unaltered. Thus, barring any dominant steric influence of ion pairing in NBu_4BF_4 compared to $HOEt_2BF_4$, these experiments indicate that the reaction of $HOEt_2BF_4$ is not initiated by fluoride (BF_4^-) lone pairs.

An alternative to the more obvious direct protonation of $W(CO)_3(PCy_3)_2$ would be coordination of $OHEt_2^+$ to tungsten via oxygen. Intramolecular migration of the proton from oxygen to tungsten in $W(OHEt_2)(CO)_3(PCy_3)_2^+$ would then be followed by dissociation of OEt_2 (or its displacement by BF_4^-). In this regard, the steric $OHEt_2^+$ analogues EtOH, $EtNH_2$, pyridine, and thiophene have been shown to bind to $W(CO)_3(PCy_3)_2$ as opposed to Et_2NH and Et_3N which do not.[1,15]

With regard to the original goal of this work, protonation of $W(CO)_3(PCy_3)_2$ with a Bronsted acid of a "noncoordinating" conjugate base has been shown to give a kinetically labile, even if 18-electron, species. An exploration of the chemical reactivity of this operational equivalent of the 16-electron hydride $WH(CO)_3(PCy_3)_2^+$ thus seems warranted.

(11) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

(12) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *J. Am. Chem. Soc.* **1983**, *105*, 7302.

(13) For fluxionality of η^1-BF_4^-, see: Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6056. Cutler, A. R.; Todara, A. B. *Organometallics* **1988**, *7*, 1782.

(14) Mootz, D.; Steffen, M. *Z. Anorg. Allg. Chem.* **1981**, *482*, 193.

(15) G. Kubas; unpublished work.