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Isolation and Characterization of Salts of the Organometallic Synthon $[Tp^*W(NCMe)(CO)_3]^+$ and Its Propionitrile Analogue

Michael S. Malarek, Brett A. Logan, Jonathan M. White, and Charles G. Young*

School of Chemistry, University of Melbourne, Victoria 3010, Australia

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Summary: Trifluoromethanesulfonate and tetrafluoroborate salts of the previously in situ-generated synthetic precursor $[Tp^*W(NCMe)(CO)_3]^+$ *and a propionitrile analogue,* $[Tp^*W(NCEt)(CO)_3](CF_3SO_3)$*, have been isolated and fully characterized. The complex cations exhibit a carbonyl-capped octahedral structure with* C_s *symmetry and undergo slow nitrile ligand exchange.*

Introduction

Certain cationic complexes, viz., $[Tp^*W(CO)(NCMe)(alkyne)]^+$,[1,2] $[Tp^*W(CO)(alkyne)_2]^+$,[3] $[Tp^*W(CO)_3]^+$,[2,4] and $[Tp^*W(NCR)(CO)_3]^+$,[5−7] have been pivotal in the development of tungsten hydrotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) organometallic chemistry.[8,9] While the alkyne complexes have been isolated and thoroughly characterized, little is known about the highly reactive, hitherto intractable (in situ-generated) tricarbonyl species.

The tricarbonyl cations produced in the reactions of $Tp^*WI(CO)_3$ with silver salts depend on the solvent employed. In dichloromethane, 16-electron $[Tp^*W(CO)_3]^+$ (ν(CO) 2117 and 2054 cm^{-1}) is proposed to form, although token solvation to produce an 18-electron species has been canvassed; a related cation is generated upon ferrocenium oxidation of $Tp^*W(CO)_3$ in dichloromethane.[2,4] In acetonitrile, the reaction product is formulated as the 18-electron, σ-bonded nitrile complex $[Tp^*W(NCMe)(CO)_3]^+$ on the basis of infrared data (lit. ν(CO) 2045 and 1956 (br) cm^{-1});[5] the same complex is generated upon halide abstraction from $Tp^*WX(CO)_3$ (X = Cl, Br) in acetonitrile.[7] The benzonitrile analogue, $[Tp^*W(NCPh)(CO)_3]^+$, has also been reported.[6] These cations are exploited in the synthesis of alkyne, phosphine, metallacyclic, and amido complexes, such as $[Tp^*W(CO)_2(RC{\equiv}CR')]BF_4$,[2] $[Tp^*W(CO)_3(PR_3)]PF_6$ (R = Me, Et, Ph, etc.),[4] $Tp^*W\{C({=}O)\text{-}N(R)\text{-}C(Me){=}N(H)\}(CO)_2$ (R = H, Bu), and $Tp^*W\{N[C({=}CH_2)\text{-}N(Bu^t)\text{-}C(O)]\}(CO)_2$, respectively.[5] The nitrile complexes also react with nucleophiles producing azavinylidene complexes, $Tp^*W(CO)_2(N{=}CRNu)$ ($Nu^- = H^-, Me^-, Et^-, MeO^-$), which in turn react with electrophiles to yield imido species, $[Tp^*W(CO)_2(NCRENu)]BF_4$ ($E^+ = H^+, Ph_3C^+$)[6] (the latter process being reversed upon deprotonation[10]). Comparisons and orbital interpretations of the reactions of simple N-donor ligands bound to $[Tp^*W(CO)(PhC{\equiv}CMe)]^+$ and $[Tp^*W(CO)_2]^+$ fragments have been provided by Vogeley and Templeton.[11] The reactions of nitrile ligands, in a broader sense, are an area of considerable research interest.[12,13]

To date, all efforts to isolate and fully characterize any of the tricarbonyl complexes mentioned above have failed. Consequently, the formulations and structures of these important synthons remain uncertain or unknown. We report here the synthesis, isolation, and characterization of three salts containing the seven-coordinate cations $[Tp^*W(NCR)(CO)_3]^+$ (R = Me, Et).

Results and Discussion

Reaction of dark brown $Tp^*WI(CO)_3$ with silver salts (AgX) in acetonitrile instantly produces a suspension of silver iodide in a solution of bright yellow-orange $[Tp^*W(NCMe)(CO)_3]X$ ($X = CF_3SO_3^-$ (**1**), BF_4^- (**2**)) according to eq 1. The corresponding bromo and chloro complexes react similarly albeit more slowly, the rates of reaction being in the order I > Br > Cl.[7]

$$Tp^*WI(CO)_3 + AgX + NCMe \rightarrow [Tp^*W(NCMe)(CO)_3]X + AgI \quad (1)$$

During the reactions, solution infrared spectroscopy revealed the rapid replacement of the ν(CO) bands of the starting materials (ca. 2020 and 1920 cm^{-1}) by bands ascribed to the cationic product (2056 and 1963 cm^{-1}). The yellow filtrate obtained after removal of the silver salts was prone to aerial and photochemical decomposition and to further precipitation of silver salts upon standing. Isolation of the complexes depends critically on the prompt instigation and execution of workup and recrystallization procedures (see Experi-

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mental Section). The yellow crystalline substances were air-sensitive, decomposing over a period of hours to unidentified purple species. Compound **2** crystallized as a 1:1 acetone solvate from acetone/diethyl ether mixtures. The propionitrile derivative [Tp*W(NCEt)(CO)$_3$](CF$_3$SO$_3$) (**3**) was obtained via a nitrile exchange reaction.

Solution (CH$_2$Cl$_2$) infrared spectra of acetonitrile complexes **1** and **2** exhibited two ν(CO) bands, a sharp single band at 2056 cm^{-1} and a broader band at ca. 1960 cm^{-1}. Band shape analysis revealed that the broader band was comprised of two bands at ca. 1964 and 1951 cm^{-1}. These IR data are consistent with a structure of C_s rather than C_{3v} symmetry. Indeed, the spectra closely resemble those of Tp*WX(CO)$_3$ (X = Cl, Br, I), likely to adopt the carbonyl-capped octahedral structure established for Tp^{iPr}WI(CO)$_3$ (Tp^{iPr} = hydrotris(3-isopropylpyrazol-1-yl)borate).[7] The solid state infrared spectra exhibited ν(CO) bands at ca. 2050 and 1960 cm^{-1} as well as weak bands assigned to a monodentate acetonitrile ligand (ca. 2320 and 2290 cm^{-1}). Similar spectra, but with a clear separation of the low-energy ν(CO) bands in solution, were observed for **3**. Bands characteristic of Tp* and the anions/solvates were observed in all cases. ^{1}H NMR spectra were consistent with molecular C_s symmetry, with 1:2:2:1 and 2:1 patterns for the methyl and methine resonances, respectively. In CDCl$_3$, the acetonitrile resonances of **1** and **2**·acetone were observed at δ 2.71 and 2.65, respectively; a resonance at δ 2.18 in the spectrum of the latter was ascribed to solvate acetone. The acetonitrile methyl resonance was absent from samples synthesized using d_3-acetonitrile as solvent. Spectral changes consistent with nitrile ligand exchange were observed in spectra recorded in d_3-acetonitrile (with the nitrile resonance at δ ca. 2.44 diminishing and the resonance of free NCMe growing with time). Triplet (δ 1.20) and quartet (δ 2.36) resonances were assigned to the methyl and methylene protons, respectively, of the propionitrile ligand in **3**. The ^{13}C NMR spectrum of **2** in d_6-acetone exhibited the expected resonance pattern and a nitrile $C{\equiv}$N resonance at δ ca. 139; the carbonyl resonances could not be detected.

The structures of **1**, **2**·acetone, and **3** were determined by X-ray diffraction. Essentially identical structures were observed for the complex cations, and the discussion below pertains to all three; data for the compounds are presented in the order cited above. Views of the cations in the triflate salts **1** and **3** are presented in Figures 1 and 2, respectively. Selected bond distances and angles are presented in Table 1. The tungsten center in the discrete complex cation is coordinated by a facially tridentate Tp* ligand, three carbonyl ligands, and an end-on N-bound acetonitrile ligand. A pseudo-mirror plane passes through W, B, the pyrazole ring containing N(11), the carbonyl group −C(2)O(2), and the nitrile ligand; the C(2), W, N(1), and N(11) atoms are planar with maximum displacements of 0.0147, 0.0017, and 0.0006 Å for the W atom in the respective cations.

The coordination spheres closely approach a capped octahedral geometry with an axial carbonyl ligand (abbreviated CO_h-CO$_{ax}$). The octahedron is defined by atoms C(1), C(3), N(1), and N(n1) (n = 1−3); the capping carbonyl ligand containing C(2) lies close to the pseudo-3-fold axis projecting out of the face defined by C(1), C(3), and N(1), subtending small angles of 2.7°, 8.1°, and 1.2° to the W···B axis. Superposition of idealized CO_h and real structures produced rms atom deviations of 0.11, 0.15, and 0.05 Å for the cations of **1**, **2**·acetone, and **3**, respectively; the superimposed idealized CO_h-CO$_{ax}$ and real structures of the cation of **1** are displayed in Figure 3a. When the WN$_3$ core of the W-Tp* unit is used as the basis for the superposition, the rms atom deviations are 0.016, 0.020, and 0.011 Å, respectively, with nitrile N and carbonyl C atom displacements as follows (Δ = separation of real and idealized positions for the cations in the order stated above): $\Delta_{N(1)}$ = 0.14, 0.06, and 0.08 Å, $\Delta_{C(1)}$ = 0.07, 0.23, and 0.05 Å, $\Delta_{C(2)}$ = 0.11, 0.27, and 0.06 Å, and $\Delta_{C(3)}$ = 0.04, 0.10, and 0.10 Å. The δ' angles (δ'_1, δ'_2, and δ'_3) for the cations, as defined by Muetterties and Guggenberger,[14] are 18.4°, 17.5°, and 12.5° for **1**, 22.1°, 3.5°, and 12.7° for **2**·acetone, and 18.1°, 16.8°, and 14.9° for **3**; these compare well with the δ' angles expected for an idealized CO_h

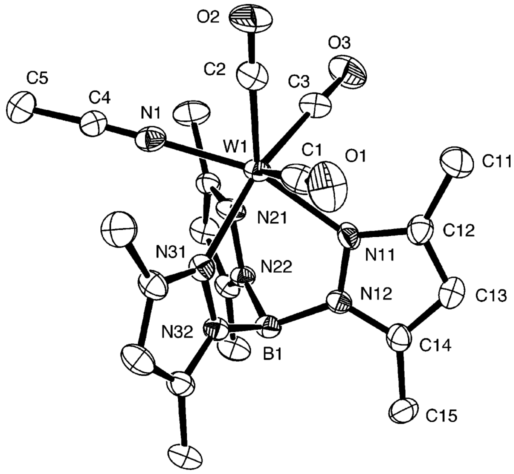

Figure 1. Structure of the cation in **1**. The numbering schemes for the pyrazole rings containing N(21) and N(31) parallel that shown for the ring containing N(11). Thermal ellipsoids are drawn at the 30% probability level, and H atoms are excluded for clarity.

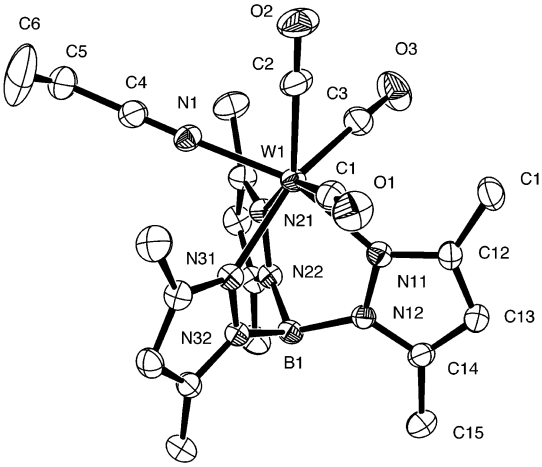

Figure 2. Structure of the cation in **3**. See Figure 1 caption for details.

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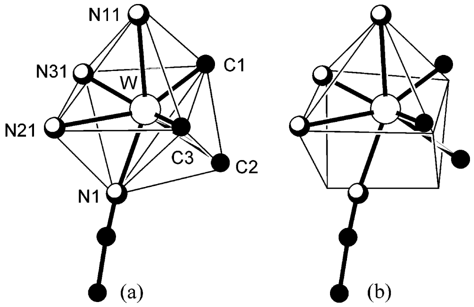

Figure 3. Comparisons of the coordination geometry of the cation in **1** with idealized capped octahedral (a) and capped trigonal prismatic (b) coordination spheres. The idealized geometries are represented as wireframe polyhedra, the real structures (in identical orientations) by balls and sticks.

Table 1. Selected Bond Distances and Angles

	1	**2**·acetone	**3**
	Distances (Å)		
W−N(1)	2.157(5)	2.147(9)	2.147(3)
W−C(1)	1.996(8)	1.992(11)	2.008(4)
W−C(2)	1.987(7)	1.994(10)	1.985(4)
W−C(3)	2.013(7)	2.013(11)	1.990(5)
W−N(11)	2.191(5)	2.195(8)	2.182(3)
W−N(21)	2.220(5)	2.226(6)	2.216(3)
W−N(31)	2.205(5)	2.228(7)	2.220(3)
C(1)−O(1)	1.139(8)	1.153(12)	1.133(5)
C(2)−O(2)	1.148(7)	1.153(11)	1.146(5)
C(3)−O(3)	1.128(7)	1.156(13)	1.145(5)
N(1)−C(4)	1.127(7)	1.158(13)	1.129(5)
C(4)−C(5)	1.456(9)	1.454(15)	1.452(6)
	Angles (deg)		
N(1)−W−C(1)	112.3(2)	118.0(4)	113.43(15)
N(1)−W−C(2)	73.4(2)	75.0(4)	73.13(15)
N(1)−W−C(3)	111.1(2)	109.0(4)	110.88(16)
N(1)−W−N(11)	160.28(18)	157.8(3)	158.68(12)
N(1)−W−N(21)	80.36(18)	78.7(3)	79.22(12)
N(1)−W−N(31)	80.54(18)	78.9(3)	79.83(12)
C(1)−W−C(2)	71.6(3)	70.5(4)	73.03(17)
C(1)−W−C(3)	110.5(3)	107.6(4)	110.18(17)
C(1)−W−N(11)	79.0(2)	75.0(4)	77.51(14)
C(1)−W−N(21)	157.5(2)	152.9(3)	156.01(15)
C(1)−W−N(31)	81.5(2)	80.1(3)	79.72(14)
C(2)−W−C(3)	72.3(3)	72.9(4)	71.7(2)
C(2)−W−N(11)	126.3(2)	127.3(4)	128.19(15)
C(2)−W−N(21)	130.8(2)	136.5(4)	130.95(15)
C(2)−W−N(31)	131.0(2)	124.0(4)	129.10(17)
C(3)−W−N(11)	77.7(2)	81.3(4)	80.04(17)
C(3)−W−N(21)	79.8(2)	84.0(3)	81.79(15)
C(3)−W−N(31)	156.7(2)	163.1(3)	159.15(17)
N(11)−W−N(21)	84.11(17)	83.0(3)	84.56(11)
N(11)−W−N(31)	85.49(17)	86.5(3)	84.54(12)
N(21)−W−N(31)	82.56(17)	82.9(2)	82.87(10)
W−C(1)−O(1)	176.2(7)	178.1(10)	174.1(4)
W−C(2)−O(2)	178.1(7)	178.6(10)	178.0(5)
W−C(3)−O(3)	174.9(6)	176.8(9)	176.5(5)
W−N(1)−C(4)	175.1(5)	177.9(8)	177.5(3)
N(1)−C(4)−C(5)	178.0(8)	177.7(12)	178.7(5)

geometry, viz., $\delta'_1 = \delta'_2 = \delta'_3 = 16.2°$. The above data show that the cation of **2**·acetone is the more distorted of the three, most probably due to lattice packing effects.

As expected, C(1), C(3), and N(1) are splayed away from the capping C(2) atom. The W atoms of the three complexes lie 0.622(4), 0.607(5), and 0.611(2) Å out of the planes defined by C(1), C(3), and N(1), and 1.398(3), 1.404(4), and 1.400(2) Å out of the planes defined by the three N(*n*1) atoms; these two faces are parallel, with dihedral angles of just 4.2(4)°, 6.1(3)°, and 2.7(2)°. This distortion is reflected in the angles subtended with the W···B axis in the three complexes, viz., for W−C(1), 107.1°, 101.9°, and 105.8°; W−C(3), 106.2°, 112.7°, and 108.6°; W−N(1), 109.4°, 107.5°, and 107.7°; W−N$_{av}$, 50.6°, 50.7°, and 50.6°; and the average *trans* N/C$_{face}$−W−N angles of 158.2°, 158.4°, and 158.0°. The B···W−C(2) angles are 177.3°, 171.9°, and 178.8°, respectively, consistent with the presence of a pseudosymmetry axis. The nitrile ligands are essentially linear with experimentally identical W−N distances at ca. 2.15 Å. The W−C and W−N(*n*1) distances lie in the ranges 1.985(4)−2.013(7) and 2.182(3)−2.228(7) Å, respectively. The pyrazole rings are planar and the carbonyl ligands are essentially linear in all cases.

The structure of the cation of **1** is compared to the closest idealized capped trigonal prismatic (CTP) structure, with N(11) (the capping atom), W, N(1), and C(2) in a σ_v plane, in Figure 3b; atoms C(1) and N(1) are displaced by ca. 0.7 and 0.6 Å, respectively, from their idealized positions, the displacements of the other atoms being ca. 0.1−0.3 Å; the same is true of the other structures. The δ' angles for the CTP geometry, $\delta'_1 = \delta'_2 = 0°$, and $\delta'_3 = 41.5$ °, differ substantially from those determined for the complexes.

A variety of structures are adopted by seven-coordinate complexes of the type $LM(CO)_3X$ (L = Tp derivative; M = Mo, W; X = Hal, CH_2CN, SnR_3, H, PR_3). Complexes such as Tp*Mo$(CO)_3(SnPh_3)$, Tp*Mo$(CO)_3(SnClMe_2)$, $(MeGapz_3)Mo(CO)_3(SnPh_3)$,[15,16] Tp*W$(CO)_3(PMe_3)$, and Tp*W$(CO)_3(PPhMe_2)$[4] exhibit CO_h structures with effective C_{3v} symmetry, the substitutents of the non-carbonyl ligand being eclipsed with respect to the pyrazolyl groups of Tp*, the carbonyl ligands staggered. Piano-stool structures are adopted by TpMo$(CO)_3$Br,[17] TpMo$(CO)_3(CH_2CN)$,[18] and Tp*MH$(CO)_3$ (M = Mo,[19] W[20]); here, the less sterically demanding (carbonyl or hydride) ligands eclipse a pyrazole group (when viewed along the M−B vector). The hitherto unique carbonyl-capped octahedral structure of Tp^{iPr}WI$(CO)_3$ features a staggered arrangement of the facial coligands and the bulky isopropylpyrazolyl groups.[7] The structures of the title complexes are closely related to that of Tp^{iPr}WI$(CO)_3$ but with the nitrile in place of iodide. With these structures in hand, there is a roughly equal representation of the three seven-coordinate structural types in carbonyl-Mo/W trispyrazolylborate complexes.

Experimental Section

Materials and Methods. All reactions were performed under an atmosphere of dinitrogen using dried, deoxygenated solvents and standard Schlenk techniques. Samples of Tp*WI$(CO)_3$[7,21] were prepared by literature methods, and all other reagents were analytical reagent grade or above. Infrared spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer, and ^{1}H NMR spectra were obtained using Varian

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Table 2. Crystallographic Data

	1	**2**·acetone	**3**
formula	$C_{21}H_{25}BF_3N_7O_6SW$	$C_{23}H_{31}B_2F_4N_7O_4W$	$C_{22}H_{27}BF_3N_7O_6SW$
fw	755.20	751.02	769.23
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	14.2114(17)	12.013(8)	14.6582(7)
b, Å	14.0071(17)	13.266(9)	13.8294(6)
c, Å	14.5748(18)	19.970(13)	15.0128(7)
β, deg	104.087(2)	104.964(12)	106.6300(10)
V, Å^3	2814.0(6)	3075(3)	2916.0(2)
Z	4	4	4
ρ, g cm^{-3}	1.783	1.622	1.752
unique/$I > 2\sigma(I)$	6407/4439	6801/5069	6640/5410
μ, cm^{-1}	42.48	38.21	41.01
R	0.0402	0.0687	0.0322
R_w	0.0960	0.1905	0.0764
GOF	1.008	1.045	0.943

Unity 300 and Varian Unity Plus 400 spectrometers. Microanalyses were performed by Atlantic Microlabs Inc, Norcross, GA.

Syntheses. [Tp*W(NCMe)(CO)$_3$](CF$_3$SO$_3$) (1). Solid AgO$_3$SCF$_3$ (0.288 g, 1.12 mmol) was added to a stirred solution of Tp*WI(CO)$_3$ (0.944 g. 1.36 mmol) in acetonitrile (30 mL). After 5 min the solution was filtered through Celite. The solution was then reduced to dryness and the residue recrystallized from acetone/diethyl ether to produce yellow crystals of **1** (yield: 0.35 g, 41%). Best results were obtained when the workup/recrystallization steps were promptly instigated and executed. Anal. Calcd for $C_{21}H_{25}BF_3N_7O_6SW$: C, 33.40; H, 3.34; N, 12.98. Found: C, 33.45; H, 3.37; N, 12.86. IR (KBr, cm^{-1}): ν(BH) 2575w; ν(CO) 2054s, 1970s, 1954s; ν(C≡N) 2321vw, 2287w; ν(CN) 1544m. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2055s, 1964s. ^{1}H NMR (NCCD$_3$): δ 2.18 (s, 3H), 2.27 (s, 6H), 2.46 (s, 6H), 2.49 (s, 3H) (6CH_3 of Tp*); 2.43 (s, 3H, CH_3CN); 6.15 (s, 1H), 6.16 (s, 2H) (3CH of Tp*). ^{1}H NMR (CDCl$_3$): δ 2.07 (s, 3H), 2.31 (s, 6H), 2.46 (s, 6H), 2.49 (s, 3H) (6CH_3 of Tp*); 2.71 (s, 3H, CH_3CN); 6.06 (s, 1H), 6.13 (s, 2H) (3CH of Tp*).

[Tp*W(NCMe)(CO)$_3$]BF$_4$ (2). Solid AgBF$_4$ (0.379 g, 1.95 mmol) was added to a stirred solution of Tp*WI(CO)$_3$ (1.00 g. 1.44 mmol) in acetonitrile (30 mL). After 5 min the solution was filtered through Celite. The yellow filtrate was reduced to dryness and the residue recrystallized from acetone/diethyl ether, to produce yellow crystals of **2**·acetone (yield: 0.29 g, 35%). Best results were obtained when the workup/recrystallization steps were promptly instigated and executed. The solvent acetone can be removed by warming the crystals under vacuum. Characterization data are for **2**·acetone. Anal. Calcd for $C_{23}H_{31}B_2F_4N_7O_4W$: C, 36.78; H, 4.16; N, 13.05. Found: C, 36.75; H, 4.26; N, 13.18. IR (KBr, cm^{-1}): ν(BH) 2573w; ν(CO) 2045s, 1948s,br; ν(C≡N) 2324vw, 2292w; ν(C═O) 1703m, ν(CN) 1544m. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2054s, 1960s. ^{1}H NMR (NCCD$_3$): δ 2.09 (s, 6H, O═C(CH_3)$_2$); 2.07 (s, 3H), 2.28 (s, 6H), 2.47 (s, 6H), 2.50 (s, 3H) (6CH_3 of Tp*); 2.44 (s, 3H, CH_3CN); 6.16 (s, 1H), 6.18 (s, 2H) (3CH of Tp*). ^{1}H NMR (CDCl$_3$): δ 2.18 (s, 6H, O═C(CH_3)$_2$); 2.07 (s, 3H), 2.31 (s, 6H), 2.46 (s, 6H), 2.48 (s, 3H) (6CH_3 of Tp*); 2.65 (s, 3H, CH_3CN); 6.04 (s, 1H), 6.12 (s, 2H) (3CH of Tp*). ^{13}C{^{1}H} NMR (d_6-acetone): δ 4.46 (CH$_3$CN); 12.62 (2C), 13.24, 15.46 (2C), 16.06 (6CH$_3$ of Tp*); 109.23 (2C), 109.93 (3CH of Tp*); 138.97 (CH$_3$$C$N);148.52 (2C), 151.27, 152.96 (2C), 153.95 (6CMe of Tp*).

[Tp*W(NCEt)(CO)$_3$](CF$_3$SO$_3$) (3). A sample of **1** (100 mg, 0.15 mmol) was stirred in propionitrile (10 mL) for 2−3 h. The solvent was then evaporated and the residue recrystallized from acetone/diethyl ether to produce yellow crystals of **3** (yield: 60 mg, 60%). Anal. Calcd for $C_{22}H_{27}BF_3N_7O_6SW$: C, 34.35; H, 3.54; N, 12.75. Found: C, 33.94; H, 3.51; N, 12.64. IR (KBr, cm^{-1}): ν(BH) 2573w; ν(CO) 2054s, 1974s, 1950s; ν(C≡N) 2285w; ν(CN) 1544. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2053s, 1969s, 1949s. ^{1}H NMR (NCCD$_3$): δ 1.20 (t, 3H, CH_3CH$_2$CN), 2.36 (q, 2H, CH$_3$CH_2CN); 2.07 (s, 3H), 2.28 (s, 6H), 2.46 (s, 6H), 2.49 (s, 3H) (6CH_3 of Tp*); 6.18 (s, 1H), 6.19 (s, 2H) (3CH of Tp*). ^{1}H NMR (CDCl$_3$): δ 1.26 (t, 3H, CH_3CH$_2$CN), 3.08 (q, 2H, CH$_3$CH_2CN); 2.08 (s, 3H), 2.32 (s, 6H), 2.47 (s, 6H), 2.50 (s, 3H) (6CH_3 of Tp*); 6.06 (s, 1H), 6.15 (s, 2H) (3CH of Tp*).

X-ray Crystallography. Yellow crystals of the complexes were grown by slow diffusion of diethyl ether into acetone solutions of the complexes. Crystals of approximate dimensions 0.10 × 0.05 × 0.02 mm^3 (for **1**), 0.50 × 0.30 × 0.06 mm^3 (for **2**·acetone), and 0.20 × 0.15 × 0.10 mm^3 (for **3**) were selected for data collection. Intensity data were collected with a Bruker SMART Apex CCD detector using Mo Kα radiation (graphite crystal monochromator $\lambda = 0.71073$) at 293 K.[22] Accurate cell parameters and crystal orientation were obtained by least-squares refinement of 4101, 6302, and 7595 reflections with θ values between 2.3° and 23.2°, 27.1°, and 27.5° for **1**, **2**·acetone, and **3**, respectively. Data were reduced using the program SAINT and corrected for absorption using the program SMART.[22] Crystallographic data are summarized in Table 2.

The structures were solved by direct methods and difference Fourier syntheses.[22] Hydrogen atoms were included in calculated positions. Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms.

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Supporting Information Available: Crystallographic data (in CIF format) for all three compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) *SMART*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1999.