Ligand Exchange Reactions of $[Et_4N]_3[W_2(CO)_6(OMe)_3]$. A Reactive Binuclear Tungsten(0) Carbonyl Center

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The complex $[Et_4N]_3[W_2(CO)_6(OMe)_3]$ (**1**) has been shown to undergo ligand substitution of the methoxide in the presence of alcohols. This reaction proceeds provided the incoming alcohol is more acidic than the afforded methanol. The reaction is facile at room temperature, with completion of reaction being attained in less than an hour. The exchange for the substituted aryl alcohols 4-aminophenol (**2**), 4-hydroxypyridine (**3**), 3-hydroxypyridine (**4**), 4-cyanophenol (**5**), and 3-cyanophenol (**6**) was studied. Complexes **2**, **4**, **5**, and **6** were structurally characterized by X-ray crystal analysis.

Introduction

Since the first reports by Hieber,[1−4] reactions of group 6 carbonyls under basic conditions have been widely studied. Much of the interest in these complexes stems from their role in catalytic reactions, for example, aldehyde/ketone reductions and methanol carbonylations.[5−9] Numerous complexes have been isolated and structurally characterized. These complexes exhibit structural motifs which include binuclear metal centers that are either doubly or triply bridged by hydroxide, alkoxides, and aryloxides having the general formula $W_2(CO)_8(OR)_2^{2-}$ or $M_2(CO)_6(OR)_3^{3-}$ (M = Mo, W).[10−16] Also known is the triply bridged cubane-like tetraanion $M_4(CO)_{12}(OMe)_4^{4-}$ (M = Cr, Mo, W).[10,17] The subsequent reactivity of these dimers and tetramers has remained relatively undeveloped. One example is the reaction of $Cr_4(CO)_{12}(OMe)_4^{4-}$ with aqueous ammonia to afford $Cr(CO)_3(NH_3)_3$ or with concentrated hydrochloric acid in an acetonitrile solution to yield $Cr(CO)_3(CH_3CN)_3$.[17] The thiolate derivatives have been extensively studied by Zhuang and co-workers, including the oxidation of the doubly bridged $M_2(CO)_8(SR)_2^{2-}$ species (M = Mo or W).[18]

In this family of compounds, the generation of metal−metal bonds has been rarely observed, with only one reported example thus far. For this series, $[Me_4N]_3[M_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]$ (M = Mo, W),[19] only the subsequent reaction of the M−M bond has been explored.[20,21] In these cases the M−M bond was reacted with Ph_3PAu^+ and Bi^+ to yield heteronuclear clusters. These highly anionic complexes are interesting from another standpoint also. If one wanted to produce an anionic metallodendrimer or supramolecular assembly, these complexes would provide the required negative charge for its construction. This report focuses on the reactivity of the complex $[Et_4N]_3[W_2(CO)_6(OMe)_3]$ with various alcohols (HOR) where R contains a basic functionality, to afford the trisubstituted product $[Et_4N]_3[W_2(CO)_6(OR)_3]$.

Experimental Section

General Considerations. All reactions were carried out under air-free conditions in an argon-filled glovebox, or using standard Schlenk techniques. THF, diethyl ether, and hexane were freshly distilled from sodium/benzophenone ketyl; acetonitrile was freshly distilled from calcium hydride. Photolysis reactions were carried out with a 350 W mercury vapor lamp

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purchased from Ace Glass Inc. Infrared spectra were recorded on either a Mattson Genesis II or a ThermoMattson IR300 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer and referenced to the residual solvent peaks. When possible, ^{13}C assignments of the ligands were made by comparison with expected shifts for the free ligand.[22] Mass spectra were acquired using an API QStar Pulsar (MDS Sciex, Concord, Ontario) quadrupole-time-of-flight mass spectrometer (QqTOFMS) equipped with an ion-spray source.

Syntheses. $[\mathbf{Et_4N}]_3[\mathbf{W_2(CO)_6(OMe)_3}]$ (**1**) was synthesized according to the published procedure.[10] All other reagents were purchased from Aldrich Chemical Co. or Sigma Chemical Co. and used as received.

General Synthesis of $[\mathbf{Et_4N}]_3[\mathbf{W_2(CO)_6(OR)_3}]$ (OR = $\mathbf{4\text{-}OC_6H_4NH_2}$ (2), $\mathbf{4\text{-}OC_5H_4N}$ (3), $\mathbf{3\text{-}OC_5H_4N}$ (4), $\mathbf{4\text{-}OC_6H_4CN}$ (5), $\mathbf{3\text{-}OC_6H_4CN}$ (6)). The complex **1** (0.200 g, 0.2 mmol) was dissolved in CH_3CN (20 mL), and an acetonitrile solution of ROH (0.6 mmol in 30 mL of CH_3CN) was added. After stirring at room temperature for 2 h, the solvent was evaporated under reduced pressure to approximately 10 mL. The resulting solution was precipitated with 60 mL of diethyl ether. The solid obtained, $[Et_4N]_3W_2(CO)_6(OR)_3$, was washed twice with 30 mL of THF and dried under vacuum for 1 h. Complex **2** is light sensitive, decomposing in acetonitrile solution, but complexes **3**−**6** are stable in solution indefinitely, provided an inert atmosphere is present.

$[\mathbf{Et_4N}]_3[\mathbf{W_2(CO)_6(4\text{-}OC_6H_4NH_2)_3}]$ (2): beige powder; yield 0.145 g (59%). IR (cm^{-1}): CH_3CN ν (C−O) 1854 (s), 1716 (vs). ^{1}H NMR (CD_3CN): δ 7.38, 6.67, 6.45, 6.38 (m, m, m, m, 2H, 4H, 4H, 2H, $OC_6\mathit{H}_4NH_2$), 3.57 (s, br, 6H, $OC_6H_4N\mathit{H}_2$), 3.09 (m, 24H, $(CH_3C\mathit{H}_2)_4N$), 1.13 (m, 36H, $(C\mathit{H}_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 230.7 (CO), 161.5, 151.8 ($O\mathit{C}C_4H_4CN$), 139.6, 136.3 ($OCC_4H_4\mathit{C}NH_2$), 122.3−115.7 ($OC\mathit{C}_4H_4CNH_2$), 52.5 ($(CH_3\mathit{C}H_2)_4N$), 7.4 ($(\mathit{C}H_3CH_2)_4N$).

$[\mathbf{Et_4N}]_3[\mathbf{W_2(CO)_6(4\text{-}OC_5H_4N)_3}]$ (3): yellow powder; yield 0.150 g (63%). IR (cm^{-1}): CH_3CN ν(C−O) 1870 (s), 1737 (vs). ^{1}H NMR (CD_3CN): δ 8.03, 7.48 (m, m, 6H, 6H, $OC_5\mathit{H}_4N$), 3.06 (m, 24H, $(CH_3C\mathit{H}_2)_4N$), 1.12 (m, 36H, $(C\mathit{H}_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 228.8 (CO), 173.5 ($O\mathit{C}C_4H_4N$), 150.1, 118.7 ($OC\mathit{C}_4H_4N$), 52.5 ($(CH_3\mathit{C}H_2)_4N$), 7.3 ($(\mathit{C}H_3CH_2)_4N$). ES$^-$-MS (CH_3CN): *m/z* 949 $\{[Et_4N][W_2(CO)_6(4\text{-}OC_5H_4N)_3]H\}^-$.

$[\mathbf{Et_4N}]_3[\mathbf{W_2(CO)_6(3\text{-}OC_5H_4N)_3}]$ (4): yellow powder; yield 0.145 g (61%). IR (cm^{-1}): CH_3CN ν(C−O) 1865 (s), 1731 (vs). ^{1}H NMR (CD_3CN): δ 8.86, 7.85, 7.69, 6.97 (m, m, m, m, 3H, 3H, 3H, 3H, $OC_5\mathit{H}_4N$), 3.04 (m, 24H, $(CH_3C\mathit{H}_2)_4N$), 1.12 (m, 36H, $(C\mathit{H}_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 229.4 (CO), 163.8 ($O\mathit{C}C_4H_4N$), 145.8, 135.7, 127.7, 123.2 ($OC\mathit{C}_4H_4N$), 52.5 ($(CH_3\mathit{C}H_2)_4N$), 7.3 ($(\mathit{C}H_3CH_2)_4N$). ES$^-$-MS (CH_3CN): *m/z* 949 $\{[Et_4N][W_2(CO)_6(3\text{-}OC_5H_4N)_3]H\}^-$, 819 $\{[W_2(CO)_6(3\text{-}OC_5H_4N)_3]H\}^{2-}$.

$[\mathbf{Et_4N}]_3[\mathbf{W_2(CO)_6(4\text{-}OC_6H_4CN)_3}]$ (5): yellow powder; yield 0.170 g (70%). IR(cm^{-1}): CH_3CN ν(C−O) 1871 (s), 1738 (vs); ν(C−N) 2210 (s). ^{1}H NMR (CD_3CN): δ 7.70, 7.39 (m, m, 6H, 6H, $OC_6\mathit{H}_4CN$), 3.02 (m, 24H, $(CH_3C\mathit{H}_2)_4N$), 1.12 (m, 36H, $(C\mathit{H}_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 228.4 (CO), 172.2 ($O\mathit{C}C_5H_4CN$), 134.4−119.1 ($OC\mathit{C}_5H_4CN$), 97.0 ($\mathit{C}N$) 52.5 ($(CH_3\mathit{C}H_2)_4N$), 7.3 ($(\mathit{C}H_3CH_2)_4N$). ES$^-$-MS (CH_3CN): *m/z* 1150 $\{[Et_4N]_2[W_2(CO)_6(4\text{-}OC_6H_4CN)_3]\}^-$, 1021 $\{[Et_4N][W_2(CO)_6(4\text{-}OC_6H_4CN)_3]H\}^-$, 902 $\{[Et_4N][W_2(CO)_6(4\text{-}OC_6H_4CN)_2]\}^-$.

$[\mathbf{Et_4N}]_3[\mathbf{W_2(CO)_6(3\text{-}OC_6H_4CN)_3}]$ (6): yellow powder; yield 0.174 g (72%). IR (cm^{-1}): CH_3CN ν(C−O) 1868 (s), 1735 (vs); ν(C−N) 2210 (s). ^{1}H NMR (CD_3CN): δ 7.92, 7.18, 6.81 (m, m, m, 6H, 3H, 3H, $OC_6\mathit{H}_4CN$), 3.04 (m, 24H, $(CH_3C\mathit{H}_2)_4N$), 1.12 (m, 36H, $(C\mathit{H}_3CH_2)_4N$). ^{13}C NMR (CD_3CN): δ 228.9 (CO), 168.2, 165.6 ($O\mathit{C}C_5H_4CN$), 130.8−119.0 ($OC\mathit{C}_5H_4CN$), 112.8, 111.5 ($\mathit{C}N$) 52.6 ($(CH_3\mathit{C}H_2)_4N$), 7.5 ($(\mathit{C}H_3CH_2)_4N$). ES$^-$-MS (CH_3CN): *m/z* 1150 $\{[Et_4N]_2[W_2(CO)_6(3\text{-}OC_6H_4CN)_3]\}^-$, 1021 $\{[Et_4N][W_2(CO)_6(3\text{-}OC_6H_4CN)_3]H\}^-$, 902 $\{[Et_4N][W_2(CO)_6(3\text{-}OC_6H_4CN)_2]\}^-$.

Table 1. Infrared Spectra in the Carbonyl Region for Compounds 1−6

compound[a]	ν(CO)
$[Et_4N]_3[W_2(CO)_6(OMe)_3]$ (**1**)	1834(s), 1698(vs)[10]
$[Et_4N]_3[W_2(CO)_6(OPh)_3]$	1860(s), 1719(vs)[14]
$[Et_4N]_3[W_2(CO)_6(4\text{-}OC_6H_4NH_2)_3]$ (**2**)	1854(s), 1716(vs)
$[Et_4N]_3[W_2(CO)_6(4\text{-}OC_5H_4N)_3]$ (**3**)	1870(s), 1737(vs)
$[Et_4N]_3[W_2(CO)_6(3\text{-}OC_5H_4N)_3]$ (**4**)	1865(s), 1731(vs)
$[Et_4N]_3[W_2(CO)_6(4\text{-}OC_6H_4CN)_3]$ (**5**)	1868(s), 1735(vs)
$[Et_4N]_3[W_2(CO)_6(3\text{-}OC_6H_4CN)_3]$ (**6**)	1870(s), 1738(vs)

[a] Spectra recorded in CH_3CN.

X-ray Crystallography. Details of data collection and refinement are given in Table 2. Crystals of complexes **2**, **4**, **5**, and **6** were grown by vapor diffusion of ether into an acetonitrile solution at −10 °C. A brown block for **2** and yellow blocks for **4**, **5**, and **6** were fixed to a cryo-loop in paratone oil and immediately placed in a nitrogen cold stream (110 K). A Bruker SMART 1000 X-ray three-circle diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the SMART software suite, version 5.056 (Microsoft NT operating system). The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 5.0 cm from the crystal sample (CCD-PXL-KAF2, SMART 1000, 512 × 512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (Kα = 0.70173 Å with a potential of 50 kV and a current of 40 mA) and filtered with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes).

Dark currents were obtained for the appropriate exposure time of 30 s, and a rotation exposure was taken to determine crystal quality and the X-ray beam intersection with the detector. The beam intersection coordinates were compared to the configured coordinates and changes were made accordingly. The rotation exposure indicated acceptable crystal quality, and the unit cell determination was undertaken. Twenty data frames were taken at widths of 0.3° with an exposure time of 10 s. A total of 84 reflections for **2**, 113 for **4**, 224 for **5**, and 36 for **6** were centered and their positions were determined. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures (Table 2). The unit cell was verified by examination of the *hkl* overlays on several frames of data, including zone photographs. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated. This procedure consists of collection of one hemisphere of data collected using omega scans, involving the collection of 1201, 0.3° frames at fixed angles for ϕ, 2θ, and χ ($2\theta = -28°$, $\chi = 54.73°$), while varying omega. Each frame was exposed for 30 s and contrasted against a 30 s dark current exposure. The total data collection was performed for a duration of approximately 13 h at 110 K. No significant intensity fluctuations of equivalent reflections were observed.

Data reduction was accomplished using SAINTPLUS (Bruker[23]). All structures were solved by direct methods using the SHELX program suite,[24] which provided the positions of the tungsten atoms and some of the atoms of the ligands. Subsequent least-squares refinements revealed the positions of the

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(23) *SAINT-Plus* 6.02 ed.; Bruker: Madison, WI, 1999.

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Table 2. Crystal Data, Data Collection, and Structure Refinement for 2, 4, 5, and 6

	2	**4**	**5**	**6**
empirical formula	$C_{50}H_{81}N_7O_9W_2$	$C_{49}H_{78}N_8O_9W_2$	$C_{53}H_{75}N_7O_9W_2$	$C_{110}H_{156}N_{16}O_{18}W_4$
fw	1291.92	1290.89	1321.90	2725.91
temperature, K	110			
wavelength, Å	0.71073			
cryst syst	orthorhombic	orthorhombic	orthorhombic	triclinic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$
unit cell dimens	$a = 11.92(4)$ Å	$a = 11.83(2)$ Å	$a = 15.070(6)$ Å	$a = 11.971(7)$ Å
				$\alpha = 106.512(9)°$
	$b = 17.63(6)$ Å	$b = 17.26(2)$ Å	$b = 19.220(8)$ Å	$b = 18.639(11)$ Å
				$\beta = 97.301(10)°$
	$c = 26.02(9)$ Å	$c = 26.39(4)$ Å	$c = 19.295(8)$ Å	$c = 28.82(2)$ Å
				$\gamma = 100.956(10)°$
	$V = 5465(32)$ Å^3	$V = 5389(13)$ Å^3	$V = 5589(4)$ Å^3	$V = 5939(6)$ Å^3
	$Z = 4$	$Z = 4$	$Z = 4$	
density (calcd), Mg/m^3	1.570	1.591	1.571	1.524
abs coeff, mm^{-1}	4.264	4.325	4.172	3.928
cryst size, mm	.05 × 0.10 × 0.10	.08 × 0.17 × 0.21	.12 × 0.15 × 0.20	.15 × 0.18 × 0.20
θ range for data collection, deg	1.40 to 28.26	1.41 to 28.38	1.50 to 28.35	1.17 to 27.74
index ranges	$-15 \le h \le 13$	$-15 \le h \le 15$	$-19 \le h \le 15$	$-15 \le h \le 15$
	$-23 \le k \le 22$	$-23 \le k \le 21$	$-25 \le k \le 21$	$-23 \le k \le 23$
	$-34 \le l \le 21$	$-28 \le l \le 34$	$-22 \le l \le 25$	$-37 \le l \le 36$
collection method	0.3 deg ω scans for 0.1667 min/scan			
no. of reflns collected	35 452 [R(int) = 0.0523]	35 019 [R(int) = 0.0403]	36 231 [R(int) = 0.0314]	50 832 [R(int) = 0.0724]
no. of ind reflns	13 140 [9848 obs, $I > 2\sigma(I)$]	12 938 [10 432 obs, $I > 2\sigma(I)$]	13 346 [12 485 obs, $I > 2\sigma(I)$]	25 998 [16 341 obs, $I > 2\sigma(I)$]
abs corr	SADABS[a]			
refinement	full-matrix least-squares on F^2			
no. of data/restraints/params	13 137/56/655	12 935/0/617	13 345/0/641	25 998/9/1281
goodness-of-fit on F^2	1.065	1.003	1.000	1.104
final R indices (obs data)	R1 = 0.0399	R1 = 0.0319	R1 = 0.0187	R1 = 0.0633
	wR2 = 0.0753	wR2 = 0.0576	wR2 = 0.0373	wR2 = 0.1423
R indices (all data)	R1 = 0.0721	R1 = 0.0473	R1 = 0.0224	R1 = 0.1162
	wR2 = 0.0908	wR2 = 0.0877	wR2 = 0.0568	wR2 = 0.1690
abs structure param	−0.022(10)	0.000(6)	−0.023(3)	
largest diff peak and hole, e/Å^3	1.754 and −0.936	1.509 and −0.779	0.966 and −0.525	3.421 and −1.891

[a] Sheldrick, G. M.; University of Gottingen: Gottingen, Germany, 1997.

remaining atoms in the structure. Unless noted otherwise, all non-hydrogen atoms were refined anisotropically.

Results and Discussion

Synthesis. The triply bridged binuclear complex $[Et_4N]_3[W_2(CO)_6(OMe)_3]$ (**1**) has been shown to undergo facile ligand exchange under ambient conditions in acetonitrile with a variety of alcohols to afford the trisubstituted product (eq 1). This reaction proceeds provided the incoming alcohol has a lower pK_a than the afforded methanol.

$$W_2(CO)_6(OMe)_3^{\,3-} + 3HOR \rightarrow W_2(CO)_6(OR)_3^{\,3-} + 3MeOH \quad (1)$$

The exchange reaction has been carried out for a number of substituted aryl alcohols, and the infrared spectra of these compounds are listed in Table 1. Due to the air sensitivity of these molecules, satisfactory elemental analysis has not been possible.

For the more acidic aryl alcohols, substitution is complete within 20 min, as indicated by the shift to higher wavenumbers in the IR spectrum for the carbonyl ligands. Attempts to isolate the monosubstituted mixed ligand product by addition of only 1 equiv of ROH yielded only the trisubstituted complex in low yield. This substitution reaction is general; that is, substitution will occur for any of the triply bridged complexes provided the incoming alcohol is more acidic than the leaving alcohol. For example, when $[Et_4N]_3[W_2(CO)_6(OPh)_3]$ is treated with 3 equiv of 4-cyanophenol (pK_a = 8.21 vs 9.88 for phenol),[25] complete exchange occurs within 3 h. If the less acidic 4-aminophenol (pK_a = 10.80)[25] is used, no exchange is observed.

X-ray Crystallography. X-ray crystal structure determinations were carried out for compounds **2**, **4**, **5**, and **6**. Crystals of **3** suitable for X-ray analysis have not yet been obtained. The complexes are isostructural and compare favorably to the previously reported $[Et_4N]_3$-$[W_2(CO)_6(OPh)_3]$ complex. Each contains a W_2O_3 core with three terminal carbonyls on each tungsten atom. Three molecules of Et_4N cation are present to balance the charge of each anion. Hydrogen atoms were placed in calculated positions. The W−C, as well as the $C-O_{(carbonyl)}$, bond lengths for all complexes fall well within normally observed values.

The average W−O distance is 2.11 Å for **2**, 2.22 Å for **4** and **6**, and 2.23 Å for **5**; these compare to 2.22 Å for the phenoxide complex.[14] The W−O−W bond angles average 96.2° for **2**, 96.4° for **4**, and 96.6° for **5** and **6**, nearly the same as the 96.6° reported for the phenoxide. For the $O-C_{(ring)}$ bond lengths, the average for **2** and **4** is 1.34 Å, and for **5** and **6** it is 1.33 Å; these lengths imply the presence of some double-bond character, hence the approximate trigonal planar geometry. The geometry around the tungsten atoms is that of a distorted octahedron for all structures, very similar to that of the phenoxide derivative.

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[25] Liptak, M. D.; Gross, K. C.; Seybold, P. G.; Feldgus, S.; Shields, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6421−6427.

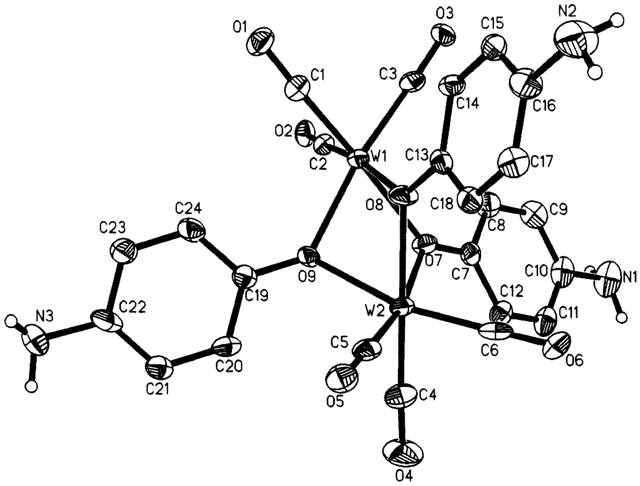

Figure 1. Thermal ellipsoid plot of **2** with atomic numbering scheme. Ellipsoids are shown at 40% level. Ring hydrogen atoms are omitted for clarity.

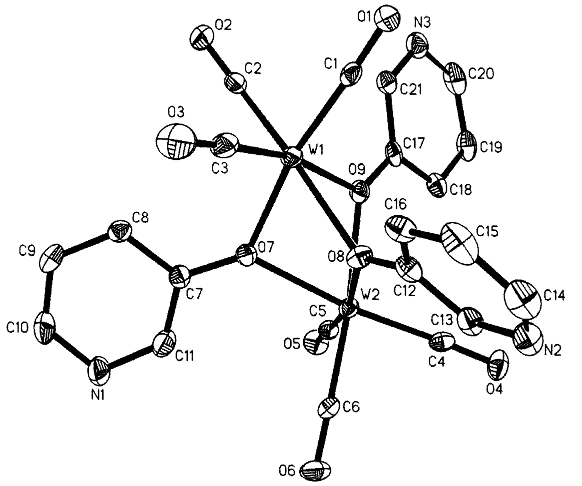

Figure 2. Thermal ellipsoid plot of **4** with atomic numbering scheme. Ellipsoids are shown at 40% level. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å)[a] and Angles (deg) for Complex 2

W(1)−C(2)	1.914(9)	W(1)−C(3)	1.930(10)
W(1)−C(1)	1.930(10)	W(1)−O(8)	2.204(9)
W(1)−O(7)	2.212(7)	W(1)−O(9)	2.236(7)
W(2)−C(4)	1.899(10)	W(2)−C(6)	1.916(11)
W(2)−C(5)	1.919(10)	W(2)−O(7)	2.195(7)
W(2)−O(8)	2.206(9)	W(2)−O(9)	2.215(8)
O(7)−C(7)	1.351(10)	O(8)−C(13)	1.359(8)
O(9)−C(19)	1.329(10)	N(1)−C(10)	1.444(12)
N(2)−C(16)	1.432(11)	N(3)−C(22)	1.440(11)

C(2)−W(1)−C(3)	83.8(4)	C(2)−W(1)−C(1)	86.5(3)
C(3)−W(1)−C(1)	81.5(4)	C(2)−W(1)−O(8)	170.5(2)
C(3)−W(1)−O(8)	102.6(3)	C(1)−W(1)−O(8)	101.3(3)
C(2)−W(1)−O(7)	100.9(3)	C(3)−W(1)−O(7)	103.9(4)
C(1)−W(1)−O(7)	171.2(3)	O(8)−W(1)−O(7)	70.9(2)
C(2)−W(1)−O(9)	101.8(3)	C(3)−W(1)−O(9)	171.8(3)
C(1)−W(1)−O(9)	104.7(4)	O(8)−W(1)−O(9)	71.1(2)
O(7)−W(1)−O(9)	69.3(3)	C(4)−W(2)−C(6)	84.3(4)
C(4)−W(2)−C(5)	87.1(4)	C(6)−W(2)−C(5)	89.2(4)
C(4)−W(2)−O(7)	102.6(3)	C(6)−W(2)−O(7)	99.2(4)
C(5)−W(2)−O(7)	167.7(3)	C(4)−W(2)−O(8)	173.6(3)
C(6)−W(2)−O(8)	97.9(3)	C(5)−W(2)−O(8)	98.9(3)
O(7)−W(2)−O(8)	71.2(2)	C(4)−W(2)−O(9)	105.4(3)
C(6)−W(2)−O(9)	166.6(3)	C(5)−W(2)−O(9)	100.4(4)
O(7)−W(2)−O(9)	70.0(3)	O(8)−W(2)−O(9)	71.5(2)
C(7)−O(7)−W(2)	128.6(5)	C(7)−O(7)−W(1)	133.9(5)
W(2)−O(7)−W(1)	96.6(3)	C(13)−O(8)−W(1)	132.8(4)
C(13)−O(8)−W(2)	128.4(5)	W(1)−O(8)−W(2)	96.6(2)
C(19)−O(9)−W(2)	130.0(5)	C(19)−O(9)−W(1)	133.6(5)
W(2)−O(9)−W(1)	95.4(3)	O(7)−C(7)−C(8)	121.5(8)
O(7)−C(7)−C(12)	122.3(7)	C(11)−C(10)−N(1)	121.8(9)
C(9)−C(10)−N(1)	119.4(9)	O(8)−C(13)−C(18)	121.6(6)
O(8)−C(13)−C(14)	120.9(7)	C(17)−C(16)−N(2)	122.6(8)
C(15)−C(16)−N(2)	119.5(8)	O(9)−C(19)−C(24)	121.3(8)
O(9)−C(19)−C(20)	121.7(7)	C(21)−C(22)−N(3)	123.8(7)
C(23)−C(22)−N(3)	118.4(8)		

[a] Estimated standard deviations are given in parentheses.

Table 4. Selected Bond Lengths (Å)[a] and Angles (deg) for Complex 4

W(1)−C(3)	1.905(6)	W(1)−C(2)	1.907(6)
W(1)−C(1)	1.926(6)	W(1)−O(7)	2.210(4)
W(1)−O(9)	2.210(4)	W(1)−O(8)	2.236(4)
W(2)−C(5)	1.902(6)	W(2)−C(4)	1.924(6)
W(2)−C(6)	1.935(6)	W(2)−O(8)	2.224(4)
W(2)−O(7)	2.228(4)	W(2)−O(9)	2.230(5)
O(7)−C(7)	1.321(6)	O(8)−C(12)	1.342(6)
O(9)−C(17)	1.346(6)	N(1)−C(10)	1.349(7)
N(1)−C(11)	1.372(7)	N(2)−C(14)	1.332(8)
N(2)−C(13)	1.355(7)	N(3)−C(20)	1.333(7)
N(3)−C(21)	1.337(7)		

C(3)−W(1)−O(7)	99.6(2)	C(2)−W(1)−O(7)	101.4(2)
C(1)−W(1)−O(7)	169.8(2)	C(3)−W(1)−O(9)	168.9(2)
C(2)−W(1)−O(9)	101.4(2)	C(1)−W(1)−O(9)	100.5(2)
O(7)−W(1)−O(9)	71.13(12)	C(3)−W(1)−O(8)	101.1(2)
C(2)−W(1)−O(8)	169.7(2)	C(1)−W(1)−O(8)	101.5(2)
O(7)−W(1)−O(8)	70.4(2)	O(9)−W(1)−O(8)	70.32(12)
C(5)−W(2)−O(8)	167.6(2)	C(4)−W(2)−O(8)	104.3(2)
C(6)−W(2)−O(8)	103.9(2)	C(5)−W(2)−O(7)	99.3(2)
C(4)−W(2)−O(7)	172.6(2)	C(6)−W(2)−O(7)	101.8(2)
O(8)−W(2)−O(7)	70.3(2)	C(5)−W(2)−O(9)	100.4(2)
C(4)−W(2)−O(9)	103.2(2)	C(6)−W(2)−O(9)	171.3(2)
O(8)−W(2)−O(9)	70.16(14)	O(7)−W(2)−O(9)	70.42(13)
C(7)−O(7)−W(1)	130.6(3)	C(7)−O(7)−W(2)	132.1(3)
W(1)−O(7)−W(2)	96.7(2)	C(12)−O(8)−W(2)	132.9(3)
C(12)−O(8)−W(1)	128.7(3)	W(2)−O(8)−W(1)	96.1(2)
C(17)−O(9)−W(1)	130.5(3)	C(17)−O(9)−W(2)	132.8(3)
W(1)−O(9)−W(2)	96.63(12)	C(10)−N(1)−C(11)	114.1(6)
C(14)−N(2)−C(13)	116.4(5)	C(19)−N(3)−C(21)	116.2(5)
O(7)−C(7)−C(11)	122.2(5)	O(7)−C(7)−C(8)	121.6(5)
N(1)−C(10)−C(9)	124.7(6)	N(1)−C(11)−C(7)	126.8(5)
O(8)−C(12)−C(13)	121.0(5)	O(8)−C(12)−C(16)	121.5(5)
N(2)−C(13)−C(12)	123.8(5)	N(2)−C(14)−C(15)	124.1(6)
O(9)−C(17)−C(21)	121.8(5)	O(9)−C(17)−C(18)	120.8(5)
N(3)−C(20)−C(19)	124.1(5)	N(3)−C(21)−C(17)	125.0(5)

[a] Estimated standard deviations are given in parentheses.

The molecular structure of complex **2** is shown in Figure 1, and selected bond lengths and angles are provided in Table 3. Complex **2** exhibits a hydrogen-bonding distance of 3.061 Å between N1 and N2 on an adjacent molecule; no other hydrogen bonding is observed. The average C−N distance is 1.439 Å, appropriate for an amine. The rings of the aminophenol ligands are twisted slightly with respect to the W−W axis with the bridging oxygen atom having a nearly trigonal planar geometry; the average angle around the oxygen atom is 119.5°. The W−O−C−C torsion angles for this complex range from 1.2° to 28.1°. One molecule of Et_4N^+ is disordered with a 59:41 ratio of the two positions. One molecule of acetonitrile is cocrystallized in **2**.

A thermal ellipsoid drawing of **4** is shown in Figure 2, and selected bond lengths and angles are given in Table 4. The average angle about the O atom of the 3-hydroxypyridine is 119.7°, giving a distorted trigonal planar geometry. The W−O−C−C torsion angles range from 0.7° to 27.6° for **4**. The position of the N atoms of the pyridyl rings was determined by refining all atoms of the ring as carbon first and then naming the atoms

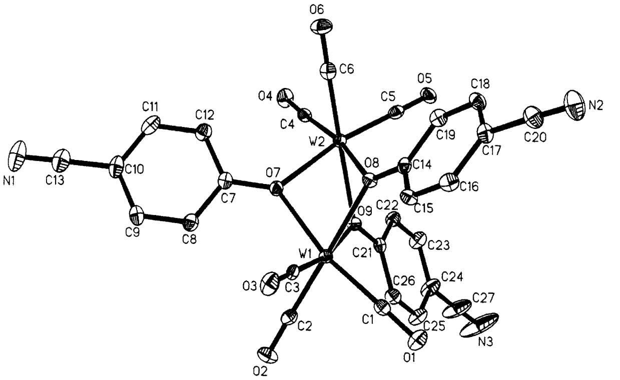

Figure 3. Thermal ellipsoid plot of **5** with atomic numbering scheme. Ellipsoids are shown at 40% level. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å)[a] and Angles (deg) for Complex 5

W(1)−C(3)	1.912(3)	W(1)−C(2)	1.920(3)
W(1)−C(1)	1.932(3)	W(1)−O(7)	2.221(2)
W(1)−O(9)	2.229(2)	W(1)−O(8)	2.231(2)
W(2)−C(4)	1.919(3)	W(2)−C(5)	1.919(3)
W(2)−C(6)	1.927(3)	W(2)−O(7)	2.226(2)
W(2)−O(8)	2.236(2)	W(2)−O(9)	2.244(2)
O(7)−C(7)	1.321(3)	O(8)−C(14)	1.333(3)
O(9)−C(21)	1.336(3)	N(1)−C(13)	1.143(4)
N(2)−C(20)	1.143(4)	N(3)−C(27)	1.149(5)
C(3)−W(1)−C(2)	85.51(12)	C(3)−W(1)−C(1)	88.26(12)
C(2)−W(1)−C(1)	84.53(13)	C(3)−W(1)−O(7)	98.37(10)
C(2)−W(1)−O(7)	105.58(10)	C(1)−W(1)−O(7)	168.23(10)
C(3)−W(1)−O(9)	168.34(10)	C(2)−W(1)−O(9)	101.40(10)
C(1)−W(1)−O(9)	101.65(10)	O(7)−W(1)−O(9)	70.83(7)
C(3)−W(1)−O(8)	102.25(10)	C(2)−W(1)−O(8)	171.57(10)
C(1)−W(1)−O(8)	98.85(10)	O(7)−W(1)−O(8)	70.32(7)
O(9)−W(1)−O(8)	70.41(7)	C(4)−W(2)−C(5)	82.60(13)
C(4)−W(2)−C(6)	84.55(13)	C(5)−W(2)−C(6)	87.03(12)
C(4)−W(2)−O(7)	99.05(10)	C(5)−W(2)−O(7)	169.75(10)
C(6)−W(2)−O(7)	103.18(11)	C(4)−W(2)−O(8)	169.19(10)
C(5)−W(2)−O(8)	108.07(11)	C(6)−W(2)−O(8)	97.47(11)
O(7)−W(2)−O(8)	70.14(7)	C(4)−W(2)−O(9)	107.18(10)
C(5)−W(2)−O(9)	99.35(10)	C(6)−W(2)−O(9)	167.19(10)
O(7)−W(2)−O(9)	70.46(7)	O(8)−W(2)−O(9)	70.04(7)
C(7)−O(7)−W(1)	131.4(2)	C(7)−O(7)−W(2)	131.5(2)
W(1)−O(7)−W(2)	97.04(7)	C(14)−O(8)−W(1)	129.2(2)
C(14)−O(8)−W(2)	134.4(2)	W(1)−O(8)−W(2)	96.43(7)
C(21)−O(9)−W(1)	130.3(2)	C(21)−O(9)−W(2)	131.9(2)
W(1)−O(9)−W(2)	96.27(7)	O(7)−C(7)−C(12)	122.1(3)
O(7)−C(7)−C(8)	120.4(3)	N(1)−C(13)−C(10)	179.0(4)
O(8)−C(14)−C(15)	121.3(3)	O(8)−C(14)−C(19)	120.4(3)
N(2)−C(20)−C(17)	178.2(4)	O(9)−C(21)−C(22)	121.2(3)
O(9)−C(21)−C(26)	120.9(3)	N(3)−C(27)−C(24)	176.2(5)

[a] Estimated standard deviations are given in parentheses.

with the largest displacement parameters as nitrogen. This resulted in an unsymmetrical structure. When viewed down the W−W axis, two nitrogen atoms are pointing one way and the other is pointing in the opposite direction. No disorder is apparent for the 3-hydroxypyridyl rings. Two molecules of acetonitrile are cocrystallized in **4**.

The molecular structure of **5** is shown in Figure 3, and selected bond lengths and angles are given in Table 5. For **5**, the average angle about the 4-cyanophenol ligand is 119.8° and the W−O−C−C torsion angles range from 2.4° to 14.6°. One molecule of acetonitrile is present in **5**.

A thermal ellipsoid plot for complex **6** is provided in Figure 4, and selected bond lengths and angles are given in Table 6. The average C−N distance is 1.14 Å, appropriate for a cyanide functionality, and the average angle around the O atom is 119.9°. The W−O−C−C torsion angles for **6** range from 0.5° to 15.7°. Complex **6** has two ordered molecules of acetonitrile and an ether molecule disordered with an acetonitrile in a 43:57 ratio. Two independent trianions are present in the unit cell for complex **6** with only minor differences between the two structures. The acetonitrile solvent molecules were restrained to behave similarly in complex **6**. All non-hydrogen atoms of all molecules were refined anisotropically except for the disordered ether and acetonitrile of compound **6**. Additional features of the X-ray structure are discussed in the context of the NMR spectra.

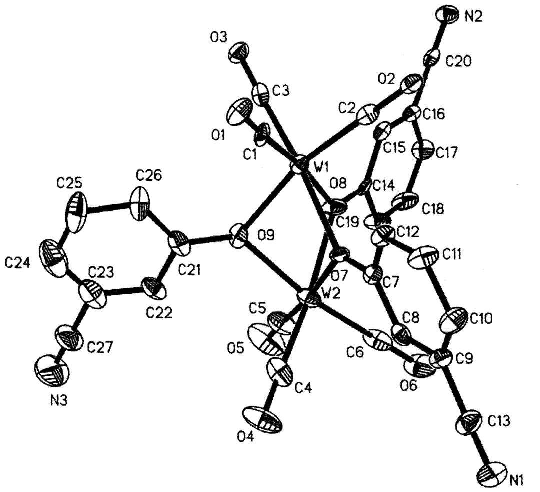

Figure 4. Thermal ellipsoid plot of one of the trianions of **6** with atomic numbering scheme. Ellipsoids are shown at 40% level. Hydrogen atoms are omitted for clarity.

NMR Spectroscopy. The ^{1}H and ^{13}C NMR spectra for the complexes **2**−**6** show an asymmetry present in the molecules. This asymmetry is manifested most prominently in the 4-aminophenol (**2**) and 3-cyanophenol (**6**) derivatives. For each of the compounds a proper integration versus the protons of the Et_4N cation was attained in the ^{1}H NMR spectrum.

For complex **2** in the ^{1}H NMR spectrum, the proton resonances for two of the rings appear to be nearly equivalent and the resonances for the third ring are quite removed from the other two. The features of this spectrum persist even upon heating to 60 °C; no change is observed in the ^{1}H NMR spectrum. The reason for this inequivalence is not obvious from the crystal structure and is currently under further study. The ^{13}C NMR spectrum shows a single peak at 230 ppm for the metal carbonyl carbons and eight signals for the ring carbons. The *C*-O signals are at 161.5 and 151.8 ppm, and the *C*-NH_2 signals are at 136.4 and 139.6 ppm in ratios of 2:1, respectively. The remaining four signals for the unsubstituted ring carbons are also in a ratio of 2:1.

The ^{1}H NMR spectrum of **3** shows only slight asymmetry. The proton signals are as expected, doublets which show that additional inequivalences are present. The metal carbonyl carbons appear at 228.7 ppm in the ^{13}C NMR spectrum, and the *C*-O for the 4-hydroxypyridyl ligand is at 173.5 ppm. The OCC_4H_4N carbons appear as single signals at 150.0 and 118.7 ppm.

The asymmetry in complex **4** is displayed in the ^{1}H NMR spectrum by a slight splitting of the peak for the

Table 6. Selected Bond Lengths (Å)[a] and Angles (deg) for Complex 6

W(1)−C(2)	1.895(11)	W(1)−C(1)	1.913(11)
W(1)−C(3)	1.946(10)	W(1)−O(9)	2.199(7)
W(1)−O(8)	2.211(6)	W(1)−O(7)	2.226(6)
W(2)−C(6)	1.910(12)	W(2)−C(4)	1.919(12)
W(2)−C(5)	1.922(12)	W(2)−O(7)	2.203(7)
W(2)−O(8)	2.225(6)	W(2)−O(9)	2.230(7)
W(3)−C(30)	1.911(11)	W(3)−C(28)	1.918(11)
W(3)−C(29)	1.918(11)	W(3)−O(18)	2.218(6)
W(3)−O(16)	2.227(6)	W(3)−O(17)	2.229(7)
W(4)−C(32)	1.906(12)	W(4)−C(31)	1.912(11)
W(4)−C(33)	1.935(10)	W(4)−O(17)	2.195(6)
W(4)−O(16)	2.198(6)	W(4)−O(18)	2.234(6)
O(7)−C(7)	1.318(11)	O(8)−C(14)	1.346(11)
O(9)−C(21)	1.325(12)	O(16)−C(34)	1.324(11)
O(17)−C(41)	1.325(11)	O(18)−C(48)	1.335(12)
N(1)−C(13)	1.154(13)	N(2)−C(20)	1.124(12)
N(3)−C(27)	1.15(2)	N(4)−C(40)	1.145(14)
N(5)−C(47)	1.131(13)	N(6)−C(54)	1.14(2)

C(2)−W(1)−C(1)	83.0(4)	C(2)−W(1)−C(3)	89.8(4)
C(1)−W(1)−C(3)	83.6(4)	C(2)−W(1)−O(9)	167.2(3)
C(1)−W(1)−O(9)	103.2(4)	C(3)−W(1)−O(9)	101.9(3)
C(2)−W(1)−O(8)	102.4(3)	C(1)−W(1)−O(8)	172.1(3)
C(3)−W(1)−O(8)	102.0(3)	O(9)−W(1)−O(8)	70.4(2)
C(2)−W(1)−O(7)	97.7(3)	C(1)−W(1)−O(7)	103.3(3)
C(3)−W(1)−O(7)	170.4(3)	O(9)−W(1)−O(7)	70.2(2)
O(8)−W(1)−O(7)	70.6(2)	C(6)−W(2)−C(4)	86.0(5)
C(6)−W(2)−C(5)	82.7(5)	C(4)−W(2)−C(5)	86.1(5)
C(6)−W(2)−O(7)	101.8(4)	C(4)−W(2)−O(7)	99.6(4)
C(5)−W(2)−O(7)	172.9(4)	C(6)−W(2)−O(8)	102.5(4)
C(4)−W(2)−O(8)	168.1(4)	C(5)−W(2)−O(8)	103.1(4)
O(7)−W(2)−O(8)	70.7(2)	C(6)−W(2)−O(9)	170.0(4)
C(4)−W(2)−O(9)	101.0(4)	C(5)−W(2)−O(9)	104.9(4)
O(7)−W(2)−O(9)	70.0(2)	O(8)−W(2)−O(9)	69.6(2)
C(30)−W(3)−C(28)	86.4(5)	C(30)−W(3)−C(29)	85.2(5)
C(28)−W(3)−C(29)	84.4(4)	C(30)−W(3)−O(18)	102.7(4)
C(28)−W(3)−O(18)	168.3(3)	C(29)−W(3)−O(18)	103.5(4)
C(30)−W(3)−O(16)	101.7(4)	C(28)−W(3)−O(16)	101.2(3)
C(29)−W(3)−O(16)	171.3(4)	O(18)−W(3)−O(16)	70.1(2)
C(30)−W(3)−O(17)	170.6(3)	C(28)−W(3)−O(17)	99.7(4)
C(29)−W(3)−O(17)	102.4(4)	O(18)−W(3)−O(17)	70.4(2)
O(16)−W(3)−O(17)	70.1(2)	C(32)−W(4)−C(31)	85.5(4)
C(32)−W(4)−C(33)	84.6(4)	C(31)−W(4)−C(33)	86.6(4)
C(32)−W(4)−O(17)	101.8(3)	C(31)−W(4)−O(17)	100.1(4)
C(33)−W(4)−O(17)	171.0(4)	C(32)−W(4)−O(16)	101.9(4)
C(31)−W(4)−O(16)	169.5(3)	C(33)−W(4)−O(16)	101.4(3)
O(17)−W(4)−O(16)	71.3(2)	C(32)−W(4)−O(18)	170.4(3)
C(31)−W(4)−O(18)	101.5(3)	C(33)−W(4)−O(18)	102.3(4)
O(17)−W(4)−O(18)	70.7(2)	O(16)−W(4)−O(18)	70.3(2)
C(7)−O(7)−W(2)	132.9(6)	C(7)−O(7)−W(1)	130.3(6)
W(2)−O(7)−W(1)	96.8(2)	C(14)−O(8)−W(1)	132.1(6)
C(14)−O(8)−W(2)	131.0(5)	W(1)−O(8)−W(2)	96.6(2)
C(21)−O(9)−W(1)	133.7(7)	C(21)−O(9)−W(2)	129.2(7)
W(1)−O(9)−W(2)	96.8(3)	C(34)−O(16)−W(4)	131.9(6)
C(34)−O(16)−W(3)	131.4(6)	W(4)−O(16)−W(3)	96.7(2)
C(41)−O(17)−W(4)	131.0(6)	C(41)−O(17)−W(3)	131.8(6)
W(4)−O(17)−W(3)	96.7(2)	C(48)−O(18)−W(3)	132.7(6)
C(48)−O(18)−W(4)	131.3(6)	W(3)−O(18)−W(4)	95.9(2)

[a] Estimated standard deviations are given in parentheses.

unique proton at 8.85 and 8.86 ppm. The other peaks in the spectrum show additional asymmetry also. The ^{13}C NMR spectrum shows the metal carbonyl peak at 229.4 ppm, and the *C*-O signal is at 163.8 ppm. The remaining four ring carbon atoms have single resonances from 123 to 145 ppm in the proper ratio.

The ^{1}H NMR spectrum of **5** consists of a set of doublets that show additional peaks that are due to asymmetry in the molecule. This asymmetry causes the peaks to appear similar to a quartet. The ^{13}C NMR spectrum has a single peak at 228.4 ppm for the metal carbonyl carbons with the signal for the $C_{(ring)}$-O at 172.2 ppm. There is a single *C*-N peak at 97.0 ppm. The unsubstituted carbons of the 4-cyanophenol have two sets of peaks at 133.3 and 134.4 ppm, and 123.3 and 121.8 ppm in a ratio of 2:1, respectively. This is the only occurrence of an asymmetry in the unsubstituted ring carbons but not in the substituted carbons.

The ^{1}H NMR spectrum of **6** shows four sets of resonances for the ring protons. The observed peaks do not, however, show clean splitting, due to two different environments for the rings. The ^{13}C NMR spectrum for the 3-cyanophenol derivative **6** shows one resonance for the metal carbonyl carbons at 228.9 ppm and a series of peaks between 110 and 170 ppm for the ring and cyano carbons of the bridging ligand. Most interesting is that the *C*-O$_{(ring)}$ peaks in a ratio of roughly 2:1 at 168 and 165 ppm are seen. Similarly, the resonances attributed to the other ring carbons are present in 2:1 ratios, with the *C*N resonances being at 112.8 and 111.5 ppm, at a ratio of 1:2. These peaks may be explained by noting that in the X-ray crystal structure the 3-cyanophenol ligands have different orientations; that is, viewed down the W−W axis two CN's are pointing one direction and the third is pointing in the opposite direction. With the C−O$_{(ring)}$ distance being somewhat shorter than a single bond (~1.32 Å), hindrance to rotation around the bond can cause the two orientations of the ligand to give separate resonances.

Conclusions. Despite the continued interest in alkoxy-bridged complexes of the group 6 metal carbonyls, exchange reactions of the zerovalent binuclear triply bridged tungsten complexes have, to our knowledge, remained unreported. This report demonstrates that exchange reactions for methoxide not only are facile but have a potential utility, in that additional functionality can be incorporated into the complex. The exchange reaction is not limited to methoxide derivatives. Provided the leaving alcohol is more basic than the incorporated alcohol, the exchange reaction is favorable.

By incorporating amine, pyridyl, and cyano functionalities into the triply bridged complex, additional reactivity can be accomplished. Initial results show that for the pyridyl-containing derivatives **3** and **4**, the pyridyl nitrogen maintains enough basicity to interact with $ZnCl_2$. For example, a shift in the IR spectrum is seen when 2 equiv of **3** or **4** is added to $ZnCl_2$, from 1865 and 1731 cm^{-1} for **3** to 1870 and 1734 cm^{-1} for the adduct. The produced adduct is insoluble after precipitation with ether, and efforts are currently underway to solublize this compound.

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Supporting Information Available: A listing of the final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **2**, **4**, **5**, and **6** is available. A thermal ellipsoid plot of the second independent trianion of complex **6** is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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