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η^2-Nitriles as Four-Electron-Donor Ligands for Tungsten(II) and Their Comparison to η^2-Alkynes

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A series of octahedral tungsten coordination compounds have been prepared containing chloride, phosphine, and pyridyl ligands. The electron-rich, 16-electron complex $WCl_2(PMe_3)_2(bpy)$ undergoes chloride substitution with acetonitrile, benzonitrile, and pivalonitrile to form complexes of the type $[WCl(PMe_3)_2(bpy)(L)]^+$, in which the nitrile (L) is η^2-bound to the metal. These unusual side-bound nitrile complexes exhibit electrochemical, spectroscopic, magnetic, and structural features similar to those of the ubiquitous "four-electron-donor" alkyne complexes of Mo(II) and W(II) previously reported and theoretically evaluated. Thus, the model used to describe the bonding interactions of alkyne complexes is extended to include η^2-nitrile complexes. The nitrile is proposed to stabilize the W(II) center through donation of electron density from both its $\pi_\parallel$ and $\pi_\perp$ orbitals while its $\pi_\parallel{}^*$ orbital simultaneously renders it a π acid. The W(II) alkyne complexes $WCl_2(PMe_3)_3(\eta^2\text{-2-pentyne})$ and $[W(bpy)(PMe_3)_2(\eta^2\text{-2-pentyne})]^{2+}$ have also been prepared in order to make a direct comparison with their nitrile analogs. Crystal structures of the complexes $[W(bpy)(PMe_3)_2Cl(\eta^2\text{-}CH_3CN)]^+$ and $WCl_2(PMe_3)_3(\eta^2\text{-}CH_3CN)$ show that the nitrogen and carbon of the nitrile group are nearly equidistant from the metal (ca. 2.00 Å) and that the N–C bond is lengthened by as much as 0.12 Å compared to that of the free ligand. In addition, crystal structures are reported for $WCl_2(PMe_3)_2(bpy)$ and $WCl_3(PMe_3)_2(py)$. $WCl_3(PMe_3)_2(py)$: a (Å) = 10.025(3), b (Å) = 22.228(6), c (Å) = 8.232(1), orthorhombic, $P2_12_12_1$ (No. 19), $Z = 4$. $WCl_2(PMe_3)_2(bpy)$: a (Å) = 13.975(5), b (Å) = 9.408(3), c (Å) = 18.456(6), β = 103.38(3), (monoclinic, $P2_1/c$ (No. 14), $Z = 4$. $WCl_2(PMe_3)_3(\eta^2\text{-}CH_3CN)$: a (Å) = 16.792(5), b (Å) = 12.611(3), c (Å) = 18.971(5), β (deg) = 97.78(3), monoclinic, $P2_1/c$ (No. 14), $Z = 8$.

Introduction

Over the past decade, an extensive body of data has been assembled supporting the notion that transition-metal–alkyne complexes, when formally unsaturated (i.e. 16 electron), can be stabilized by the alkyne ligand acting as a "four-electron donor".[1] This term is derived from the ability of the alkyne $\pi_\perp$ orbital to donate electron density to the metal in addition to the more classical σ-donor and π-acceptor functions of the $\pi_\parallel$ system. In 1986, Wilkinson and Hursthouse[2] reported the first example of a structurally characterized η^2-nitrile complex, $MoCp_2(\eta^2\text{-}CH_3CN)$. In this case, the Mo(II) is formally saturated (18 electron), and correspondingly, the nitrile would be viewed as a classic two-electron donor. Herein we describe a series of formally *unsaturated* octahedral tungsten(II) compounds in which both η^2-nitrile and η^2-alkyne ligands can be characterized in similar coordination environments. Thus, the direct comparison of alkynes and nitriles can be made in a system where these ligands, in a formal sense, can serve as *four-electron* donors. A portion of this work has been previously communicated.[3]

Experimental Section

Infrared spectra were recorded of KBr pellets on a Mattson Cygnus 100 FTIR spectrometer. Electronic spectra were recorded on an HP 8452A diode array spectrophotometer. Routine ^1H and ^{13}C NMR spectra were recorded on a General Electric QE-300 or GN-300 spectrometer and are reported as shifts in ppm from tetramethylsilane. Electrochemical experiments were performed under nitrogen using a PAR Model 362 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded (Kipp & Zonen BD90 XY recorder) in a standard three-electrode cell from +1.50 to −2.3 V with a glassy-carbon working electrode. All potentials are reported vs NHE unless otherwise noted and were determined in *N,N*-dimethylacetamide (~0.5 M tetrabutylammonium hexafluorophosphate (TBAH)) using ferrocene ($E_{1/2}$ = 0.55 V) or cobaltocenium hexafluorophosphate ($E_{1/2}$ = −0.78 V) *in situ* as a calibration standard. The peak-to-peak separation ($E_{p,a} - E_{p,c}$) was between 70 and 100 mV for all reversible couples reported unless otherwise noted (where $E_{p,a}$ and $E_{p,c}$ refer to the potential at peak anodic current and peak cathodic current, respectively). This work was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Co. glovebox. Microanalytical data were obtained on a Perkin-Elmer PE2400 CHN analyzer.

Structure Determinations. All X-ray experiments were carried out on a Rigaku AFC6S diffractometer at −100 or −120 °C using Mo Kα radiation (λ = 0.710 69 Å). Pertinent details of the data collections and structure determinations are listed in Table I. Crystals of the compounds were mounted on glass fibers and quickly transferred to the cold N_2 stream of the diffractometer. Unit cells were determined using the setting angles of 25 high-angle reflections. The intensities of three standard reflections were monitored during each data collection, showing neither significant decay nor instrument instability. Empirical absorption corrections were applied on the basis of the ψ scans of several reflections. All calculations were performed on a VAXstation 3520 computer using the TEXSAN 5.0 crystallographic software package.[4] The structures were solved by direct methods (SIR88).[5] Full-matrix least-squares refinement was carried out with anisotropic thermal displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located from

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(1) For a recent review, see: Templeton, J. L. Four-Electron Alkyne Ligands in Molybdenum(II) and Tungsten(II) Complexes. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: San Diego, CA, 1989; Vol. 29, p 1.

(2) Wright, T. C.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* 1986, 2017.

(3) Barrera, J.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* 1991, *113*, 8178.

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Table I. Crystallographic Experimental Details for Compounds 1, 3, and 7

	1	3	7
empirical formula	$WC_3P_2NC_{11}H_{23}$	$WCl_4P_2N_2C_{17}H_{28}$	$WCl_2P_3NC_{11}H_{30}$
color, habit	orange, needle	black, prism	green, plate
space group (No.)	$P2_12_12_1$ (19)	$P2_1/c$ (14)	$P2_1/c$ (14)
cryst syst	orthorhombic	monoclinic	monoclinic
cell dimens			
a (Å)	10.025(3)	13.975(5)	16.792(5)
b (Å)	22.228(6)	9.408(3)	12.611(3)
c (Å)	8.232(1)	18.456(6)	18.971(5)
α (deg)	90	90	90
β (deg)	90	103.38(3)	97.78(3)
γ (deg)	90	90	90
Z	4	4	8
2θ(max) (deg)	46.0	50.0	46.0
no. of obsd rflns, $I > 3\sigma(I)$	1209	3105	2963
R	0.021	0.038	0.040
R_w	0.030	0.051	0.054
temp (°C)	−120	−100	−100

difference Fourier maps and included as fixed contributions to the structure factors.

Solvents. All distillations were performed under nitrogen, and all solvents were deoxygenated by purging with nitrogen for at least 15 min. Methylene chloride was refluxed over P_2O_5 and distilled. Diethyl ether, hexanes, and benzene were refluxed over Na/benzophenone and distilled. Methanol was refluxed over $Mg(OMe)_2$, prepared in situ from Mg^0 activated by I_2, and distilled. 1,2-Dimethoxyethane (DME) and toluene were refluxed over Na^0 and distilled. Acetonitrile was refluxed over CaH_2 and distilled. *N,N*-Dimethylacetamide (DMAc) was stirred over CaH_2 for 72 h and vacuum-distilled. Acetone (Burdick and Jackson) was deoxygenated prior to use. Deuterated solvents were stirred over various drying agents and vacuum-transferred (C_6D_6, Na/K alloy; CD_3CN, CaH_2; CD_2Cl_2 and $CDCl_3$, P_2O_5). $WCl_4(PMe_3)_3$,[6] $WCl_2(PMe_3)_4$,[6] and WCl_4L_2[7] were prepared according to published procedures.

$WCl_3(PMe_3)_2(py)$ (1). $WCl_4(PMe_3)_3$ (2.516 g, 4.54 mmol) was suspended in toluene (40 mL) and OEt_2 (20 mL). Dry pyridine (5 mL) was added and the reaction mixture stirred for 15 min. Na/Hg (26.7 g, 0.405%, 4.7 mmol) was added slowly over a 2-min period, and the solution turned a dark orange. The reaction mixture was stirred at room temperature for 2 h and then filtered through Celite. The solvent was removed in vacuo to give an orange-green solid, which was extracted with hexanes (5 × 4 mL) to remove the W(II) complexes formed during the reaction. The remaining solid was dissolved in a slight excess of CH_2Cl_2. Upon the addition of Et_2O and hexanes, an orange precipitate formed. This solid was collected and reprecipitated as described above to give an orange, crystalline solid: yield 1.246 g, 53%. ^1H NMR (CD_2Cl_2): δ 35.82 (s, 2H, py, $w_{h/2}$ = 17 Hz), −22.60 (s, 9H, PMe_3, $w_{h/2}$ = 36 Hz), −25.91 (s, 9H, PMe_3, $w_{h/2}$ = 34 Hz), −59.95 (s, 2H, py, $w_{h/2}$ = 76 Hz), −72.48 (s, 1H, py, $w_{h/2}$ = 34 Hz). CV (100 mV s^{-1}; Bu_4NPF_6; DMAc): $E_{p,a}$ = +0.21 V, $E_{1/2}$ = −1.21 V. Anal. Calcd for $WC_{11}H_{23}NP_2Cl_3$: C, 25.34; H, 4.45; N, 2.69. Found: C, 25.14; H, 4.39; N, 2.56.

$WCl_3(py)_3$ (2). $WCl_4(py)_2$ (1.81 g, 3.75 mmol) was suspended in benzene (60 mL) and OEt_2 (40 mL). Pyridine (5 mL) was added and the solution stirred at room temperature for 15 min. An excess of Na/Hg was added and the reaction mixture stirred overnight. The solids were collected on a fine frit, dried under vacuum, and extracted with acetone (125 mL). After the extracts were filtered through Celite, the acetone was removed under vacuum to give an orange-red solid: yield 1.321 g, 67%. ^1H NMR (acetone-d_6): δ 56.8 (s, 4H, $w_{h/2}$ = 16 Hz), 2.87 (s, 2H, $w_{h/2}$ = 16 Hz), 2.14 (s, H, $w_{h/2}$ = 16 Hz), 1.21 (s, 2H, $w_{h/2}$ = 16 Hz), −125.5 (s, 2H, $w_{h/2}$ = 37 Hz), −134.7 (s, 4H), $w_{h/2}$ = 116 Hz). CV (100 mV s^{-1}; TBAH; DMAc): $E_{1/2}$ = −0.18 V, $E_{1/2}$ = −1.80 V, NHE. Anal. Calcd for $WC_{15}H_{15}N_3Cl_3$: C, 34.15; H, 2.87; N, 7.97. Found: C, 34.09; H, 3.02; N, 7.19. Attempts to purify this material further were unsuccessful.

$WCl_2(bpy)(PMe_3)_2$ (3).[6] $WCl_4(bpy)$ (2.08 g, 4.32 mmol) was suspended in toluene (50 mL) and OEt_2 (30 mL) and cooled to −5 °C. PMe_3 (1.3 mL, 12.6 mmol) was added, followed by Na/Hg (0.59%, 35.4 g, 9 mmol). The suspension was stirred at 0 °C for a period of 30 min, then warmed slowly to room temperature, and stirred overnight. The orange-brown mixture was filtered through Celite and the solids washed with toluene/OEt_2 (2 × 5 mL). The solvent was removed in vacuo, and the black crystalline solid was suspended in hexanes (5 mL). The suspension was filtered and the solid washed with hexanes and dried in vacuo: yield 1.35 g, 56%. Recrystallization at −20 °C from CH_2Cl_2/OEt_2/hexanes (1:2:4) results in analytically pure material. ^1H NMR (CD_3CN): δ 43.04 (d, 2H, bpy), 17.01 (d, 2H, bpy), 10.53 (d, 2H, bpy), −5.95 (t, 2H, bpy), 4.96 (br s, 18H, PMe_3). CV (100 mV s^{-1}; TBAH; DMAc): $E_{p,a}$ = 0.55 V; $E_{1/2}$ = −0.34 V; $E_{1/2}$ = −1.66 V, NHE. Anal. Calcd for $WC_{16}H_{26}N_2P_2Cl_2$: C, 34.13; H, 4.65; N, 4.98. Found: C, 33.74; H, 4.60; N, 4.73.

$WCl_2(PMe_3)_2(py)_2$ (4). Compound 1 (0.257 g, 0.49 mmol) was suspended in benzene (12 mL) and OEt_2 (6 mL). Dry pyridine (0.135 g) was added and the solution stirred for 5 min. Na/Hg (2.97, 0.42%, 0.54 mmol) was slowly added (1 min), and the solution turned from orange to a deep blue. The solution was stirred for 30 min and filtered through Celite. The solvent was removed under vacuum to give a blue solid: yield 0.242 g, 87%. Recrystallization from OEt_2 at −20 °C resulted in analytically pure material. ^1H NMR (C_6D_6): δ 19.21 (d, 4H, py), 15.66 (t, 2H, py), 12.32 (br s, 4H, py), −1.55 (br s, 18H, PMe_3). CV (100 mV s^{-1}; TBAH; DMAc): $E_{p,a}$ = 0.62 V, $E_{1/2}$ = −0.75 V, $E_{p,c}$ = −2.04 V, NHE. Anal. Calcd for $WC_{16}H_{28}N_2P_2Cl_2$: C, 34.01; H, 4.99; N, 4.96. Found: C, 33.77; H, 4.89; N, 4.84.

$WCl_2(PMe_3)_3(py)$ (5). $WCl_4(PMe_3)_3$ (0.705 g, 1.27 mmol) was suspended in benzene (18 mL) and OEt_2 (6 mL). Dry pyridine (1.385 g, 17.5 mmol) was added, followed by the addition of Na/Hg (14.6, 0.42%, 2.67 mmol). The reaction mixture was stirred for 1.5 h and filtered through Celite. Upon evaporation of the solvent, the resulting dark solid was washed with hexanes (2 × 2 mL) and dried in vacuo (0.582 g). The majority of impurities was extracted away with OEt_2/hexanes (3 × 5 mL, 1:1) over a 6-h period. The final solid was 96% $WCl_2(PMe_3)_3(py)$, judging from ^1H NMR and cyclic voltammetry: yield 0.395 g, 55%. ^1H NMR (C_6D_6): δ 25.46 (t, 1H, py), 17.62 (br s, 2H, py), 15.43 (d, 2H, py), 0.15 (br s, 18H, PMe_3), −2.60 (br s, 9H, PMe_3). CV (100 mV s^{-1}; TBAH; DMAc): $E_{p,a}$ = 0.76 V, $E_{1/2}$ = −0.59 V, $E_{p,c}$ = −2.24 V, NHE.

$WCl_2(PMe_3)_3(\eta^2\text{-}NCCH_3)$ (7). $WCl_4(PMe_3)_3$ (1.25 g, 2.26 mmol) was added to a 200-mL flask and dissolved in toluene (40 mL) and acetonitrile (35 mL) to form a cherry red solution. Na/Hg (0.4%, 26.5 g, 4.6 mmol) was added, and the solution was stirred for 2.5 h. The reaction mixture was filtered through Celite and the solvent removed in vacuo to give a green-brown oil. The oil was dissolved in CH_2Cl_2 (4 mL) and then treated with OEt_2, resulting in a brown precipitate. This mixture was filtered and the filtrate evaporated to give another brown oil. This procedure was repeated until a pale green solid formed from the ether/hexanes washings upon evaporation: yield 0.778 g, 66%. ^1H NMR (C_6D_6): δ 3.23 (d, 3, J_{HP} = 1.3 Hz, CH_3CN), 1.54 (t, 18, J_{HP} = 3.0 Hz, PMe_3), 0.76 (d, 9, J_{HP} = 8.5 Hz, PMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 230.4 (m, CN), 26.4 (s, $NC\mathit{C}H_3$), 24.0, (d, J_{CP} = 29 Hz), 17.7 (bd s). CV (100 mV s^{-1}; TBAH; DMAc): $E_{p,a}$ = 0.35 V, $E_{p,c}$ = −1.76 V, NHE. Anal. Calcd for $WC_{11}H_{30}NP_3Cl_2$: C, 25.21; H, 5.77; N, 2.67. Found: C, 25.23; H, 6.20; N, 2.71.

$[WCl(bpy)(PMe_3)_2(\eta^2\text{-}NCC(CH_3)_3)]PF_6$ (8). A THF solution of $TlPF_6$ (4 mL, 0.125 g, 0.354 mmol) was added to $W(PMe_3)_2$

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(4) TEXSAN: Single Crystal Structure Analysis Software, Version 5.0; Molecular Structure Corp., The Woodlands, TX 77381, 1989.

(5) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(6) Sharp, P. *Organometallics* **1984**, *3*, 1217.

(7) Schaefer King, M. A.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1972.

(bpy)Cl_2 (**3**; 0.190 g, 0.337 mmol) in trimethylacetonitrile (2 mL), and the reaction mixture was stirred (20 °C) for 6 h. The green solution was filtered through Celite and the solvent removed in vacuo. The resulting green residue was dissolved in a minimum of acetone (6 mL), and upon the slow addition of OEt_2, a green oil formed. The green solution was decanted off the oil into a second flask, and a crystalline solid precipitated over a period of 2 h. A small amount of OEt_2 was added to facilitate the precipitation. The solid was collected, washed with OEt_2/acetone (3:1), and dried in vacuo: yield 0.138 g, 54%. ^1H NMR (acetone-d_6): δ 9.58 (d), 8.80 (d), 8.75 (d), 8.20 (t), 7.68 (t), 7.12 (t), 6.71 (t), 6.54 (d), (bpy, 1H each), 1.73 (s, 9H, PMe_3), 1.20 (t, J_{HP} = 4.1 Hz, 18H, PMe_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 240 (t, J_{CP} = 10.1 Hz, N*C*R), 153, 149, 148, 143, 140, 139, 125, 124, 122, 121 (bpy), 46 (NC*C*Me$_3$), 31 (NCC(*C*H$_3$)$_3$), 14.2 (t, J_{CP} = 14.0 Hz, P(*C*H$_3$)$_3$). CV (100 mV s^{-1}; TBAH; DMAc): $E_{p,a}$ = 0.48 V, $E_{1/2}$ = −0.93 V, $E_{p,c}$ = −1.62 V, NHE. Anal. Calcd for $WC_{21}H_{35}N_3P_3CF_6$: C, 33.38; H, 4.67; N, 5.56. Found: C, 33.48; H, 4.46; N, 5.29.

[WCl(bpy)(PMe$_3$)$_2$(η^2-NC(C$_6$H$_5$))]PF$_6$ (9). A THF solution of $TlPF_6$ (1 mL, 0.123 g, 0.352 mmol) was added to $W(PMe_3)_2(bpy)Cl_2$ (**3**; 0.189 g, 0.336 mmol) dissolved in THF (6 mL) and benzonitrile (2 mL), and the reaction mixture was stirred for 4 h. The green suspension was filtered through Celite and the solvent removed in vacuo. The resulting green residue was dissolved in acetone (2 mL), and upon the slow addition of OEt_2 a precipitate formed. The suspension was filtered, and the crystalline green solid was washed with OEt_2/acetone (5:1) and dried in vacuo: yield 0.168 g, 57%. ^1H NMR (acetone-d_6): δ 9.63 (d, 1H), 8.84 (d, 1H), 8.77 (d, 1H), 8.28 (t, 1H), 7.50 (m, 1H), 7.12 (t, 1H), 6.97 (t, 1H), 6.72 (d, 1H) (bpy), 7.70 (m, 5H, Ph), 1.22 (t, J_{HP} = 8.1 Hz, 18H, PMe_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 236.5 (t, J_{CP} = 11.5 Hz, N*C*Ph), 152.8, 143.1, 140.9, 139.4, 131.3, 129.6, 129.5, 125.3, 124.0, 122.5, 122.4, 13.3 (t, J_{CP} = 14.1 Hz, PMe_3). CV (100 mV s^{-1}; TBAH; DMAc): $E_{p,c}$ = 0.53 V (2e$^-$), $E_{1/2}$ = −0.94 V, $E_{p,a}$ = −1.54 V, NHE. Anal. Calcd for $WC_{23}H_{31}N_3P_3ClF_6$: C, 35.61; H, 4.03; N, 5.42. Found: C, 34.53; H, 3.76; N, 5.17. Attempts to further purify this compound were unsuccessful.

WCl$_2$(PMe$_3$)$_3$(η^2-MeC$\equiv$CEt) (10). $WCl_4(PMe_3)_3$ (1.94 g, 3.5 mmol) was suspended in benzene 60 mL) and OEt_2 (20 mL). The alkyne (1.81 g, 26.6 mmol) was added to the reaction flask followed by the gradual addition of Na/Hg (40.2 g, 0.42%, 7.35 mmol). The reaction mixture was stirred for 4 h followed by filtration of the reaction mixture through Celite. The filtrate was evaporated, resulting in a dark blue oil. This oil was purified on activated, neutral alumina (CH_2Cl_2, dark blue fraction) to give 1.08 g (1.96 mmol, 56%) of product. ^1H NMR (C_6D_6): δ 3.11 (q, J_{HP} = 1.2 Hz, J_{HH} = 7.5 Hz, 2H, CH_2), 2.78 (d, J_{HP} = 1.8 Hz, 3H, CCH_3), 1.57 (t, J_{HP} = 3.6 Hz, 18H, PMe_3), 0.95 (t, J_{HH} = 7.5 Hz, 3H, CH$_2$*C*H$_3$), 0.85 (d, J_{HP} = 6.9 Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 218 (m J_{CP} = 6.6 Hz, $J_{CP'}$ = 16.9 Hz, C$\equiv$C), 214 (m, J_{CP} = 6.6 Hz, $J_{CP'}$ = 17.3 Hz, C$\equiv$C), 31.2 (s, CH_2), 25.4 (d, J_{CP} = 111 Hz, PMe_3), 23.0 (s, C*C*H$_3$), 19.0 (t, J_{CP} = 46.5 Hz, PMe_3), 13.7 (s, CH$_2$*C*H$_3$). CV (100 mV s^{-1}; TBAH; DMAc): $E_{1/2}$ = 0.01 V, $E_{p,a}$ = 2.18 V (2e$^-$), NHE. Anal. Calcd For $WC_{14}H_{35}P_3Cl_2$: C, 30.51; H, 6.40. Found: C, 30.48; H, 6.76.

[W(PMe$_3$)$_3$(bpy)(η^2-MeC$\equiv$CEt)](PF$_6$)$_2$ (11). $WCl_2(PMe_3)_3$(η^2-MeC$\equiv$CEt) (**10**; 0.172 g, 0.31 mmol) was dissolved in THF (4 mL), and bipyridine (0.067 g, 0.43 mmol) was added. A THF solution of $TlPF_6$ (2 mL, 0.230 g, 0.655 mmol) was added dropwise to the reaction flask, and a precipitate formed immediately. The reaction mixture was stirred for 1.5 h at room temperature followed by filtration. The resulting blue solid was washed with THF (4 × 1 mL) and dried in vacuo. The solid was then extracted with acetone (6 × 1.5 mL), and the extracts were filtered through the original frit. Slow addition of OEt_2 (6 mL) to the filtrate resulted in a blue precipitate. This solid was collected, washed with OEt_2, and dried in vacuo: yield 0.174 g, 61%. ^1H NMR (acetone-d_6): δ 8.94 (d, 1H), 8.74 (d, 1H), 8.55 (t, 1H), 8.33 (d, 1H), 8.14 (t, 1H), 7.91 (t, 1H), 7.34 (t, 1H), 7.01 (d, 1H) (bpy), 3.94 (q, 2H, CH_2), 3.62 (d, J_{HP} = 1.5 Hz, 3H, CCH_3), 1.70 (d, J_{HP} = 8.4 Hz, 9H, PMe_3), 1.46 (t, 3H, CH_2CH_3), 1.33 (t, J_{HP} = 3.9 Hz, 18H, PMe_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 241.5 (t, J_{CP} = 14.1 Hz, C$\equiv$C), 238.7 (t, J_{CP} = 13.9 Hz, C$\equiv$C), 152.3, 151.1, 150.5 (d, J_{CP} = 9.5 Hz), 148.0, 142.3, 139.9, 129.5, 127.5, 126.1, 125.8, 32.6 (*C*H$_2$CH$_3$), 24.5 (C*C*H$_3$), 23.1 (d, J_{CP} = 31.2 Hz, PMe_3), 17.4 (t, J_{CP} = 13.8 Hz, PMe_3), 12.4 (CH$_2$*C*H$_3$). CV (100 mV s^{-1}; TBAH; DMAc): $E_{1/2}$ = 0.77 V, $E_{1/2}$ = −0.96 V, $E_{1/2}$ = −1.28 V, NHE. Anal. Calcd for $WC_{24}H_{43}N_2P_2F_{12}$: C, 31.12; H, 4.68; N, 3.02. Found: C, 30.69; H, 4.65; N, 3.01.

Results

Inorganic W(III) and W(II) Pyridyl Complexes. Following the lead of Sharp,[6] neutral tungsten(III) and tungsten(II) complexes were prepared from the stoichiometric reduction of tungsten(IV) in the presence of a slight excess of the desired ligand. Treatment of $WCl_4(PMe_3)_3$ with 1 equiv of Na^0 (amalgamated) in the presence of pyridine results in the tungsten(III) complex $WCl_3(PMe_3)_2(py)$ (**1**). The related complex $WCl_3(py)_3$ (**2**) was obtained under similar conditions from the reduction of $WCl_4(py)_2$.[8] Tungsten(II) complexes were prepared from W(IV) by a two-electron reduction with sodium in the presence of the desired ligand. Thus, $WCl_2(bpy)(PMe_3)_2$ (**3**) was prepared via the reduction of $WCl_4(bpy)$ in the presence of PMe_3,[6] and the reduction of $WCl_4(PMe_3)_3$ in the presence of pyridine resulted in $WCl_2(PMe_3)_3(py)$ (**5**). The bis(pyridine) analog to **3**, $WCl_2(PMe_3)_2(py)_2$ (**4**), was obtained cleanly from the one-electron reduction of $WCl_3(PMe_3)_2(py)$ in the presence of pyridine. However, our attempt to prepare **5** by reduction of the tungsten(III) complex $WCl_3(PMe_3)_2(py)$ and addition of 3 equiv of PMe_3 led to $WCl_2(PMe_3)_4$ as the only major product. All attempts to prepare either $WCl_2(PMe_3)_3(py)$ or $WCl_2(PMe_3)_2(py)_2$ cleanly via the phosphine substitution of $WCl_2(PMe_3)_4$ were unsuccessful.

Unlike those of mononuclear molybdenum(III) complexes,[9] the octahedral d^3 tungsten complexes **1** and **2** exhibit relatively sharp ($w_{h/2}$ = 16–120 Hz) but unresolved ^1H NMR spectra, consistent with that observed for $WCl_3(PMe_3)_3$.[6] In comparison, the octahedral tungsten(II) complexes **3**-**5** show fully resolved, Knight-shifted ^1H NMR signals, as have been reported for other octahedral W(II) compounds.[6,10] The pseudotriplet resonance exhibited in the ^1H NMR spectrum of $WCl_2(PMe_3)_2(py)_2$ (**4**) indicates that the phosphines are in a *trans* configuration, as is the case for the bpy analog (**5**).[11] In addition, a preliminary X-ray diffraction study of **4** indicates that the chloride ligands are in a *cis* orientation analogous to compound **3** and **7** (*vide infra*).

Low-temperature structure determinations have been carried out for a representative sample of octahedral tungsten(II) and tungsten(III) with phosphine and pyridyl ligands. The corresponding ORTEP drawings of $WCl_3(PMe_3)_2(py)$ (**1**) and $WCl_2(PMe_3)_2(bpy)$ (**3**) are shown in Figures 1 and 2, respectively. For the most part, W–P, W–N, and W–Cl distances are typical of those reported by other workers.[12] However, in the W(II)–bipyridyl

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(8) This reaction may be carried out using an excess of reducing agent without overreduction. In an earlier report $WCl_3(py)_3$ was prepared from $W(CO)_4Cl_2$ and pyridine at 140 °C: Westland, A. D.; Muriithi, N. *Inorg. Chem.* **1972**, *11*, 2971.

(9) *mer*-$MoCl_3(PMe_2Ph)_3$ exhibits the line width $w_{h/2} \approx$ 360 Hz for the methyl hydrogens: Poli, R.; Gordon, J. G. *Inorg. Chem.* **1991**, *30*, 4550.

(10) Sharp, P. R.; Bryan, J. C.; Mayer, J. M. *Inorg. Synth.* **1990**, *28*, 326.

(11) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1.

(12) Hills, A.; Hughes, D. L.; Leigh, G. J.; Prieto-Alcon, R. *J. Chem. Soc., Dalton Trans.* **1991**, 1515. Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

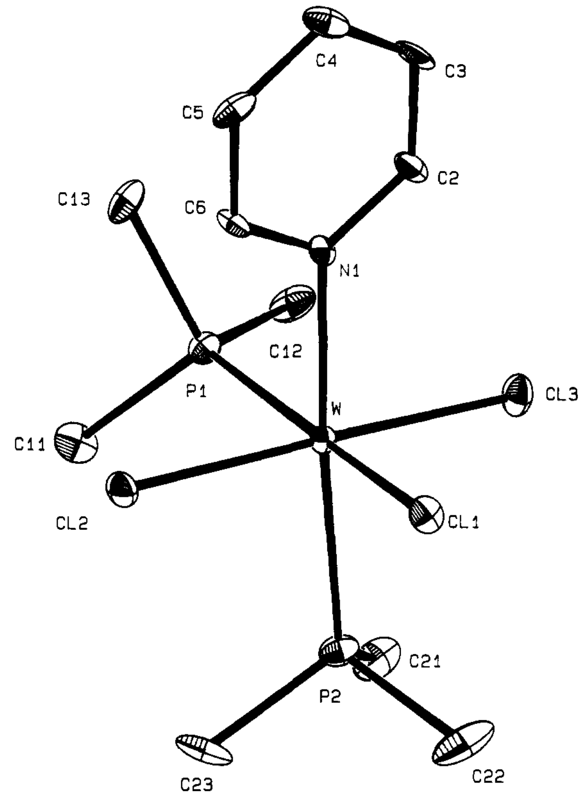

Figure 1. ORTEP drawing of the compound $[W(PMe_3)_2(py)Cl_3]$ (**1**).

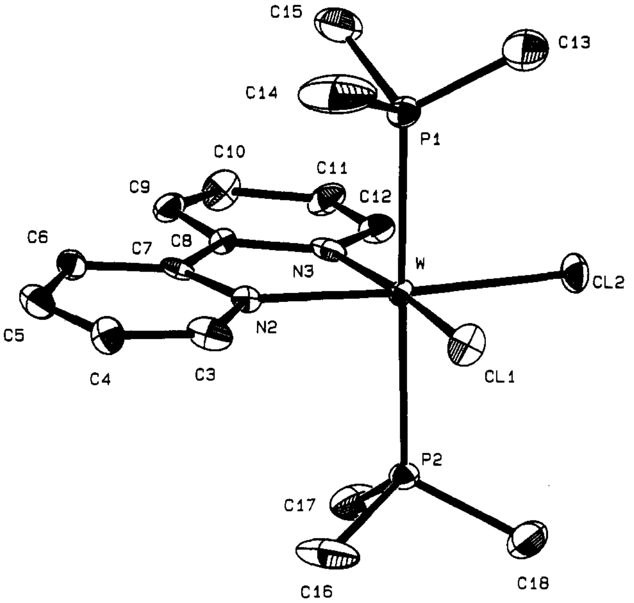

Figure 2. ORTEP drawing of the compound $W(PMe_3)_2(bpy)Cl_2$ (**3**).

complex **3**, extremely short W–N distances (2.071(7) and 2.085(6) Å, cf. 2.28 Å) and distortions in the bpy framework, compared to the free ligand (e.g. C(7)–C(8) = 1.43(1) Å, cf. 1.49 Å; C(3)–N(2) = 1.38(1) Å and C(12)–N(3) = 1.37(1) Å, cf. 1.341 Å), are consistent with a substantial metal-to-ligand π back-donation, as was earlier demonstrated in the compound $Mo(bpy)_2(OPr\text{-}i)_2$.[13] Selected bond distances and angles for the structures of **1** and **3** appear in Tables II and III.

Table II. Selected Bond Lengths (Å) for the Compounds 1, 3, and 7[a]

	$WCl_3(PMe_3)_2(py)$ (**1**)		
W–Cl(1)	2.431(2)	W–P(1)	2.496(3)
W–Cl(2)	2.418(3)	W–P(2)	2.493(3)
W–Cl(3)	2.411(3)	W–N(1)	2.258(8)
	$WCl_2(PMe_3)_2(bpy)$ (**3**)		
W–Cl(1)	2.448(2)	C(3)–C(4)	1.37(1)
W–Cl(2)	2.450(2)	C(4)–C(5)	1.39(1)
W–P(1)	2.499(2)	C(5)–C(6)	1.37(1)
W–P(2)	2.491(2)	C(6)–C(7)	1.42(1)
W–N(2)	2.085(6)	C(8)–C(9)	1.40(1)
W–N(3)	2.071(7)	C(9)–C(10)	1.37(1)
C(7)–C(8)	1.43(1)	C(10)–C(11)	1.38(1)
C(3)–N(2)	1.38(1)	C(11)–C(12)	1.37(1)
C(12)–N(3)	1.37(1)	N(2)–C(7)	1.35(1)
C(3)–C(4)	1.37(1)	N(3)–C(8)	1.39(1)
C(4)–C(5)	1.39(1)		
	$WCl_2(PMe_3)_3(\eta^2\text{-}NCMe)$ (**7**)		
W(1)–C(1)	1.97(1)	W(2)–C(3)	1.98(1)
W(1)–N(1)	2.02(1)	W(2)–N(2)	1.99(1)
W(1)–Cl(1)	2.444(4)	W(2)–Cl(3)	2.444(4)
W(1)–Cl(2)	2.495(4)	W(2)–Cl(4)	2.473(4)
W(1)–P(1)	2.503(4)	W(2)–P(4)	2.506(4)
W(1)–P(2)	2.498(4)	W(2)–P(5)	2.473(4)
W(1)–P(3)	2.483(4)	W(2)–P(6)	2.513(4)
C(1)–N(1)	1.26(2)	C(3)–N(2)	1.27(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

Table III. Selected Bond Angles (deg) for the Compounds 1, 3, and 7[a]

	$WCl_3(PMe_3)_2(py)$ (**1**)		
Cl(2)–W–P(1)	86.0(1)	Cl(3)–W–P(1)	91.1(1)
Cl(2)–W–N(1)	91.0(2)	P(1)–W–P(2)	94.5(1)
	$WCl_2(PMe_3)_2(bpy)$ (**3**)		
N(2)–W–N(3)	74.9(2)	Cl(1)–W–P(1)	88.42(8)
Cl(1)–W–N(2)	97.7(2)	Cl(1)–W–P(2)	87.27(7)
Cl(2)–W–N(3)	96.0(2)	P(1)–W–P(2)	175.68(7)
Cl(1)–W–Cl(2)	91.46(7)		
	$WCl_2(PMe_3)_3(\eta^2\text{-}NCMe)$ (**7**)		
N(2)–C(3)–C(4)	129(1)	P(4)–W(2)–P(5)	99.1(1)
N(2)–W(2)–C(3)	37.4(5)	N(1)–C(1)–C(2)	127(1)
Cl(4)–W(2)–N(2)	155.6(3)	N(1)–W(1)–C(1)	36.8(5)
Cl(4)–W(2)–Cl(3)	86.6(1)	Cl(2)–W(1)–N(1)	155.8(3)
P(4)–W(2)–P(6)	162.9(1)	Cl(1)–W(1)–Cl(2)	86.9(1)
P(4)–W(2)–P(5)	99.1(1)	P(1)–W(1)–P(2)	165.5(1)
N(1)–C(1)–C(2)	127(1)	P(1)–W(1)–P(3)	91.8(1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

η^2-Alkyne Compounds. Reduction of $WCl_4(PMe_3)_3$ in the presence of 2-pentyne results in the neutral, tungsten(II) alkyne complex $WCl_2(PMe_3)_3(\eta^2\text{-}MeC{\equiv}CEt)$ (**10**). This diamagnetic material exhibits a quartet at 3.23 ppm and a triplet at 1.05 ppm assigned to the ethyl group and a doublet at 2.90 ppm (J_{HP} = 1.5 Hz) assigned to the methyl group of the coordinated alkyne.[14] The $^{13}C\{^1H\}$ NMR spectrum exhibits two multiplets at 218 ppm (J_{CP} = 6.6 Hz, $J_{CP'}$ = 16.9 Hz) and 214 ppm (J_{CP} = 6.6 Hz, $J_{CP'}$ = 17.3 Hz) attributed to the alkyne carbons, values which are consistent with the alkyne functioning as a four-electron donor.[15] The addition of 2.1 equiv of $TlPF_6$ and bipyridine to a THF solution of $WCl_2(PMe_3)_3(\eta^2\text{-}MeC{\equiv}CEt)$ (**10**) results in the dicationic complex $[W(PMe_3)_3(bpy)(\eta^2\text{-}MeC{\equiv}CEt)](PF_6)_2$ (**11**). The ^1H NMR spectrum shows eight distinct bipyridine resonances

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(13) Chisholm, M. H.; Huffman, J. C.; Rothwell, I. P; Bradley, P. G.; Kress, N.; Woodruff, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 4945.

(14) In contrast, the free ligand exhibits a multiplet at 1.93 ppm, a triplet at 0.92 ppm, and a second triplet at 149 ppm, respectively.

(15) (a) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *97*, 1970. (b) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956.

Table IV. Refined Atomic Coordinates for Compounds 1, 3, and 7

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
			Compound 1				
W	−0.00223(5)	0.12312(1)	0.80783(4)	C(4)	0.418(1)	0.1789(5)	0.504(1)
Cl(1)	−0.1058(3)	0.1230(1)	0.5408(3)	C(5)	0.377(1)	0.1194(5)	0.517(1)
Cl(2)	0.0487(3)	0.0172(1)	0.7825(3)	C(6)	0.262(1)	0.1048(4)	0.603(1)
Cl(3)	−0.0576(3)	0.2273(1)	0.8535(3)	C(11)	0.087(1)	0.0553(5)	0.202(1)
P(1)	0.1245(3)	0.1189(1)	1.0685(3)	C(12)	0.115(1)	0.1841(5)	1.199(1)
P(2)	−0.2217(3)	0.998(1)	0.9357(4)	C(13)	0.305(1)	0.1104(5)	1.034(1)
N(1)	0.1881(8)	0.1479(4)	0.677(1)	C(21)	−0.261(1)	0.1376(6)	1.125(1)
C(2)	0.226(1)	0.2048(4)	0.660(1)	C(22)	−0.361(1)	0.1218(6)	0.806(2)
C(3)	0.338(1)	0.2211(5)	0.576(1)	C(23)	−0.255(1)	0.0220(5)	0.982(1)
			Compound 3				
W	0.22651(2)	0.11197(3)	0.16090(2)	C(7)	0.2296(6)	0.3939(8)	0.2358(4)
Cl(1)	0.2779(2)	−0.1039(2)	0.2336(1)	C(8)	0.1967(6)	0.427(1)	0.1583(4)
Cl(2)	0.2011(2)	−0.0206(2)	0.0437(1)	C(9)	0.1754(6)	0.5639(9)	0.1282(5)
Cl(3)	0.5162(2)	0.1758(3)	0.4523(1)	C(10)	0.1384(7)	0.5794(9)	0.0533(5)
Cl(4)	0.6868(2)	0.1573(3)	0.5775(1)	C(11)	0.1280(6)	0.461(1)	0.0075(4)
P(1)	0.4025(2)	0.1532(3)	0.1588(1)	C(12)	0.1520(6)	0.330(1)	0.0380(4)
P(2)	0.0552(2)	0.0545(2)	0.1687(1)	C(13)	0.4599(8)	0.036(1)	0.1034(6)
N(2)	0.2440(4)	0.2538(7)	0.2498(3)	C(14)	0.4839(8)	0.150(2)	0.2494(6)
N(3)	0.1874(5)	0.3085(7)	0.1125(3)	C(15)	0.4235(7)	0.328(1)	0.1237(6)
C(3)	0.2692(6)	0.211(1)	0.3236(4)	C(16)	0.0411(7)	0.042(1)	0.2626(5)
C(4)	0.2813(6)	0.3074(9)	0.3805(4)	C(17)	−0.0355(7)	0.187(1)	0.1260(6)
C(5)	0.2691(6)	0.452(1)	0.3657(5)	C(18)	0.0032(8)	−0.111(1)	0.1266(7)
C(6)	0.2460(6)	0.498(1)	0.2931(5)	C(19)	0.6428(7)	0.173(1)	0.4796(5)
			Compound 7				
W(1)	0.33027(4)	0.20698(5)	0.02540(3)	C(11)	0.548(1)	0.166(2)	0.084(1)
W(2)	0.84151(4)	0.22664(4)	0.23444(3)	C(12)	0.453(1)	0.133(2)	0.1881(9)
Cl(1)	0.2609(2)	0.2094(3)	0.1306(2)	C(13)	0.488(1)	0.342(2)	0.153(1)
Cl(2)	0.3291(3)	0.4046(3)	0.0309(2)	C(21)	0.118(1)	0.125(1)	−0.008(1)
Cl(3)	0.9017(2)	0.0602(3)	0.2021(2)	C(22)	0.169(1)	0.213(2)	−0.1316(9)
Cl(4)	0.9537(2)	0.2380(3)	0.3330(2)	C(23)	0.139(1)	0.343(1)	−0.0184(8)
P(1)	0.4565(3)	0.2173(3)	0.1120(2)	C(31)	0.445(1)	0.151(2)	−0.1187(8)
P(2)	0.1899(3)	0.2219(3)	−0.370(2)	C(32)	0.346(1)	0.332(2)	−0.150(1)
P(3)	0.4023(3)	0.2607(4)	−0.0749(2)	C(33)	0.482(1)	0.353(2)	−0.061(1)
P(4)	0.9402(3)	0.2995(3)	0.1590(2)	C(41)	0.934(1)	0.232(1)	0.0744(8)
P(5)	0.8108(3)	0.3914(3)	0.2961(2)	C(42)	1.045(1)	0.283(1)	0.1932(7)
P(6)	0.7740(3)	0.1115(3)	0.3168(2)	C(43)	0.941(1)	0.437(1)	0.1297(8)
N(1)	0.3810(8)	0.062(1)	0.0259(6)	C(51)	0.709(1)	0.441(1)	0.269(1)
N(2)	0.7269(8)	0.2210(9)	0.1909(6)	C(52)	0.870(1)	0.509(1)	0.288(1)
C(1)	0.316(1)	0.063(1)	−0.0154(8)	C(53)	0.812(1)	0.389(1)	0.3913(8)
C(2)	0.276(1)	−0.028(1)	−0.0588(8)	C(61)	0.831(1)	0.072(1)	0.3997(8)
C(3)	0.767(1)	0.274(1)	0.1505(7)	C(62)	0.741(1)	−0.015(1)	0.2783(8)
C(4)	0.737(1)	0.332(1)	0.0830(8)	C(63)	0.680(1)	0.155(1)	0.3440(8)

between 7 and 9 ppm, a doublet at 1.70 ppm (9H), and a pseudotriplet at 1.46 ppm (18H) assigned to trimethylphosphine ligands in a *mer* configuration. In comparison to its precursor (**10**), the alkyne proton and carbon resonances of the cationic complex (**11**) are shifted downfield, consistent with the increased acidity of the metal center. As with other known alkyne complexes, the infrared spectra (KBr) of **10** and **11** do not reveal a ν(C≡C) absorption in the range 1620–2700 cm^{-1}.

η^2-Nitrile Compounds. Addition of $TlPF_6$ to an acetonitrile solution of $WCl_2(bpy)(PMe_3)_2$ results in the cationic complex $[WCl(bpy)(PMe_3)_2(\eta^2\text{-}NCCH_3)]PF_6$ (**6**).[3] Similar to the η^2-alkyne complexes above, this formally 16-electron, six-coordinate complex exhibits a diamagnetic ^{1}H NMR spectrum. The ^{13}C{^{1}H}NMR spectrum of **6** exhibits a triplet at 235 ppm (J_{CP} = 13 Hz) assigned to the nitrile carbon, but the infrared spectrum (KBr) of **6** does not reveal a ν(CN) stretch in the range 1700–2300 cm^{-1}. The η^2-nitrile complexes $[WCl(bpy)(PMe_3)_2(\eta^2\text{-}NCC(CH_3)_3)]PF_6$ (**8**) and $[WCl(bpy)(PMe_3)_2(\eta^2\text{-}NC(C_6H_5))]PF_6$ (**9**) are prepared in a similar fashion from the corresponding nitrile. These complexes also show no infrared absorptions over the range 1650–2300 cm^{-1}. Various spectroscopic properties are summarized for the nitrile compounds **6**–**9** in Tables V and VI. Representative absorption spectra of the cationic η^2-alkyne (**11**) and the η^2-nitrile (**6**) are shown in Figure 6, with each complex showing an absorption between 500 and 700 nm. Attempts to prepare the halogenated η^2-nitrile complexes $[WCl(bpy)(PMe_3)_2(\eta^2\text{-}NCCH_2X)]PF_6$(X = F, Cl) by the methods described above were unsuccessful.

Reduction of $WCl_4(PMe_3)_3$ in toluene/CH_3CN results in the olive green η^2-acetonitrile complex $WCl_2(PMe_3)_3(\eta^2\text{-}NCCH_3)$ (**7**). The ^{13}C NMR spectrum displays a low-filed multiplet at 230.4 ppm (interaction from the two types of phosphines) assigned to the nitrile carbon. The proton spectrum exhibits a doublet at 3.23 ppm (J_{HP} = 1.3 Hz) for the acetonitrile, along with a doublet at 0.76 ppm and pseudotriplet at 1.54 ppm indicating a *mer* configuration of trimethylphosphines.

A crystal of the neutral complex $WCl_2(PMe_3)_3(\eta^2\text{-}NCCH_3)$ (**7**) was structurally characterized by X-ray diffraction, and the corresponding ORTEP drawing for one of two independent molecules found in the asymmetric unit is shown in Figure 3. The average W–C (1.98(1) Å) bond length is slightly shorter and the nitrile C–C–N angle is more distorted (128(1)°), relative to the cationic complex **6**, consistent with an increased amount of metal-to-ligand back-bonding for the neutral species. The average W–N (2.01(1) Å) and C–N (1.27(1) Å) bond lengths are identical with those of **6** within experimental error. Similar to the case for $[W(PMe_3)_2(pby)(\eta^2\text{-}CH_3CN)]^+$ (**6**), the neutral

Table V. Summary of Spectroscopic and Structural Properties of Various η^2-Nitrile, η^2-Alkyne, and η^2-Alkene W(II) Complexes

complex	*N*	M–C (Å)	M–N(C) (Å)	C–N(C) (Å)	Δ (Å)	N(C)–C–C (deg)	^{13}C NMR (ppm)	Δ$G^‡$ (kcal/mol)	ref
$[W(bpy)(PMe_3)_2Cl(CH_3CN)]^+$	4	2.00	2.01	1.26	0.11	130	235	11.9	this work
$[W(bpy)(PMe_3)_2Cl(t\text{-}BuCN)]^+$	4						240	9.9	this work
$[W(bpy)(PMe_3)_2Cl(PhCN)]^+$	4						236	8.4	this work
$W(PMe_3)_3Cl_2(CH_3CN)$	4	1.98	2.01	1.27	0.12	128	230	13.3	this work
$W(PMe_3)_3Cl_2(MeC{\equiv}CEt)$	4						218, 214	9.1	this work
$[W(PMe_3)_3(bpy)(MeC{\equiv}CEt)]^{2+}$	4						241, 239	10.8	this work
$W(CO)(HC{\equiv}CH)(S_2CNEt_2)_2$	4	2.02	2.04	1.29	0.09	130, 136	206, 207	11.7	21b
$Mo(CO)(PhC{\equiv}CH)(PEt_3)_2Br_2$	4	1.98	1.99	1.27	0.08	134	225, 225		21c
$[Mo(dmpe)_2Cl(CH_3CN)]^+$	4	1.98	1.96	1.22	0.07	130			21a
$Mo(Cp)_2(CH_3CN)$	2	2.11	2.22	1.20	0.05	139			2
$W(CO)_2(dppe)(DMAC)_2$	2	2.18	2.15	1.30	0.10	137		17.7	21d
$W(CO)_3(dppe)(HC{\equiv}CPh)$	2						98.2, 88.7		21d
$Ir(Cp)(PPh_3)(NCC_6H_4Cl)$	2	2.10(2)	2.17(1)	1.23(3)	0.08(3)	136			23b
$Ir(Cp^*)(CO)(NCC_6H_4Cl)$	2	2.04	2.18	1.22	0.06	141			23b

Table VI. UV/Vis Absorption Data for Various η^2-Alkyne and η^2-Nitrile W(II) Complexes

compd	wavelength (nm)	$10^{-3}\,\epsilon$ ($M^{-1}\,cm^{-1}$)
$[WCl(PMe_3)_2(bpy)(\eta^2\text{-}NCCH_3)]PF_6$ (**6**)	310^a	13.5
	448^a	2.9
	668^a	5.5
$[WCl(PMe_3)_2(bpy)(\eta^2\text{-}NC(C_6H_5))]PF_6$ (**8**)	308^a	14.1
	398^a	2.7
	668^a	6.7
$[WCl(PMe_3)_2(bpy)(\eta^2\text{-}NCC(CH_3)_3)]PF_6$ (**9**)	310^a	12.6
	460^a	3.0
	684^a	4.9
$WCl_2(PMe_3)_3(\eta^2\text{-}NCCH_3)$ (**7**)	224^b	9.2
	258^b	6.9
	360^b	0.83
	674^b	0.022
$WCl_2(PMe_3)_3(\eta^2\text{-}2\text{-pentyne})$ (**10**)	224^b	9.4
	252^b	9.8
	584^b	0.086
$[W(PMe_3)_3(bpy)(\eta^2\text{-}2\text{-pentyne})](PF_6)_2$ (**11**)	304^a	12.2
	316^a	11.3
	392^a	2.4
	584^a	3.1
$WCl_2(PMe_3)_2(bpy)$ (**3**)	220^b	20.2
	246^b	20.2
	290^b	18.7
	340^b	18.1
	434^b	11.1
	518^b	6.5

^{a} Spectrum recorded in CH_3OH. ^{b} Spectrum recorded in CH_2Cl_2.

η^2-nitrile ligand in compound **7** displays a distinct trans influence; the average tungsten–chloride bond *trans* to the acetonitrile (2.484(4) Å) is ~0.04Å longer than the tungsten–chloride bond trans to trimethylphosphine (2.444(4) Å). A summary of the described reactions appears in Figure 4.

Variable-Temperature ^{1}H NMR Studies. The ^{1}H NMR spectra of the reported η^2-nitrile complexes **6**–**9** at 20 °C each exhibit a pseudotriplet for the equivalent *trans* trimethylphosphine ligands. This observation suggests that either the nitrile is rotating about the M–CN bond at a rate greater than the NMR time scale or it is oriented in a plane perpendicular to the trans phosphines. However, crystal structure determinations for **6** and **7** shows that the acetonitrile ligand is oriented parallel to the phosphine–tungsten bonds. Thus, a variable-temperature ^{1}H NMR study was undertaken to gain information on the rotational barrier for the η^2-nitrile complexes **6**–**9**. At −70 °C, the *trans*-phosphine resonances in the ^{1}H NMR (acetone-d_6) spectrum of $[WCl(bpy)(PMe_3)_2(\eta^2\text{-}NCCH_3)]PF_6$ (**6**) were observed as a pair of doublets separated by 34 Hz. Coalescence was observed at −32 °C, and a value of Δ$G^‡$ = 11.9 ± 0.2 kcal/mol was calculated for rotation of the acetonitrile ligand about the M–CN bond.[16] The low-temperature ^{1}H NMR spectrum of the neutral complex $WCl_2(PMe_3)_3(\eta^2\text{-}NCCH_3)$ is slightly more complicated, since the inherent chemical shifts of the two *trans* trimethylphosphines are nearly identical. As a result, at −65 °C the pseudotriplet converts into a broad doublet. From the small difference in frequencies (Δν ≈ 2 Hz) and an estimate of the coalescence temperature (−35 ± 5 °C), a value of Δ$G^‡$ = 13.2 ± 0.5 kcal/mol was calculated for rotation of the acetonitrile about the M–CN bond. This value is confirmed by a low-temperature $^{31}P\{^1H\}$ NMR study,[17] which determined a value of 13.3 ± 0.2 kcal/mol.

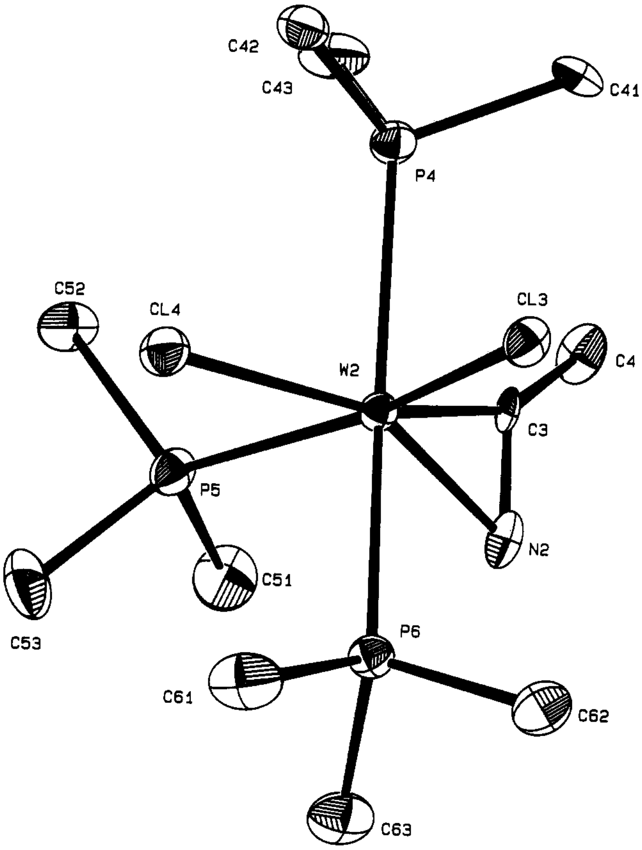

Figure 3. ORTEP drawing of the complex $WCl_2(PMe_3)_3(\eta^2\text{-}NCCH_3)$ (**7**).

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[16] Sandström, J. In *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

[17] For ^{31}P NMR: δ(20 °C) −35.05, −35.73 ppm (H_3PO_4); Δν = 58 Hz, T_c = 0 °C.

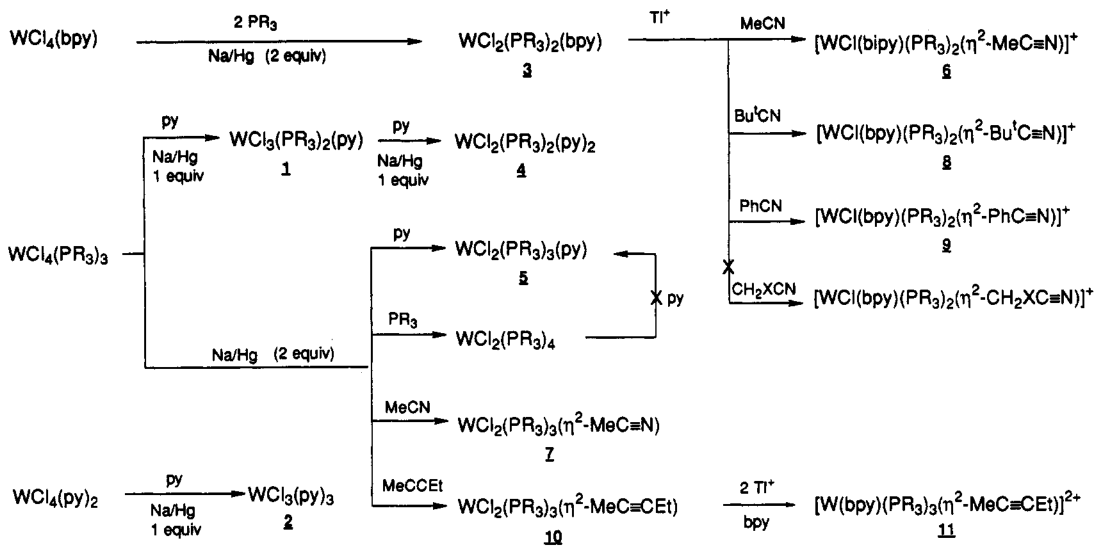

Figure 4. Reaction scheme summarizing the syntheses of various octahedral W(III) and W(II) complexes.

At −85 °C, the ^{1}H NMR spectrum of [WCl(bpy)(PMe$_3$)$_2$(η^2-NC(C$_6$H$_5$))]PF$_6$ (**8**) exhibits two broad singlets (or two unresolved doublets) separated by 64 Hz. Coalescence is observed at −65 °C, and a value of $\Delta G^{\ddagger} = 9.9 \pm 0.2$ kcal/mol is determined for the rotation barrier of the benzonitrile ligand about the M–CN bond. Interestingly, no change is observed in the ^{1}H NMR spectrum of [WCl(bpy)(PMe$_3$)$_2$(η^2-NCC(CH$_3$)$_3$)]PF$_6$ (**9**) from +55 to −65 °C. However, the ^{31}P{^{1}H} NMR spectrum at 20 °C (acetone-d_6, vs H$_2$PO$_4$) exhibits a singlet at −25.0 ppm (^{31}P NMR, J_{PH} = 69 Hz), which resolves into two resonances below $T_c = -80 \pm 3$ °C. This coalescence temperature along with $\Delta\nu$ = 550 Hz corresponds to $\Delta G^{\ddagger} = 8.4 \pm 0.2$ kcal/mol. Given that the phosphine ligands in **8** and **9** are in a *trans* configuration, this observation of inequivalent phosphines suggests a conformational miniumum in which the nitrile C≡N bond axis is parallel to the P–W–P axis, as is illustrated in the ORTEP drawings of **6** and **7**.

The rotational barriers for the alkyne ligand in WCl$_2$(PMe$_3$)$_3$(η^2-MeC≡CEt) (**10**) and [W(PMe$_3$)$_3$(bpy)(η^2-MeC≡CEt)](PF$_6$)$_2$ (**11**) were measured most conveniently by identifying the coalescence temperature for the methylene resonance of the 2-pentyne ligand. For the neutral complex **10**, coalescence is observed at -82 ± 5 °C and a $\Delta\nu$ value of 68 Hz corresponds to $\Delta G^{\ddagger} = 9.1 \pm 0.2$ kcal/mol. Coalescence for the dicationic analog **11** is observed at −47 °C ($\Delta\nu$ = 60 Hz), corresponding to a rotational barrier of 10.8 ± 0.2 kcal/mol. For a *mer* arrangement of phosphine ligands, this observation indicates that the conformational minimum has the alkyne C≡C bond axis parallel to the P–W–P axis. Thus, the alkyne and η^2-nitrile ligands exhibit striking similarities with regard to both the magnitude of the barrier to rotation and their ground-state orientation. Barriers to rotation for both the alkyne and nitrile ligands are summarized in Table V.

Electrochemistry. Virtually all of these W(III) and W(II) complexes exhibit rich electrochemical activity. In particular, complexes that contain pyridyl ligands often exhibit more than one reversible couple in cyclic voltammetry experiments carried out at routine scan rates. For comparison, a summary of electrochemical data for complexes **1**–**11** is presented in Table VII, and the cyclic voltammograms of WCl$_2$(PMe$_3$)$_2$(bpy) and [WCl(PMe$_3$)$_2$(bpy)(η^2-NCCH$_3$)]$^+$ are shown in Figure 5.

Table VII. Summary of Electrochemical Data for Various W(II) and W(III) Complexes

complex[d]	IV/III	III/II	II/I	I/0
WCl$_3$(py)$_3$ (**2**)	−0.18	−1.80		
WCl$_3$(PMe$_3$)$_2$(py) (**1**)	0.21[a]	−1.21		
WCl$_2$(PMe$_3$)$_4$	0.73[a]	−0.51	−2.25[b,c]	
WCl$_2$(PMe$_3$)$_3$(py) (**5**)	0.76[a]	−0.59	−2.24[c]	
WCl$_2$(PMe$_3$)$_2$(py) (**4**)	0.62[a]	−0.75	−2.04[c]	
WCl$_2$(PMe$_3$)$_2$(bpy) (**3**)	0.55[a]	−0.34	−1.66	
WCl$_2$(PMe$_3$)$_3$(η^2-NCCH$_3$) (**7**)		0.35[a]	−1.76[c]	
[WCl(PMe$_3$)$_2$(bpy)(η^2-NCC(CH$_3$)$_3$)]$^+$ (**8**)		0.48[a]	−0.93	−1.62[c]
[WCl(PMe$_3$)$_2$(bpy)(η^2-NCCH$_3$)]$^+$ (**6**)		0.48[a]	−1.07	−1.62[c]
[WCl(PMe$_3$)$_2$(bpy)(η^2-NC(C$_6$H$_5$))]$^+$ (**9**)		0.53[a,b]	−0.94	−1.54[c]
WCl$_2$(PMe$_3$)$_3$(η^2-MeC≡CEt) (**10**)		0.01	−2.18[b]	
[W(PMe$_3$)$_3$(bpy)(η^2-MeC≡CEt)]$^{2+}$ (**11**)		0.77	−0.96	−1.28[c]

[a] Irreversible anodic peak. [b] Two-electron process. [c] Irreversible cathodic peak. [d] Cyclic voltammetric data were obtained in *N*,*N*-dimethylacetamide at 100 mV/s and are reported vs NHE (*in situ* reference: FeCp$_2$/FeCp$_2^+$ 0.62 V, CoCp$_2^+$/CoCp$_2$ −0.78 V).

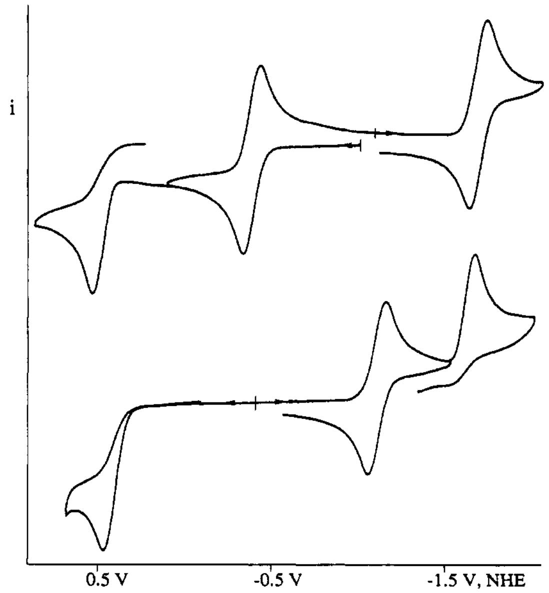

Figure 5. Cyclic voltammograms of the complexes WCl$_2$(PMe$_3$)(bpy) (**3**; above) and [WCl(PMe$_3$)$_2$(bpy)(η^2-NCCH$_3$)]$^+$ (**6**; below).

Discussion

Despite the unusual nature of η^2-nitrile complexes, their spectroscopic data are limited and theoretical treatments that describe the bonding between the η^2-nitrile ligand

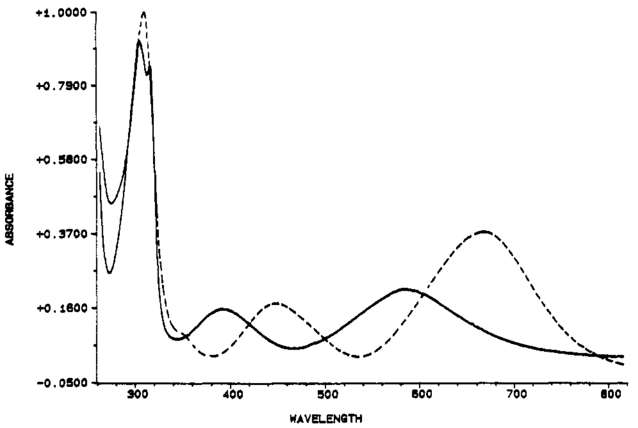

Figure 6. UV/vis absorption spectra for the compounds $W(PMe_3)_2(bpy)(\eta^2\text{-}CH_3CN)Cl]^+$ (**6**; dashed line) and $[W(PMe_3)_3(bpy)(2\text{-pentyne})]^{2+}$ (**11**; solid line).

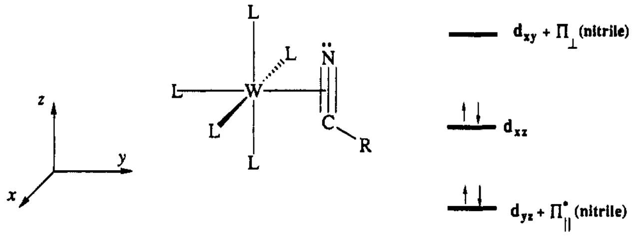

Figure 7. Metal dπ orbitals for an η^2-nitrile complex neglecting π interactions of ancillary ligands.

and the metal are lacking. For the case of alkyne ligands, Templeton[1] and Hoffmann[18] have shown that these ligands can function either as two-, three-, or "four-electron" donors, depending on the nature of the metal and the ancillary ligands. As with alkenes, the alkyne $\pi_{\|}$ and $\pi_{\|}$* orbitals enter into σ-donor and π-back-bonding interactions with the metal. Additionally, provided that the metal is not electronically saturated, the alkyne can be an effective π donor through its $\pi_{\perp}$ orbital (Figure 7). Compared to alkynes, nitriles have $\pi_{\|}$ and $\pi_{\perp}$ orbitals which are lower in energy, and this feature would decrease the stability of an η^2-nitrile complex relative to its carbon analogs, particularly for the case of electron-deficient metals. On the other hand, electron-rich metal systems can be stabilized through the relatively low-energy $\pi_{\|}$* orbital of the nitrile, which can interact more favorably with metal d_{π} electrons. The majority of the reported W(II) and Mo(II) alkyne complexes have carbonyls or other π-acidic ligands which may render the metal unsuitable for binding nitriles in a η^2 fashion. In contrast, the W(II) pyridyl/phosphine complexes reported herein are relatively electron-rich systems with alkylphosphine or pyridine ligands as the only potential π acids.

That the nitrile ligands of **6**–**9** may be significant π donors (i.e. "four-electron donors") is suggested by both spectroscopic and structural results. The alkyne complexes **10** and **11** show ^{13}C data (214–239 ppm) typical of other "four-electron-donor" alkyne species (Table V). In marked contrast, "two-electron-donor" ($N = 2$) alkynes, which are present in 18-electron complexes, display peaks in the range 100–120 ppm, values near those of the free ligand.[19] The complexes **6**–**9** display ^{13}C nitrile resonances between 230 and 240 ppm, values slightly *downfield* of the "four-electron-donor" alkynes. Although the increased electronegativity of nitrogen compared to that of carbon certainly contributes to the downfield chemical shift for the nitrile carbons in **6**–**9**,[20] an increase in chemical shift of over 100 ppm from the free ligand value must be attributed primarily to π interactions (both $\pi_{\|}$ and $\pi_{\perp}$).

An interesting difference between the nitrile and alkyne complexes and the other 16e⁻ complexes reported here is that the former are diamagnetic. The diamagnetism of the d^4 nitrile complexes suggests a two-below-one splitting of the metal dπ orbitals (Figure 7). If π interactions from the ancillary ligands are neglected, the interaction of the occupied nitrile of alkyne $\pi_{\perp}$ orbital with the unoccupied tungsten d_{xy} orbital would cause such a separation in the dπ orbitals, and this may be the primary cause of the diamagnetism observed for compounds **6**–**11**. Even with the nitrile ligand acting as a π acid, the HOMO/LUMO split would not be significant unless the nitrile were also acting as a π donor.

The structural features for the acetonitrile complexes **6** and **7** are also similar to those reported for octahedral W(II) and Mo(II) alkyne complexes, as illustrated in Table V.[21] The M–C and M–N distances for **6** and **7** are very short, being nearly identical with those values reported for 16-electron "four-electron-donor" ($N = 4$) alkyne complexes which have M–C bonds in the range 2.02–2.04 Å.[22] In contrast, the electronically saturated 18-electron analogs, "two-electron-donor" ($N = 2$) alkyne complexes, typically have M–C bonds that exceed this average by ~0.1 Å (Table V). Parallel to the situation observed with the W(II) alkyne complexes, the η^2-nitrile ligands in **6** and **7** are severely distorted. For example, the corresponding C–N bond distance in $[W(PMe_3)_3Cl_2(\eta^2\text{-}CH_3CN)]$ (**7**) is lengthened by 0.12 Å and the N–C–C bond angle is 128° (a distortion of 52° from linear). Similar findings are reported for the 16-electron complex $[Mo(dmpe)_2Cl(\eta^2\text{-}CH_3CN)]^+$.[23a] In comparison, the limited number of structurally characterized η^2-nitrile complexes which are formally saturated (i.e. 18 electrons; $N = 2$) have significantly longer metal–nitrile bond lengths and greater N–C–C angles (Table V).[23]

The η^2-nitrile (**6**–**9**) and alkyne (**10**, **11**) complexes show fluxional behavior consistent with rotational conformers of the M–(η^2-L) bond.[24] For the nitrile complexes, barriers to rotation in the range $\Delta G^* = 8.4$–13.3 kcal/mol, values which are similar to those of their η^2-alkyne analogs (**10**, **11**) and a variety of other octahedral Mo(II) and W(II) alkyne complexes.[25] For the series $[W(PMe_3)_2(bpy)Cl(\eta^3\text{-R-CN})]^+$ the barrier to rotation (kcal/mol) decreases as R varies from CH_3 (11.9) to C_6H_5 (9.9) to $C(CH_3)_3$ (8.4). In all three cases, static NMR spectra show inequivalent phosphine resonances of equal intensity, suggesting that

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[18] Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466.

[19] Reference 1, p 51.

[20] Differences in electronegativity between uncoordinated alkynes and nitriles result in ^{13}C signals which differ by ca. 40 ppm (e.g. acetonitrile 117.7 ppm, 2-hexyne 80.9 ppm).

[21] (a) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, W. *J. Am. Chem. Sco.* **1978**, *100*, 1318. (b) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532. (c) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707. (d) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 1401.

[22] Brisdon, B. J.; Hodson, A. G. W.; Mahon, M. F.; Molloy, K. C.; Walton, R. A. *Inorg. Chem.* **1990**, *27*, 2701.

[23] (a) Anderson, S. J.; Wells, F. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1988**, *7* (24), 2615. (b) Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 650.

[24] In the case of the η^2-nitriles an η^2–η^1 linkage isomerization could also account for the coalescence of the phosphine signals.

[25] Reference 1, p 52, Table IV.

the nitrile lies in a configuration which eclipses the trans phosphine ligands. This orientation is shown explicitly in the ORTEP drawing of the η^2-acetonitrile complex **7** (Figure 3). Although electronic differences of the nitrile may be significant, the increased steric bulk of the substituent (i.e. *tert*-butyl > phenyl > methyl) destabilizes this lowest energy conformation and this factor alone would account for a decrease in the conformational barrier (increase in rate) over the series **9** > **8** > **6**. The rotational barrier for the neutral η^2-nitrile **7** is the highest observed for the series (13.3 kcal/mol). Given that a chloride ligand occupies a cis coordination site relative to the η^2-nitrile in both **6** and **7** (Figure 3), the rotational process which causes coalescence of the phosphine resonances can occur via a conformer where R eclipses the halide. Thus, in comparing the two acetonitrile complexes $[W(PMe_3)_2(bpy)Cl(\eta^2\text{-}CH_3CN)]^+$ (**6**) and $WCl_2(PMe_3)_3(\eta^2\text{-}CH_3CN)$ (**7**), we attribute the increase in rotational barrier for the latter to electronic rather than steric differences.[24] Specifically, the tungsten in the neutral compound **7** is expected to be a stronger π base than in its cationic counterpart; thus, the increased metal–nitrile bond order in **7** would lead to a higher rotational barrier in this compound.

Virtually all of the W(II) and W(III) complexes reported show well-defined electrochemistry, and a summary of these results is provided in Table VII. Considering first the complexes devoid of side-bound ligands, the most general feature is that chloride ligands, which are excellent π donors, stabilize the higher oxidation states (with respect to metal reduction). Correspondingly, the IV/III, III/II, II/I, and I/0 reduction potentials all shift to more positive values as the number of chloride ligands decrease. Interestingly, the replacement of the two pyridine ligands of $WCl_2(PMe_3)_2(py)_2$ (**4**) by bipyridine (i.e. **3**) causes a dramatic positive shift of the III/II and II/I potentials of approximately 400 mV. These data indicate that a bipyridine ligand can stabilize W(II) and W(I) (relative to their respective oxidation products) to a much greater degree than a comparable number of pyridine or trimethylphosphine ligands. We have seen a similar trend in our investigation of heterocyclic complexes of Re(III).[26] These data are in variance with the general observation that electrochemical properties of bipyridine complexes do not significantly differ from those of their pyridine analogs.[27] For instance, the compounds *cis*-$[Ru(NH_3)_4L_2]^{2+}$, where $L_2 = (py)_2$ and bpy, have III/II couples which differ by only 10 mV and the compounds $[Os(bpy)_2(L_2)]^{2+}$ differ by only 70 mV. This discrepancy most likely arises from differences in π-back-bonding interactions which are only significant when the heterocycle is bound to a highly reducing metal center. Consistent with this notion, the difference of the W(III/IV) couple for **3** and **4** is only 70 mV (Table VII).

The η^2-nitrile (**6**–**9**) and η^2-alkyne (**10**, **11**) complexes have III/II and II/I potentials that are shifted considerably positive to those for their phosphine, pyridine, and chloride analogs. This shift presumably reflects a combination of the increased π acidity and decreased σ-donor capacity of these η^2 ligands. Specifically, the III/II potential for $WCl_2(PMe_3)_3(\eta^2\text{-}NCCH_3)$ (**7**) is approximately 950 mV more positive than that of $WCl_2(PMe_3)_3(py)$ (**5**), a difference due solely to the replacement of a pyridine ligand by a nitrile. For comparison, Lever has calculated an average shift of ~600 mV for CO and about 500 mV for ethylene relative to pyridine.[27] When a chloride of $WCl_2(PMe_3)_2(bpy)$ (**3**) is replaced by acetonitrile (i.e. **6**; Figure 5), the III/II couple shifts about 800 mV positive. In contrast to the neutral compounds reported, all the cationic η^2-nitrile and alkyne complexes show II/I reductions that are chemically reversible at 100 mV/s, an observation which indicates a greater kinetic stability[28] for the neutral or cationic W(I) species (generated from **6**, **8**, **9**, and **11**) relative to their anionic analogs.

A study of the neutral complexes $WCl_2(PMe_3)_3(\eta^2\text{-}MeC{\equiv}CEt)$ (**10**) and $WCl_2(PMe_3)_3(\eta^2\text{-}CH_3CN)$ (**7**) allows for a direct comparison of chemical, electrochemical, and spectroscopic properties of an η^2 nitrile complex with those of its alkyne analog, since the complexes are coordinated to an identical metal fragment, $\{WCl_2(PMe_3)_3\}$. These compounds display similar $^{13}C\{^1H\}$ and ^1H NMR spectra with the nitrile carbon in **7** showing a $^{13}C\{^1H\}$ signal (230.4 ppm) slightly downfield relative to those of the alkyne in **10** (218, 214 ppm). For $WCl_2(PMe_3)_3(\eta^2\text{-}CH_3CN)$ (**7**), the nitrile rotational barrier of 13.3 kcal/mol is about 4 kcal/mol greater than that of the alkyne in **10**. The replacement of the alkyne in $WCl_2(PMe_3)_3(\eta^2\text{-}MeC{\equiv}CEt)$ (**10**) by acetonitrile (**7**) causes both the III/II and II/I potentials to shift positive by approximately 350 mV. The greater $\pi_\parallel$ and weaker $\pi_\perp$ interactions in the case of the nitrile ligand account for this discrepancy. The alkyne complex $WCl_2(PMe_3)_3(\eta^2\text{-}MeC{\equiv}CEt)$ (**10**) displays a single, weak absorption maximum in the visible region at 564 nm (17 100 cm^{-1}; ϵ = 86 M^{-1} cm^{-1}). For the nitrile complex $WCl_2(PMe_3)_3(\eta^2\text{-}CH_3CN)$ (**7**), this absorption shifts to 654 nm (14 800 cm^{-1}; ϵ = 22 M^{-1} cm^{-1}). In the case of four-electron-donor complexes of both molybdenum and tungsten, Templeton has assigned the observed visible transitions in the range λ 550–720 nm (ϵ = 70–250 M^{-1} cm^{-1}) to the metal dd manifold.[29] The interaction between the ligand $\pi_\perp$ orbital and the LUMO of the metal (i.e. d_{xy} in Figure 7) is expected to be greater for alkyne than for nitrile ligands, as the latter are more electron-deficient. The observed bathochromic shift in **7** is consistent with a smaller HOMO–LUMO energy gap compared to its alkyne analog and is parallel to the trend observed by Templeton when an electron-rich alkyne is replaced by a more electron-deficient one.

Conclusions

A series of octahedral W(II) coordination compounds have been prepared containing chloride, phosphine, and pyridyl ligands. In the case of $WCl_2(PMe_3)_2(bpy)$, the substitution of a chloride for a nitrile allows for the synthesis of complexes in which the nitrile is η^2-bound to the metal. These unusual η^2-nitrile complexes show electrochemical, spectroscopic, magnetic, dynamic, and structural features strikingly similar to those of their alkyne analogs. Correspondingly, the new η^2-nitrile complexes reported are considered in the context of the model used successfuly for "four-electron-donor" alkynes; i.e., the nitrile stabilizes the W(II) through donation of electron

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[26] We find that terpyridyl stabilizes lower oxidation states relative to pyridine in the rhenium(III) compounds: $ReCl_3(py)_3$, IV/III 0.50 V, III/II −1.03 V; $ReCl_3$(terpyridine), IV/III 0.48 V, III/II −0.50 V.

[27] Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271 (pyridine, E_L = 0.25 V; 2,2′-bipyrdine, E_L = 0.26 V).

[28] The cationic and neutral W(I) species generated in the electrochemical experiment are most likely more stable in *both* a thermodynamic and kinetic sense, as compared to their anionic counterparts, but this has not been confirmed by the electrochemical measurements described.

[29] Reference 1, p 64.

density from both its $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals while its $\pi_{\parallel}^*$ orbital simultaneously renders it a π acid. A direct comparison between a η^2-nitrile and η^2-alkyne ligand for the tungsten(II) fragment $\{WCl_2(PMe_3)_3\}$ finds that substitution of acetonitrile by 2-pentyne decreases the III/II and II/I reduction potentials, decreases the ligand–metal rotational barrier, and increases the energy of the observed dd transition. Taken together, these data support the hypothesis that an η^2-nitrile ligand is a better π acid but less of a π base than an η^2-alkyne ligand.

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Supplementary Material Available: Tables of experimental details, thermal parameters, and bond distances and angles for compounds 1, 3, 6, and 7 and a table of atomic position parameters and an ORTEP drawing for compound 6 (25 pages). Ordering information is given on any current masthead page.

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