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Molybdenum and Tungsten Cyclopentadienone Complexes. 1. Synthesis and Characterization

Klaus Mauthner,[1a] Christian Slugovc,[1a] Kurt Mereiter,[1b] Roland Schmid,[1a] and Karl Kirchner*,[1a]

Institute of Inorganic Chemistry and Institute of Mineralogy, Crystallography, and Structural Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

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The labile complexes $M(CO)_3(CH_3CN)_3$ (M = Mo, W) undergo facile oxidative addition reactions with 4-bromo-2-cyclopentenone to give $M(\eta^3\text{-}C_5H_5O)(CO)_2(CH_3CN)_2Br$ **1a** and **2**. Complex **1a** crystallizes in space group $P2_1/m$ (No. 11) with $a = 8.631$ (2) Å, $b = 12.852$ (3) Å, $c = 6.659$ (2) Å, $\beta = 109.27$ (1)°, $V = 697.3$ (3) Å^3, and $Z = 2$. The structure was refined to $R(F) = 0.023$ ($F \geq 4\sigma F$). **1** and **2** react with potassium tris(pyrazolyl)borate ($K[HBpz_3]$), 2,2′-bipyridyl (bipy), and bis(diphenylphosphino)methane (dppm) to give neutral η^3-cyclopentenoyl complexes of types $M(\eta^3\text{-}C_5H_5O)(CO)_2(HBpz_3)$ **3a** and **4**, $M(\eta^3\text{-}C_5H_5O)(CO)_2(bipy)Br$ **5** and **6**, and $M(\eta^3\text{-}C_5H_5O)(CO)_2(dppm)Br$ **7** and **8**, respectively, in high yields. Single crystal structural studies have been carried out for complexes **3a**, **4**, and **8**. **3a** crystallizes in space group *Pbca* (No. 61) with $a = 19.819$ (3) Å, $b = 13.899$ (3) Å, $c = 13.088$ (2) Å, $V = 3605$ (1) Å^3, and $Z = 8$, and the structure was refined to $R(F) = 0.026$ ($F \geq 4\sigma F$). **4** is isostructural with **3a** and crystallizes in space group *Pbca* (No. 61) with $a = 19.726$ (6) Å, $b = 13.924$ (6) Å, $c = 13.080$ (4) Å, $V = 3593$ (2) Å^3, and $Z = 8$, and the structure was refined to $R(F) = 0.028$ ($F \geq 4\sigma F$). **8** crystallizes in space group $P\bar{1}$ (No. 2) with $a = 10.143$ (3) Å, $b = 10.972$ (4) Å, $c = 13.708$ (5) Å, $\alpha = 82.52$ (2)°, $\beta = 85.07$ (2)°, $\gamma = 84.77$ (1)°, $V = 1502.0$ (9) Å^3, and $Z = 2$. The structure was refined to $R(F) = 0.029$ ($F \geq 4\sigma F$). Treatment of complexes **3**−**8** with $Ph_3C^+PF_6^-$ in methylene chloride solution led to facile hydride abstraction and formation of the stable cationic η^4-cyclopentadienone complexes $[M(\eta^4\text{-}C_5H_4O)(CO)_2(HBpz_3)]PF_6$ **9a** and **10**, $[M(\eta^4\text{-}C_5H_4O)(CO)_2(bipy)Br]PF_6$ **11** and **12**, and $[W(\eta^4\text{-}C_5H_4O)(CO)_2(dppm)Br]PF_6$ (**13**). Complex **10** has been found to crystallize in space group *Pcab* (No. 61) with $a = 18.242$ (4) Å, $b = 17.145$ (4) Å, $c = 13.188$ (3) Å, $V = 4125$ (2) Å^3, and $Z = 8$. The structure was refined to $R(F) = 0.029$ ($F \geq 4\sigma F$). **13** crystallizes in space group $P2_1/n$ (No. 14) with $a = 11.796$ (3) Å, $b = 17.512$ (7) Å, $c = 17.210$ (5) Å, $\beta = 93.67$ (1)°, $V = 3548$ (2) Å^3, and $Z = 4$. The structure was refined to $R(F) = 0.040$ ($F \geq 4\sigma F$).

Introduction

Cyclopentadienone (C_5H_4O) is a rare but, nevertheless, interesting and useful π-ligand in transition metal complexes as previously shown.[2,3] In an attempt to further elaborate the organometallic chemistry of this ligand, we have undertaken the study of molybdenum and tungsten cyclopentadienone complexes. While with respect to diene functionalization reactions the use of cyclopentadienyl-based molybdenum diene intermediates has been explored in recent years (in one example also with diene = cyclopentadienone[3]),[4] other metal−ligand sets such as molybdenum tris(pyrazolyl)borate ($HBpz_3$), 2,2′-bipyridyl (bipy), or bis(diphenylphosphino)methane (dppm) have received relatively little attention. Moreover, there are no reports on the synthesis and reactivity of tungsten cyclopentadienone complexes in the literature.

As the first part of our study, we report on the syntheses and characterization of $[M(\eta^4\text{-}C_5H_4O)(CO)_2(HBpz_3)]^+$, $[M(\eta^4\text{-}C_5H_4O)(CO)_2(bipy)Br]^+$ (M = Mo, W), and $[W(\eta^4\text{-}C_5H_4O)(CO)_2(dppm)Br]^+$ and their respective molybdenum and tungsten η^3-cyclopentenoyl precursor complexes. X-ray structure determinations of representative complexes are presented.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and/or a glovebox. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[5] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $Mo(\eta^3\text{-}C_5H_5O)(CO)_2(CH_3CN)_2Br$ (**1a**),[3] $Mo(\eta^3\text{-}C_5H_4O\text{-}Me)(CO)_2(CH_3CN)_2Br$ (**1b**),[3] and

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(1) (a) Institute of Inorganic Chemistry; (b) Institute of Mineralogy, Crystallography, and Structural Chemistry.

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K[$HBpz_3$][6] were prepared by literature methods. Infrared spectra were recorded on a Perkin-Elmer 16PC FT IR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC 250 spectrometer operating at 250.13 and 62.86 MHz, respectively, and were referenced to residual solvent protons. Microanalyses were carried out by the Microanalytical Laboratories, University of Vienna.

Synthesis. W(η^3-C_5H_5O)$(CO)_2(CH_3CN)_2$Br (2). This complex has been prepared by following the published procedure for the analogous molybdenum complexes **1** utilizing $W(CO)_6$ as starting material.[3] Complex **2** was isolated as a mixture of *exo* and *endo* conformers in a ratio of about 1:1. Yield: 56%. Anal. Calcd for $C_{11}H_{11}BrN_2O_3W$: C, 27.36; H, 2.30; Br, 16.54; N, 5.80. Found: C, 27.23; H, 2.36; Br, 16.23; N, 5.92. ^1H NMR (δ, dmso-d_6, 20 °C): 4.34 (dd, 1H, J = 17.0, 2.6 Hz), 3.93 (m, 1H), 3.88 (m, 1H), 3.75−3.68 (m, 1H), 2.33 (d, 1H, J = 17.0 Hz), 2.07 (s, 6H), 4.38 (dd, 1H, J = 17.4, 2.7 Hz), 3.93 (m, 1H), 3.88 (m, 1H), 3.75−3.68 (m, 1H), 2.38 (d, 1H, J = 17.4 Hz), 2.07 (s, 6H). $^{13}C\{^1H\}$ NMR (δ, dmso-d_6, 20 °C): 219.2 (CO), 218.3 (CO), 201.4 (ketonic CO), 76.9, 64.0, 60.0, 41.5, 1.2 (Me), 220.0 (CO), 219.1 (CO), 198.2 (ketonic CO), 78.0, 62.5, 56.5, 42.6, 1.2 (Me).

Mo(η^3-C_5H_5O)$(CO)_2(HBpz_3)$ (3a). **1a** (1.00 g, 2.53 mmol) and K[$HBpz_3$] (0.64 g, 2.53 mmol) were dissolved in CH_2Cl_2 (10 mL), and the mixture was stirred for 12 h at room temperature. The resulting precipitate of KBr was removed by filtration, and the solvent was removed under vacuum. The remaining air-stable yellow solid was collected on a glass frit, washed with a small amount of acetone (1 mL) and anhydrous diethyl ether, and dried in vacuo. Yield: 1.1 g (97%). Anal. Calcd for $C_{16}H_{15}BMoN_6O_3$: C, 43.08; H, 3.39; N,18.84. Found: C, 43.01; H, 3.37; N, 18.90. ^1H NMR (δ, CD_3NO_2, 20 °C): 8.64 (d, 1H, $HBpz_3$), 7.88−7.75 (m, 5H, $HBpz_3$), 6.44 (dd, 1H, $HBpz_3$), 6.32−6.29 (m, 2H, $HBpz_3$), 4.91 (dd, 1H), 4.75 (m, 1H), 4.51 (dd, 1H), 3.15 (dd, 1H), 2.28 (d, 1H, J = 18.0 Hz). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 213.0 (CO), 209.8 (CO), 203.14 (ketonic CO), 148.9, 145.3, 143.2, 138.2, 138.0, 136.9, 108.0, 107.3, 107.2, 84.4, 73.8, 69.1, 43.42. IR (poly(chlorotrifluoroethylene), cm^{-1}): 1958 (s, ν_{CO}), 1861 (s, ν_{CO}), 1700 (s, $\nu_{C=O}$).

Mo(η^3-C_5H_4O-Me)$(CO)_2(HBpz_3)$ (3b). This compound was synthesized analogously to **3a** with complex **1b** as starting material. Yield: 4.61g (93%). Anal. Calcd for $C_{17}H_{17}BMoN_6O_3$: C, 44.38; H, 3.72; N, 18.27. Found: C, 44.41; H, 3.80; N, 18.17. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.46 (d, 1H, $HBpz_3$), 7.66−7.59 (m, 4H, $HBpz_3$), 6.27 (dd, 1H, $HBpz_3$), 6.25 (dd, 1H, $HBpz_3$), 6.18 (dd, 1H, $HBpz_3$), 5.02 (d, 1H, J = 5.0 Hz), 4.17 (dd, 1H, J = 5.0, 2.8 Hz), 3.27 (dd, 1H, J = 17.7, 2.8 Hz), 2.54 (d, 1H, J = 17.7 Hz). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 230.7, 222.6 (CO), 201.3 (ketonic CO), 147.5, 146.3, 141.0, 137.7, 136.7, 135.1, 106.7, 106.6, 106.2, 91.3, 89.8, 58.1, 44.7, 15,1 (Me).

W(η^3-C_5H_5O)$(CO)_2(HBpz_3)$ (4). This complex was synthesized analogously to **3** with **2** as starting material. Yield: 3.60 g (81%). Anal. Calcd for $C_{16}H_{15}BN_6O_3W$: C, 35.99; H, 2.83; N,15.74. Found: C, 35.58; H, 2.78; N, 15.49. ^1H NMR (δ, acetone-d_6, 20 °C): 8.70 (d, 1H, $HBpz_3$), 8.16 (d, 1H, $HBpz_3$), 8.07 (d, 1H, $HBpz_3$), 7.87 (m, 3H, $HBpz_3$), 6.48 (dd, 1H, $HBpz_3$), 6.42 (m, 2H, $HBpz_3$), 4.65 (dd, 1H, J = 17.3, 2.6 Hz), 4.53 (dd, 1H), 4.47 (m, 1H), 4.10 (dd, 1H), 2.84 (d, 1H, J = 17.3 Hz). $^{13}C\{^1H\}$ NMR (δ, CD_3NO_2, 20 °C): 226.5 (CO), 220.3 (CO), 204.6 (ketonic CO), 150.1, 146.0, 143.6, 138.4, 138.1, 137.2, 108.6, 107.6, 107.6, 75.3, 66.6, 59.7, 43.6. IR (poly(chlorotrifluoroethylene), cm^{-1}): 1950 (s, ν_{CO}), 1846 (s, ν_{CO}), 1698 (s, $\nu_{C=O}$).

Mo(η^3-C_5H_5O)(bipy)$(CO)_2$Br (5). To a suspension of **1a** (5.0 g, 12.66 mmol) in CH_3CN (10 mL) was added bipy (2.4 g, 15.37 mmol), and the mixture was stirred for 1 h at room temperature. The resulting precipitate was collected on a glass frit, washed with anhydrous diethyl ether, and dried under vacuum. Yield: 5.76 g (97%). Anal. Calcd for $C_{17}H_{13}BrMoN_2O_3$: C, 43.52; H, 2.79; N, 5.97; Br, 17.03. Found: C, 43.48; H, 2.82; N, 5.89; Br, 17.66. ^1H NMR (δ, dmso-d_6, 20 °C): 8.68 (m, 4H, bipy), 8.22 (dd, 2H), bipy), 7.61 (dd, 2H, bipy), 4.51 (m, 1H), 4.25 (m, 1H), 4.03 (m, 1H), 3.02 (d, 1H, J = 18.6 Hz), 2.14 (d, 1H, J = 18.6 Hz). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1955 (s, ν_{CO}), 1871 (s, ν_{CO}), 1697 (s, $\nu_{C=O}$).

W(η^3-C_5H_5O)(bipy)$(CO)_2$Br (6). A suspension of $W(CO)_6$ (5.0 g, 14.21 mmol) in CH_3CN (100 mL) was refluxed for 6 days. The resulting yellow solution was treated at 40 °C with 4-bromo-2-cyclopentenone (about 5-fold excess) in 10 mL of CCl_4. The mixture was stirred for 30 min whereupon bipy (3.3 g, 21.13 mmol) in 10 mL of CH_2Cl_2 was added and stirred for additional 30 min. The solvent was evaporated, and the residue was dissolved in 20 mL of CH_3CN. On addition of diethyl ether, a red microcrystalline precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 7.30 g (92%). Anal. Calcd for $C_{17}H_{11}BrN_2O_3W$: C, 36.65; H, 2.35; N, 5.05; Br, 14.34. Found: C, 36.52; H, 2.22; N, 5.11; Br, 14.16. ^1H NMR (δ, CD_3CN, 20 °C): 8.78 (m, 2H, bipy), 8.45 (d, 2H, bipy), 8.17 (dd, 2H, bipy), 7.56 (dd, 2H, bipy), 4.62 (d, 1H, J = 17.0 Hz), 3.84 (m, 1H), 3.76 (m, 1H), 3.53 (m, 1H), 2.86 (d, 1H, J = 17.0 Hz). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1952 (s, ν_{CO}), 1862 (s, ν_{CO}), 1694 (s, $\nu_{C=O}$).

Mo(η^3-C_5H_5O)(dppm)$(CO)_2$Br (7). To a suspension of **1a** (5.0 g, 12.66 mmol) in CH_2Cl_2 (15 mL) was added dppm (5.35 g, 13.92 mmol), and the mixture was stirred for 1 h at room temperature. Then diethyl ether (20 mL) was added, and the resulting precipitate was collected on a glass frit, washed anhydrous diethyl ether, and dried under vacuum. Yield: 8.38 g (95%). Anal. Calcd for $C_{32}H_{27}BrO_3MoP_2$: C, 55.12; H, 3.90; Br, 11.46. Found: C, 55.52; H, 3.87; Br, 11.26. ^1H NMR (δ, dmso-d_6, 20 °C): 7.90−7.00 (m, 20H), 4.90−4.40 (m, 2H), 4.71 (m, 2H), 4.16 (m, 1H), 2.94 (d, 1H, J = 17.6 Hz), 1.78 (d, 1H, J = 17.6 Hz). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1992 (s, ν_{CO}), 1957 (s, ν_{CO}), 1890 (s, ν_{CO}), 1869(s, ν_{CO}), 1687 (s, $\nu_{C=O}$).

W(η^3-C_5H_5O)(dppm)$(CO)_2$Br (8). This complex was synthesized analogously to **6** with dppm as starting material. Yield: 60%. Anal. Calcd for $C_{32}H_{27}BrO_3P_2W$: C, 48.95; H, 3.47; Br, 10.18. Found: C, 48.52; H, 3.51; Br, 10.52. ^1H NMR (δ, CD_2Cl_2, 20 °C): 7.80−7.10 (m, 20H, dppm), 4.85 (m, 2H), 4.40−3.70 (m, 2H, dppm), 4.08 (d, 1H, J = 17.4 Hz), 2.81 (d, 1H, J = 17.4 Hz). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1982 (s, ν_{CO}), 1952 (s, ν_{CO}), 1881 (s, ν_{CO}), 1863 (s, ν_{CO}), 1689 (s, $\nu_{C=O}$).

[Mo(η^4-C_5H_4O)$(CO)_2(HBpz_3)$]PF_6 (9a). A solution of **3a** (347 mg, 0.778 mmol) in CH_2Cl_2 was treated with $Ph_3C^+PF_6^-$ (302 mg, 0.778 mmol) and was stirred for 3 h at room temperature. The yellow solid that separated from solution was collected on a glass frit, washed with CH_2Cl_2 (1 mL) and anhydrous diethyl ether, and dried under vacuum. Yield: 330 mg (72%). Anal. Calcd for $C_{16}H_{14}BF_6MoN_6O_3P$: C, 32.57; H, 2.39; N,14.24. Found: C, 32.39; H, 2.40; N, 14.19. ^1H NMR (δ, CD_3CN, 20 °C): 8.28 (d, 1H, $HBpz_3$), 8.01 (m, 3H, $HBpz_3$), 7.77 (d, 2H, $HBpz_3$), 6.63 (dd, 2H, H_β), 6.53 (dd, 1H, $HBpz_3$), 6.45 (m, 2H, $HBpz_3$), 4.73 (dd, 2H, H_α). $^{13}C\{^1H\}$ NMR (δ, CD_3CN, 20 °C): 205.1 (CO), 176.0 (ketonic CO), 148.1 (2C, $HBpz_3$), 147.0 ($HBpz_3$), 140.2 (3C, $HBpz_3$), 109.0 (3C, $HBpz_3$), 89.6 (C_β), 89.5 (C_α). IR (poly(chlorotrifluoroethylene), cm^{-1}): 2110 (s, ν_{CO}), 2052 (s, ν_{CO}), 1685 (s, $\nu_{C=O}$).

[Mo(η^4-C_5H_3O-2-Me)$(CO)_2(HBpz_3)$]PF_6 (9b). This compound was synthesized analogously to **9a** but with **3b** as starting material. Yield: 2.23 g (82%). Anal. Calcd for $C_{17}H_{16}BF_6MoN_6O_3P$: C, 33.80; H, 2.67; N,13.91. Found: C, 33.86; H, 2.70; N, 14.01. ^1H NMR (δ, CD_3CN, 20 °C): 8.21 (d, 1H, $HBpz_3$), 8.02−7.75 (m, 5H, $HBpz_3$), 6.80 (dd, 1H, H_β), 6.49−6.44 (m, 3H, $HBpz_3$), 6.24 (dd, 1H, H_β), 4.90 (dd, 1H, H_α), 1.21 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (δ, CD_3CN, 20 °C): 207.1, 207.0 (CO), 177.4 (ketonic CO), 149.4, 149.2, 147.4, 141.4, 141.3,

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Table 1. Crystallographic Data

	1a	3a	4	8	10	13·CH$_3$CN
formula	$C_{11}H_{11}BrMoN_2O_3$	$C_{16}H_{15}BMoN_6O_3$	$C_{16}H_{15}BN_6O_3W$	$C_{32}H_{27}BrO_3P_2W$	$C_{16}H_{14}BF_6N_6O_3PW$	$C_{34}H_{29}BrF_6NO_3P_3W$
fw	395.07	446.09	534.00	785.24	677.96	970.25
cryst size, mm	0.18 × 0.25 × 0.36	0.23 × 0.25 × 0.38	0.07 × 0.22 × 0.29	0.21 × 0.27 × 0.44	0.11 × 0.2 × 0.65	0.18 × 0.24 × 0.48
space group	$P2_1/m$ (No. 11)	*Pbca* (No. 61)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	*Pcab* (No. 61)	$P2_1/n$ (No. 14)
a, Å	8.631(2)	19.819(3)	19.726(6)	10.143(3)	18.242(4)	11.796(3)
b, Å	12.852(3)	13.899(3)	13.924(6)	10.972(4)	17.145(4)	17.512(7)
c, Å	6.659(2)	13.088(2)	13.080(4)	13.708(5)	13.188(3)	17.210(5)
α, deg				82.52(2)		
β, deg	109.27(1)			85.07(2)		93.67(1)
γ, deg				84.77(1)		
V, Å^3	697.3(3)	3605(1)	3593(2)	1502.0(9)	4125(2)	3548(2)
Z	2	8	8	2	8	4
ρ_{calc}, g cm^{-3}	1.882	1.644	1.975	1.736	2.184	1.816
T, K	297	295	295	297	296	295
μ, mm^{-1} (Mo Kα)	3.806	0.758	6.461	5.313	5.767	4.585
absorption corr.	analytical	analytical	analytical	analytical	analytical	empirical
transmiss. fact., min/max	0.64/0.82	0.85/0.89	0.29/0.63	0.34/0.57	0.38/0.59	0.92/1.14
θ_{max}, deg	27	25	25	25	25	24
index ranges	$-11 \le h \le 10$	$0 \le h \le 23$	$0 \le h \le 23$	$-11 \le h \le 12$	$0 \le h \le 21$	$0 \le h \le 13$
	$0 \le k \le 16$	$0 \le k \le 16$	$0 \le k \le 16$	$0 \le k \le 13$	$0 \le k \le 20$	$0 \le k \le 20$
	$0 \le l \le 8$	$0 \le l \le 13$	$0 \le l \le 15$	$-15 \le l \le 16$	$0 \le l \le 15$	$-19 \le l \le 19$
no. of rflns measd	1713	3105	4200	5288	3645	5614
no. of unique rflns	1591	3105	3158	5288	3645	5614
no. of rflns $F > 4\sigma(F)$	1370	2417	2222	4684	2659	4214
no. of params	107	264	255	358	323	444
$R(F)(F > 4\sigma(F))$	0.0229	0.0261	0.0276	0.0288	0.0285	0.0397
$R(F)$(all data)	0.0314	0.0427	0.0534	0.0361	0.0533	0.0653
$wR(F^2)$(all data)	0.0505	0.0550	0.05559	0.0691	0.0521	0.0949
diff Fourier peaks min/max, eÅ^{-3}	-0.42/0.28	-0.26/0.21	-0.50/0.43	-1.05/1.09	-0.48/0.49	-0.63/0.93

140.8, 121.1 (C_β), 110.0, 109.6, 109.5, 94.6 (C_β), 84.4 (C_α), 77.7 (C_α), 12.1 (Me).

[W(η^4-C_5H_4O)(CO)$_2$(HBpz$_3$)]PF$_6$ (10). This compound was synthesized analogously to **9** with complex **4** as starting material. Yield: 1.71 g (80%). Anal. Calcd for $C_{16}H_{14}BF_6N_6O_3PW$: C, 28.35; H, 2.08; B, 1.59; N, 12.40. Found: C, 28.41; H, 2.05; N, 12.36. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.83 (d, 1H, HBpz$_3$), 8.32 (d, 1H, HBpz$_3$), 8.23 (m, 4H, HBpz$_3$), 6.91 (m, 2H, H_β), 6.72 (dd, 1H, HBpz$_3$), 6.58 (m, 2H, HBpz$_3$), 4.59 (m, 2H, H_α). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 196.9 (CO), 174.5 (ketonic CO), 148.9 (HBpz$_3$), 147.8 (2C, HBpz$_3$), 140.7 (2C, HBpz$_3$), 140.3 (HBpz$_3$), 109.8 (HBpz$_3$), 109.5 (2C, HBpz$_3$), 83.2 (C_β), 81.4 (C_α). IR (poly(chlorotrifluoroethylene), cm^{-1}): 2096 (s, ν_{CO}), 2032 (s, ν_{CO}), 1680 (s, $\nu_{C=O}$).

[Mo(η^4-C_5H_4O)(bipy)(CO)$_2$Br]PF$_6$ (11). This complex was synthesized analogously to **9** except that complex **5** was utilized as starting material and the reaction time was 24 h. Yield: 330 mg (72%). Anal. Calcd for $C_{17}H_{12}BrF_6MoN_2O_3P$: C, 33.30; H, 1.97; N, 4.57. Found: C, 33.52; H, 1.82; N, 4.66. ^{1}H NMR (δ, CD$_3$CN, 20 °C): 8.75 (d, 2H, bipy), 8.55 (d, 2H, bipy), 8.33 (dd, 2H, bipy), 7.76 (dd, 2H, bipy), 6.46 (m, 2H$_\beta$), 4.64 (m, 2H$_\alpha$). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$, 20 °C): 203.7 (CO), 174.9 (C=O), 155.5 (bipy), 155.0 (bipy), 143.1 (bipy), 129.9 (bipy), 126.1 (bipy), 89.5 (C_β), 86.9 (C_α). IR (poly(chlorotrifluoroethylene), cm^{-1}): 2096 (s, ν_{CO}), 2040 (s, ν_{CO}), 1688 (s, $\nu_{C=O}$).

[W(η^4-C_5H_4O)(bipy)(CO)$_2$Br]PF$_6$ (12). This complex was synthesized analogously to **11** with **6** used as starting material. Yield: 97%. Anal. Calcd for $C_{17}H_{12}BrF_6N_2O_3PW$: C, 29.13; H, 1.73; N, 4.00; Br, 11.40. Found: C, 30.52; H, 1.82; N, 3.89; Br, 11.58. ^{1}H NMR (δ, CD$_3$NO$_2$, 20 °C): 9.06 (d, 2H, bipy), 8.69 (d, 2H, bipy), 8.49 (dd, 2H, bipy), 7.90 (dd, 2H, bipy), 6.28 (m, 2H$_\beta$), 4.32 (m, 2H$_\alpha$). ^{13}C{^{1}H} NMR (δ, CD$_3$NO$_2$, 20 °C): 194.7 (CO), 172.4 (C=O), 156.4 (bipy), 156.1 (bipy), 143.9 (bipy), 131.0 (bipy), 126.7 (bipy), 83.5 (C_β), 79.7 (C_α). IR (poly(chlorotrifluoroethylene), cm^{-1}): 2091 (s, ν_{CO}), 2028 (s, ν_{CO}), 1667 (s, $\nu_{C=O}$).

Attempted Synthesis of [Mo(η^4-C_5H_4O)(dppm)(CO)$_2$Br]PF$_6$. Following the protocol for complexes **9**−**12**, a solution of **7** (3.0 g, 4.3 mmol) in CH$_2$Cl$_2$ was treated with 1 equiv of Ph$_3$C$^+$PF$_6^-$ and stirred overnight. On addition of diethyl ether, a pale red compound precipitated which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 2.7 g. ^{1}H NMR (δ, CD$_3$CN, 20 °C): 7.84−7.19 (m, 20H, dppm), 5.12 (m, 1H), 5.00 (m, 1H), 4.60 (m, 1H), 4.20 (m, 2H), 3.71 (m, 1H). IR (poly(chlorotrifluoroethylene), cm^{-1}): 1964 (s, ν_{CO}), 1894 (s, ν_{CO}).

[W(η^4-C_5H_4O)(dppm)(CO)$_2$Br]PF$_6$ (13). This complex was synthesized analogously to **11** with **8** as starting material. Yield: 90%. Anal. Calcd for $C_{32}H_{26}BrF_6O_3P_3W$: C, 38.09; H, 2.60; Br, 15.84; P, 9.20. Found: C, 38.13; H, 2.53; Br, 16.14; P, 9.47. ^{1}H NMR (δ, CD$_3$NO$_2$, 20 °C): 8.00−7.30 (m, 20H, dppm), 5.94 (m, 1H), 5.89 (m, 1H), 5.60−5.40 (m, 2H), 4.60 (m, 1H), 4.53 (m, 1H). ^{13}C{^{1}H} NMR (δ, CD$_3$CN, 20 °C): 191.3 (CO), 191.2 (CO), 173.8 (C=O), 134−127 (C$_6$H$_5$), 89.2, 87.2, 80.1, 73.2, 38.0 (PCH$_2$P). IR (poly(chlorotrifluoroethylene), cm^{-1}): 2070 (s, ν_{CO}), 2033 (s, ν_{CO}), 1671 (s, $\nu_{C=O}$).

X-ray Structure Determination for 1a, 3a, 4, 6, 10, and 13. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation and the $\theta - 2\theta$ scan technique. Three representative reference reflections were measured every 120 min and used to correct for crystal decay and system instability. Corrections for Lorentz and polarization effects, and for absorption were applied. The structures were solved by direct methods.[7] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in idealized positions.[8] The structures were refined against F^2. Final positional parameters are given in Tables 2−7.

Results and Discussion

Synthesis and Characterization of Molybdenum and Tungsten η^3-Cyclopentenoyl Complexes.

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 ×10^3) for Mo(η^3-C_5H_5O)$(CO)_2(CH_3CN)_2$Br (1a)[a]

	x	*y*	*z*	U_{eq}
Mo	0.37830(3)	0.25000	0.47029(4)	33(1)
Br	0.09189(4)	0.25000	0.16769(6)	54(1)
C(1)	0.5664(5)	0.2500	0.7819(6)	58(1)
C(2)	0.6090(3)	0.1634(2)	0.6878(5)	59(1)
C(3)	0.7484(4)	0.1917(3)	0.6162(5)	67(1)
C(4)	0.4481(3)	0.1505(2)	0.2937(4)	40(1)
C(5)	0.2035(3)	0.0782(2)	0.7090(4)	44(1)
C(6)	0.1345(3)	0.0045(2)	0.8215(4)	55(1)
N	0.2581(3)	0.1353(2)	0.6222(3)	47(1)
O(1)[b]	0.8180(5)	0.1163(4)	0.5667(8)	83(1)
O(2)	0.4884(2)	0.0957(2)	0.1842(3)	58(1)

[a] $U_{eq} = {}^1/_3\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(a_ia_j)$. [b] The cyclopentenoyl moiety—C(1), C(2), C(3), and O(1)—shows disorder with oxygen O(1) (site ccupation factor 0.5) alternatively attached to C(3) and its mirror-symmetric equivalent C(3′) located at x, $^1/_2 - y$, z.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 ×10^3) for Mo(η^3-C_5H_5O)$(CO)_2$(HBpz$_3$) (3a)

	x	*y*	*z*	U_{eq}[a]
Mo	0.14491(1)	0.16599(2)	0.16192(2)	34(1)
C(1)	0.1704(2)	0.2126(3)	0.0077(3)	72(1)
C(2)	0.1733(2)	0.1126(3)	−0.0023(3)	64(1)
C(3)	0.2453(2)	0.0834(4)	−0.0009(3)	79(1)
C(4)	0.2821(2)	0.1677(3)	0.0427(3)	82(1)
C(5)	0.2278(2)	0.2406(3)	0.0607(4)	78(1)
O(1A)[b]	0.2642(3)	0.0035(5)	−0.0080(5)	110(3)
O(1B)[b]	0.3382(2)	0.1747(5)	0.0624(5)	113(3)
C(6)	0.1646(1)	0.0281(2)	0.1649(3)	48(1)
O(2)	0.1778(1)	−0.0522(2)	0.1727(2)	76(1)
C(7)	0.2277(2)	0.1723(3)	0.2433(3)	58(1)
O(3)	0.2751(1)	0.1739(2)	0.2930(2)	104(1)
N(1)	−0.0135(1)	0.2030(2)	0.1523(2)	39(1)
N(2)	0.0377(1)	0.1587(2)	0.1007(2)	36(1)
C(8)	0.0088(2)	0.1181(2)	0.0198(2)	46(1)
C(9)	−0.0599(2)	0.1349(2)	0.0180(3)	57(1)
C(10)	−0.0721(1)	0.1888(2)	0.1033(2)	49(1)
N(3)	0.0500(1)	0.3368(2)	0.2349(2)	41(1)
N(4)	0.1140(1)	0.3175(2)	0.2026(2)	40(1)
C(11)	0.1459(2)	0.4028(2)	0.2031(2)	53(1)
C(12)	0.1036(2)	0.4755(2)	0.2332(2)	61(1)
C(13)	0.0438(2)	0.4321(2)	0.2527(2)	54(1)
N(5)	0.0306(1)	0.1826(2)	0.3276(2)	39(1)
N(6)	0.0904(1)	0.1388(2)	0.3041(2)	37(1)
C(14)	0.1043(2)	0.0800(2)	0.3823(2)	45(1)
C(15)	0.0551(2)	0.0856(2)	0.4557(2)	52(1)
C(16)	0.0094(2)	0.1505(2)	0.4190(2)	49(1)
B	−0.0006(2)	0.2555(3)	0.2533(3)	43(1)

[a] See footnote *a* of Table 2. [b] The cyclopentenoyl moiety—C(1)–O(1B)—is disordered with the oxygen atom alternatively attached as O(1A) to C(3) or as O(1B) to C(4). Refined site occupation factors: 0.525(7) for O(1A) and 0.475(7) for O(1B).

Table 4. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 ×10^3) for W(η^3-C_5H_5O)$(CO)_2$(HBpz$_3$) (4)

	x	*y*	*z*	U_{eq}[a]
W	0.14507(1)	0.16597(2)	0.16221(2)	35(1)
C(1)	0.1709(3)	0.2127(5)	0.0086(5)	67(2)
C(2)	0.1740(3)	0.1121(5)	−0.0008(5)	63(2)
C(3)	0.2466(4)	0.0837(7)	0.0001(7)	84(2)
C(4)	0.2829(4)	0.1680(6)	0.0436(6)	79(2)
C(5)	0.2290(3)	0.2404(5)	0.0646(6)	75(2)
O(1A)[b]	0.2665(5)	0.0021(10)	−0.0055(9)	108(5)
O(1B)[b]	0.3401(4)	0.1740(9)	0.0620(10)	108(5)
C(6)	0.1648(3)	0.0280(4)	0.1661(5)	49(2)
O(2)	0.1784(2)	−0.0520(3)	0.1732(4)	72(1)
C(7)	0.2283(3)	0.1718(4)	0.2424(5)	56(2)
O(3)	0.2766(2)	0.1733(4)	0.2937(4)	102(2)
N(1)	−0.0138(2)	0.2026(3)	0.1517(3)	40(1)
N(2)	0.0379(2)	0.1587(3)	0.1017(3)	34(1)
C(8)	0.0094(3)	0.1179(4)	0.0195(4)	45(1)
C(9)	−0.0591(3)	0.1336(4)	0.0174(5)	54(2)
C(10)	−0.0723(3)	0.1875(4)	0.1017(5)	48(2)
N(3)	0.0496(2)	0.3362(3)	0.2354(3)	43(1)
N(4)	0.1140(2)	0.3166(3)	0.2026(3)	38(1)
C(11)	0.1460(3)	0.4018(4)	0.2053(5)	55(2)
C(12)	0.1040(4)	0.4741(4)	0.2336(4)	59(2)
C(13)	0.0440(4)	0.4307(4)	0.2512(5)	53(2)
N(5)	0.0299(2)	0.1826(3)	0.3272(3)	38(1)
N(6)	0.0895(2)	0.1398(3)	0.3039(3)	35(1)
C(14)	0.1042(3)	0.0811(4)	0.3815(4)	45(1)
C(15)	0.0552(3)	0.0864(4)	0.4550(4)	52(2)
C(16)	0.0087(3)	0.1504(4)	0.4190(4)	46(1)
B	−0.0020(3)	0.2539(5)	0.2522(6)	44(2)

[a] See footnote in Table 2. [b] The cyclopentenoyl moiety—C(1)–O(1B)—is disordered with the oxygen atom alternatively attached as O(1A) to C(3) or as O(1B) to C(4). Refined site occupation factors: 0.49(1) for O(1A) and 0.51(1) for O(1B).

$Mo(CO)_3(CH_3CN)_3$[9] and $W(CO)_3(CH_3CN)_3$[9] react with 4-bromo-2-cyclopentenone[10] in acetonitrile to afford the neutral η^3-cyclopentenoyl complexes Mo(η^3-C_5H_5O)$(CO)_2(CH_3CN)_2$Br (**1a**)[3] and W(η^3-C_5H_5O)$(CO)_2(CH_3CN)_2$Br (**2**) in 93 and 56% isolated yields, respectively. The methyl-substituted derivative, Mo(η^3-C_5H_4O-Me)$(CO)_2(CH_3CN)_2$Br (**1b**), was prepared in analogous fashion by utilizing 4-bromo-2-methylcyclopentenone[10] as starting material. **2** has been characterized by ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy, and elemental analysis. The spectroscopic features of **2** are very similar to those of **1a** and will not be discussed here (see Experimental Section). Conversion to complexes Mo(η^3-C_5H_5O)$(CO)_2$(HBpz$_3$) (**3a**), W(η^3-C_5H_5O)$(CO)_2$(HBpz$_3$) (**4**), Mo(η^3-C_5H_5O)$(CO)_2$(bipy)Br (**5**), and Mo(η^3-C_5H_5O)$(CO)_2$(dppm)Br (**7**) was accomplished by treatment of **1** and **2** with stoichiometric amounts of K[HBpz$_3$], bipy, and dppm, respectively, in either CH_3NO_2 or CH_3CN as the solvents in high yields. The synthesis of W(η^3-C_5H_5O)$(CO)_2$(bipy)Br (**6**) and W(η^3-C_5H_5O)$(CO)_2$(dppm)Br (**8**) was more conveniently performed as an one-pot procedure directly from $W(CO)_6$; after the carbonyl is refluxed for 6 days the resulting complex $W(CO)_3(CH_3CN)_3$ is treated with 4-bromo-2-cyclopentenone to form complex **2** in situ. Addition of the appropriate chelating ligand (1 equiv) gave on workup **6** and **8** in 92 and 60% yields. Compounds **3**–**8** are all crystalline solids ranging in color from yellow to orange. They are generally only sparingly soluble in most common organic solvents and are air-stable in the solid state and also for extended periods in solution. **3**–**8** have been fully characterized by a combination of elemental analysis and ^{1}H NMR and IR spectroscopy. Where solubility has permitted (**3** and **4**), $^{13}C\{^1H\}$ NMR spectra have been recorded. The structures of **1a**, **3a**, **4**, and **8** have been determined by X-ray crystallography.

The ^{1}H NMR spectra of **3**–**8** all show the expected resonances for the cyclopentenoyl moiety giving rise to three multiplets and two doublets assigned to the allyl protons and H_{anti} and H_{syn} protons, respectively, and are consistent with the presence of the coligands HBpz$_3$, bipy, and dppm. It is interesting to note, however, that the resonances of the anti protons of all tungsten complexes are shifted down field by about 1.3 ppm with respect to the analogous molybdenum complexes (for comparison, **3** exhibits two apparent doublets centered

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Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $W(\eta^3\text{-}C_5H_5O)(CO)_2(dppm)Br$ (8)

	x	y	z	U_{eq}[a]
W	0.50365(2)	0.16810(2)	0.20410(1)	44(1)
Br	0.62104(6)	−0.03737(5)	0.14253(4)	65(1)
P(1)	0.71075(11)	0.26337(10)	0.11687(8)	41(1)
P(2)	0.70930(11)	0.13556(10)	0.30241(8)	44(1)
C(1)	0.4159(5)	0.2056(6)	0.0614(4)	70(2)
C(2)	0.3311(6)	0.1191(7)	0.1160(5)	83(2)
C(3)	0.2156(7)	0.1976(10)	0.1588(6)	113(3)
C(4)	0.2452(7)	0.3307(9)	0.1401(6)	104(2)
C(5)	0.3853(5)	0.3195(6)	0.1024(4)	73(2)
O(1A)[b]	0.1188(6)	0.1598(7)	0.2027(7)	144(4)
O(1B)[b]	0.1530(25)	0.3595(22)	0.1831(17)	94(9)
C(6)	0.3855(5)	0.0644(5)	0.3002(4)	70(1)
O(2)	0.3153(5)	0.0100(5)	0.3539(4)	106(2)
C(7)	0.4376(5)	0.3003(5)	0.2823(3)	56(1)
O(3)	0.3930(4)	0.3747(4)	0.3286(3)	80(1)
C(8)	0.8269(4)	0.1683(4)	0.1963(3)	45(1)
C(9)	0.7655(4)	0.2470(4)	−0.0115(3)	46(1)
C(10)	0.8572(6)	0.1582(5)	−0.0404(4)	75(2)
C(11)	0.8879(7)	0.1491(6)	−0.1408(5)	94(2)
C(12)	0.8273(7)	0.2279(6)	−0.2093(4)	83(2)
C(13)	0.7370(8)	0.3174(8)	−0.1822(4)	102(2)
C(14)	0.7050(6)	0.3264(6)	−0.0832(4)	84(2)
C(15)	0.7444(4)	0.4208(4)	0.1287(3)	45(1)
C(16)	0.6485(5)	0.5046(4)	0.1646(4)	58(1)
C(17)	0.6793(6)	0.6207(5)	0.1790(5)	76(2)
C(18)	0.8068(6)	0.6534(5)	0.1608(5)	76(2)
C(19)	0.9032(6)	0.5716(5)	0.1252(5)	77(2)
C(20)	0.8737(5)	0.4569(5)	0.1088(4)	60(1)
C(21)	0.7282(5)	0.2476(4)	0.3867(3)	50(1)
C(22)	0.6431(6)	0.2468(6)	0.4698(4)	80(2)
C(23)	0.6495(8)	0.3301(8)	0.5352(5)	104(2)
C(24)	0.7378(9)	0.4174(7)	0.5174(5)	98(2)
C(25)	0.8252(8)	0.4183(6)	0.4361(5)	88(2)
C(26)	0.8195(6)	0.3337(5)	0.3702(4)	69(1)
C(27)	0.7697(5)	−0.0112(4)	0.3683(3)	50(1)
C(28)	0.6877(6)	−0.1027(5)	0.3995(4)	71(2)
C(29)	0.7350(7)	−0.2124(6)	0.4517(5)	88(2)
C(30)	0.8644(7)	−0.2285(6)	0.4726(5)	83(2)
C(31)	0.9501(6)	−0.1393(5)	0.4417(4)	74(2)
C(32)	0.9026(5)	−0.0285(5)	0.3886(4)	61(1)

[a] See footnote in Table 2. [b] The cyclopentenoyl moiety—C(1)–O(1B)—is disordered with the oxygen atom alternatively attached as O(1A) to C(3) or as O(1B) to C(4). Refined site occupation factors: 0.79(1) for O(1A) and 0.21(1) for O(1B).

Table 6. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[W(\eta^4\text{-}C_5H_4O)(CO)_2(HBpz_3)]PF_6$ (10)[a]

	x	y	z	$U_{eq}(U_{iso})$
W	0.39442(1)	0.45307(1)	0.28538(2)	32(1)
O(1)	0.2985(2)	0.4913(2)	0.0438(3)	55(1)
C(1)	0.2989(3)	0.4908(4)	0.1370(5)	45(1)
C(2)	0.2815(3)	0.4285(3)	0.2082(5)	46(1)
C(3)	0.2723(3)	0.4586(4)	0.3061(4)	51(2)
C(4)	0.2997(3)	0.5360(4)	0.3050(4)	50(2)
C(5)	0.3259(3)	0.5511(3)	0.2053(4)	48(1)
N(1)	0.5365(2)	0.5528(3)	0.2539(3)	37(1)
N(2)	0.4667(2)	0.5547(2)	0.2927(3)	36(1)
C(6)	0.4581(3)	0.6264(3)	0.3326(5)	49(2)
C(7)	0.5202(4)	0.6701(4)	0.3175(4)	54(2)
C(8)	0.5682(3)	0.6218(3)	0.2699(4)	50(2)
N(3)	0.5206(2)	0.4470(2)	0.1236(3)	36(1)
N(4)	0.4484(2)	0.4297(2)	0.1391(3)	34(1)
C(9)	0.4272(3)	0.3863(3)	0.0588(4)	37(1)
C(10)	0.4855(3)	0.3762(3)	−0.0062(4)	43(1)
C(11)	0.5430(3)	0.4149(3)	0.0360(4)	41(1)
N(5)	0.5627(2)	0.4153(3)	0.2952(3)	37(1)
N(6)	0.4959(2)	0.3985(2)	0.3377(3)	36(1)
C(12)	0.5078(3)	0.3420(3)	0.4059(4)	44(1)
C(13)	0.5813(3)	0.3226(3)	0.4085(5)	48(2)
C(14)	0.6132(3)	0.3700(3)	0.3378(4)	48(1)
B	0.5682(3)	0.4774(4)	0.2108(5)	42(2)
C(15)	0.3822(3)	0.4619(3)	0.4381(4)	42(1)
O(2)	0.3784(2)	0.4691(3)	0.5229(3)	66(1)
C(16)	0.3715(3)	0.3356(3)	0.2857(4)	37(1)
O(3)	0.3635(2)	0.2707(2)	0.2798(3)	58(1)
P[b]	0.28252(13)	0.23486(12)	0.5390(3)	38(1)
F(1)[b]	0.3650(3)	0.2425(4)	0.4988(5)	89(2)
F(2)[b]	0.2024(3)	0.2280(6)	0.5839(4)	83(2)
F(3)[b]	0.3050(3)	0.1572(4)	0.5968(5)	102(3)
F(4)[b]	0.2622(4)	0.3135(4)	0.4887(7)	141(4)
F(5)[b]	0.2617(3)	0.1871(5)	0.4444(5)	125(4)
F(6)[b]	0.3053(3)	0.2770(4)	0.6418(5)	118(3)
F(1A)[c]	0.3473(7)	0.2093(8)	0.4704(9)	55(5)
F(2A)[c]	0.2073(7)	0.2615(9)	0.5834(11)	87(11)
P(1A)[c]	0.2774(5)	0.2354(5)	0.5271(6)	101(9)
F(3A)[c]	0.3093(8)	0.2039(9)	0.6273(10)	83(7)
F(4A)[c]	0.2454(7)	0.2670(8)	0.4265(9)	58(5)
F(5A)[c]	0.2421(8)	0.1552(7)	0.5058(11)	67(6)
F(6A)[c]	0.3127(8)	0.3157(7)	0.5480(12)	76(7)

[a] See Footnote in Table 2. [b] PF_6 octahedron orientation disordered with refined site occupation factors 0.77(1). [c] PF_6 octahedron orientation disordered with refined site occupation factors 1−0.77(1) = 0.23(1), which were refined isotropically.

at 3.15 and 2.88 ppm whereas **4** shows two apparent doublets at 4.43 and 2.84 ppm). The $^{13}C\{^1H\}$ NMR spectra of **3** and **4** bear no unusual features, with the characteristic resonance of the ketonic "carbonyl" carbon observed at 203.1 and 204.6 ppm, respectively. The cis carbonyl ligands are magnetically inequivalent, giving rise to resonances at 213.0 and 209.9 ppm, and 226.5 and 204.6 ppm, respectively.

The IR spectra of **3**−**8** display the two expected peaks for a cis dicarbonyl structure in the ranges of 1955−1992 cm^{-1} and 1861−1890 cm^{-1}, respectively, together with a peak in the range of 1687−1700 cm^{-1} due to the ketonic carbonyl of the cyclopentenoyl ligand.

Synthesis and Characterization of Molybdenum and Tungsten η^4-Cyclopentadienone Complexes. Treatment of **3**−**8** with Ph_3C^+ (introduced as the PF_6^- salt) in CH_2Cl_2 led to facile hydride abstraction yielding, with the exception of **7**, the cationic cyclopentadienone complexes **9**−**13** in 72−97% isolated yields. Surprisingly, in the case of **7** no cyclopentadienone complex, as shown by ^1H NMR and IR spectroscopy, was obtained. Therefore, no attempt was made to further characterize this compound. Complexes **9**−**13** are air-stable in the solid state but decompose readily in solution. All complexes have been characterized by IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and elemental analyses. Since no tungsten cyclopentadienone complexes are reported in the literature, the structures of **10** and **13** have been determined by X-ray crystallography.

In the IR spectra of **9**−**13**, the stretching frequencies of the ketonic carbonyl group are observed at 1685, 1680, 1688, 1667, and 1671 cm^{-1}, respectively, consistent with other cyclopentadienone complexes[2,3,11] but slightly lower than are the frequencies for the free ligand observed at 1727 and 1724 cm^{-1}.[12] Thus, as expected, coordination leads to a decrease of the C=O bond strength by lowering the π-electron density from this group to the ring and the metal center. In addition, these complexes exhibit two strong absorptions in the carbonyl region (in the range of 2070−2110 and 2028−2052 cm^{-1}, respectively) consistent with a cis disposition of the two carbonyls and compatible with expectations for cationic d^4 complexes. While the molybdenum

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(12) Maier, G.; Franz, L. H.; Harten, H.-G.; Lanz, K.; Reisenbauer, H. P. *Chem. Ber.* **1985**, *118*, 3196.

Table 7. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2 ×10^3) for [W(η^4-C_5H_4O)$(CO)_2$(dppm)Br]PF_6·CH_3CN (13·CH_3CN)

	x	*y*	*z*	U_{eq}[a]
W	0.22855(2)	0.44581(2)	0.40794(2)	40(1)
Br	0.39693(6)	0.40150(5)	0.50328(4)	58(1)
P(1)	0.34454(14)	0.37732(11)	0.31011(10)	42(1)
P(2)	0.20998(15)	0.29726(11)	0.40891(11)	46(1)
C(1)	0.1723(6)	0.5910(5)	0.4428(5)	54(2)
C(2)	0.2914(6)	0.5658(4)	0.4545(5)	60(2)
C(3)	0.3340(6)	0.5487(4)	0.3825(4)	55(2)
C(4)	0.2399(7)	0.5457(4)	0.3259(4)	54(2)
C(5)	0.1422(6)	0.5617(4)	0.3641(4)	52(2)
O(1)	0.1145(5)	0.6234(3)	0.4892(3)	74(2)
C(6)	0.1487(6)	0.4552(5)	0.5100(4)	54(2)
O(2)	0.1078(5)	0.4625(4)	0.5671(3)	76(2)
C(7)	0.0768(6)	0.4233(4)	0.3511(4)	49(2)
O(3)	−0.0107(4)	0.4127(3)	0.3209(3)	63(2)
C(8)	0.3370(6)	0.2828(4)	0.3544(4)	51(2)
C(9)	0.4917(6)	0.4031(4)	0.3019(4)	47(2)
C(10)	0.5810(6)	0.3692(5)	0.3455(4)	54(2)
C(11)	0.6910(6)	0.3961(6)	0.3399(5)	65(2)
C(12)	0.7113(7)	0.4573(5)	0.2925(5)	66(2)
C(13)	0.6222(7)	0.4913(5)	0.2495(5)	70(2)
C(14)	0.5137(7)	0.4636(5)	0.2534(5)	62(2)
C(15)	0.2925(6)	0.3621(4)	0.2093(4)	49(2)
C(16)	0.1974(6)	0.4003(5)	0.1761(4)	57(2)
C(17)	0.1590(8)	0.3841(7)	0.1015(5)	89(3)
C(18)	0.2145(10)	0.3347(8)	0.0574(6)	105(4)
C(19)	0.3109(9)	0.2960(6)	0.0892(5)	88(3)
C(20)	0.3489(8)	0.3115(5)	0.1649(5)	72(2)
C(21)	0.0911(6)	0.2532(4)	0.3539(5)	53(2)
C(22)	−0.0101(7)	0.2437(5)	0.3902(5)	68(2)
C(23)	−0.1039(7)	0.2140(6)	0.3498(7)	88(3)
C(24)	−0.0998(9)	0.1941(6)	0.2748(8)	95(4)
C(25)	−0.0003(11)	0.2035(6)	0.2369(6)	102(4)
C(26)	0.0963(8)	0.2317(5)	0.2766(5)	71(2)
C(27)	0.2271(7)	0.2471(5)	0.5008(4)	61(2)
C(28)	0.1655(8)	0.2670(6)	0.5634(5)	79(3)
C(29)	0.1806(12)	0.2291(8)	0.6333(7)	110(4)
C(30)	0.2569(13)	0.1724(11)	0.6391(9)	149(7)
C(31)	0.3199(13)	0.1495(9)	0.5794(10)	170(7)
C(32)	0.3032(9)	0.1880(7)	0.5086(7)	108(4)
P(3)	0.5543(2)	0.10072(15)	0.33548(14)	67(1)
F(1)	0.5329(7)	0.0195(5)	0.3057(6)	173(4)
F(2)	0.5710(9)	0.1782(5)	0.3707(7)	234(6)
F(3)	0.5861(10)	0.1186(8)	0.2553(5)	263(7)
F(4)	0.5235(8)	0.0792(9)	0.4169(5)	240(7)
F(5)	0.6801(5)	0.0847(5)	0.3606(5)	154(3)
F(6)	0.4290(6)	0.1167(6)	0.3108(6)	206(5)
N[b]	0.1588(24)	0.0548(12)	0.3802(13)	208(12)
C(33)[b]	0.1413(41)	0.0390(18)	0.4424(17)	259(22)
C(34)[b]	0.1383(39)	0.0025(20)	0.5181(19)	399(35)

[a] See footnote in Table 2. [b] Acetonitrile solvent molecule with refined site occupancy of 0.80(2).

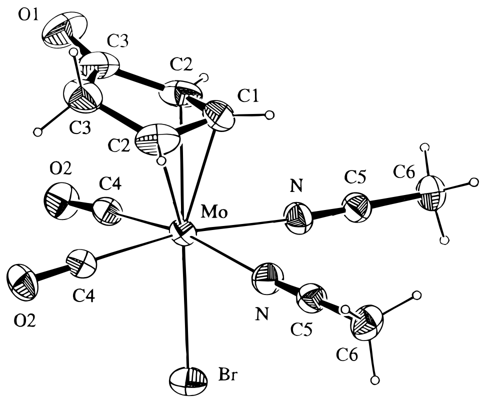


Figure 1. Structural view of Mo(η^3-C_5H_5O)$(CO)_2$(CH_3CN)-Br (**1a**). Selected bond lengths (Å): Mo−Br 2.624 (1), Mo−C(1) 2.170 (5), Mo−C(2) 2.328 (4), Mo−C(4) 1.962 (3), Mo−N 2.229 (3), C(1)−C(2) 1.392 (6), C(2)−C(3) 1.487 (7), C(3)−C(3′) 1.503 (6), C(3)−O(1) 1.213 (8), C(4)−O(2) 1.149 (4).

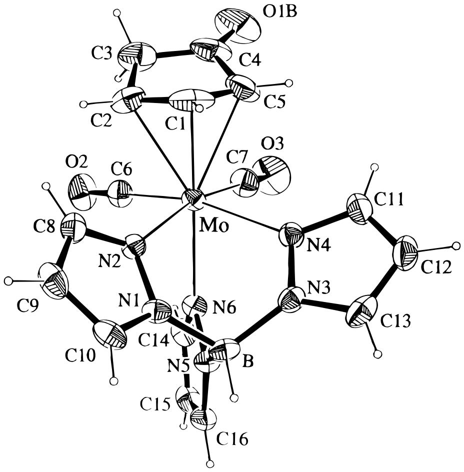


Figure 2. Structural view of Mo(η^3-C_5H_5O)$(CO)_2$($HBpz_3$) (**3a**).

complexes exhibit ν_{CO} frequencies only about 5−20 cm^{-1} higher than those of the corresponding tungsten complexes, more pronounced effects are observed on replacing $HBpz_3$ by C_5H_5. The carbonyl stretching frequencies of **9a** are 33 and 69 cm^{-1} higher than the respective carbonyl absorptions of [Mo(η^5-C_5H_5)(η^4-C_5H_4O)$(CO)_2$]$^+$, implying that the metal center in **9a** has become somewhat less electron-rich.

In the ^{1}H NMR spectra of complexes **9**−**12**, the cyclopentadienone ligand displays an AA′XX′ splitting pattern of two apparent multiplets at about 6.5 (2H) and 4.5 ppm (2H) assignable to the β- and α-protons, respectively. This assignment was afforded by comparing the ^{1}H NMR spectrum of **9a** with that of the 2-methylcyclopentadienone complex **9b** (see Experimental Section). Since complexes **9a**−**12** display mirror symmetry (not in case of the 2-methylcyclopentadienone complex **9b**), one would, therefore, expect to observe equivalent proton resonances for the dienone ligand. For complex **13**, the protons of the cyclopentadienone ligand are magnetically inequivalent, giving rise to four multiplets centered at 5.94 (1H), 5.89 (1H), 4.60 (1H), and 4.53 (1H) ppm, respectively. This is in agreement with the observed asymmetric ligand arrangement as determined by X-ray crystallography (see below). The resonances of the coligands $HBpz_3$, bipy, and dppm are in the expected ranges. The $^{13}C\{^1H\}$ NMR spectra of **9**−**13** contain no surprising features and it is sufficient to point out that the resonances of the ketonic "carbonyl" carbons are observed at 176.0, 174.5, 174.9, 172.5, and 173.8 ppm, respectively (for comparison, in [Mo(η^5-C_5H_5)(η^4-C_5H_4O)$(CO)_2$]$^+$ the resonance of the ketonic "carbonyl" carbon is found at 175.1 ppm[3]).

Crystal Structures of Mo(η^3-C_5H_5O)$(CO)_2$-$(CH_3CN)_2$Br (1a), Mo(η^3-C_5H_5O)$(CO)_2$($HBpz_3$) (3a), W(η^3-C_5H_5O)$(CO)_2$($HBpz_3$) (4), and W(η^3-C_5H_5O)-$(CO)_2$(dppm)Br (8). Structural views of complexes **1a**, **3a**, and **8** are shown in Figures 1, 2, and 3, respectively. Compound **4** is isostructural with **3a** and is not depicted because of its pronounced similarity with the latter both with respect to bond distances and thermal vibrational ellipsoids (on average the W−C/N bond distances are shorter than the corresponding Mo−C/N bond distances by only 0.007 Å). Selected bond lengths of complexes **3a**, **4**, and **8** are given in Table 8. These molecules can

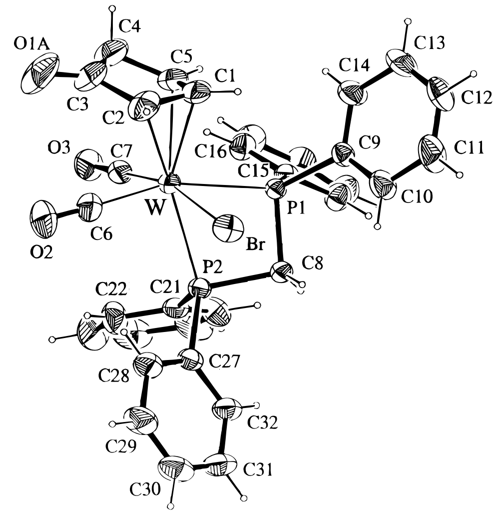
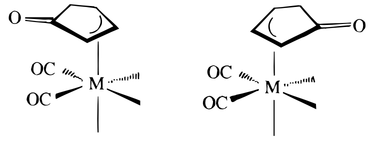


Figure 3. Structural view of W(η^3-C_5H_5O)(CO)$_2$(dppm)Br (**8**).

be described as pseudooctahedral with the assumption that the η^3-cyclopentenoyl moiety occupies one coordination site. An equatorial plane can be defined to include for complex **1a** the two carbonyls (C(4)−O(2)), and the two nitrogen atoms (N(1)), for complexes **3a** and **4** the two carbonyls (C(6)−O(2), C(7)−O(3)) and two of the nitrogen atoms (N(2), N(4) of the HBpz$_3$ ligand and for complex **8** the two carbonyls (C(6)−O(2) and C(7)−O(3)), the halogen (Br), and one of the phosphorus atoms (P(1)) of the dppm ligand. The η^3-cyclopentenoyl ligand and the halogen (Br), the third coordinating nitrogen (N(6)) of HBpz$_3$, and the second phosphorus atom of dppm (P(2)), respectively, lie trans to one another in apical positions above and below the equatorial plane. Moreover, in the solid state complexes **1a**, **3a**, **4**, and **8** are found to adopt exclusively the *exo* conformation (**I**) with respect to the orientation of the allyl moiety. In fact, the same conformation is found for all complexes featuring the M(η^3-allyl)(CO)$_2$ moiety (M = Mo, W) whose structures have been determined and it thus appears to be a general trend.[4,13,14] A rationalization of the rotational preference of the η^3-allyl group based on EHMO calculations has been given in the literature.[14] The cyclopentenoyl moieties of **1a**, **3a**, **4**, and **8** are distinctly bent and can be subdivided by two planes, one defined by C(1), C(2), and C(3) (allyl fragment) and the other defined by C(2), C(3), C(4), and C(5). The angle between this plane is 27.6 (4), 26.3 (3), 28.5 (5), and 26.8 (5)°, respectively. The cyclopentenoyl ligands of **1a**, **3a**, **4**, and **8** exhibit a disorder of the ketonic oxygen atom. For **1a**, **3a**, and **4**, equal site occupancies are observed with the oxygen atom being attached to either one of the C(3) atoms (**1a**) or C(3) and C(4) (**3a**, **4**). For **8**, presumably due to the asymmetry of this complex, a site occupancy of 77% for the oxygen atom attached to C(3) and 23% for the oxygen atom attached to C(4) is observed. The M−CO and C−O distances are both within the range of values reported for other molybdenum and tungsten carbonyl complexes. There are no structural features in complexes **1a**, **3a**, **4**, and **8** that indicate unusual deviations or distortions.



(**I**) exo (**II**) endo

Table 8. Selected Bond Lengths (Å) for the Metal Complexes in 3a, 4, 8, 10, and 13·CH$_3$CN (M = Mo,W)

	3a	**4**	**8**	**10**	**13**·CH$_3$CN
M−C1	2.179(4)	2.173(6)	2.194(5)		
M−C2	2.342(4)	2.330(7)	2.348(5)	2.335(5)	2.352(7)
M−C3				2.246(5)	2.248(7)
M−C4				2.252(5)	2.257(7)
M−C5	2.351(4)	2.333(6)	2.337(5)	2.346(5)	2.372(7)
M−C6	1.956(3)	1.961(6)	2.013(6)	2.032(5)	2.052(8)
M−C7	1.957(3)	1.950(6)	1.951(5)	2.057(6)	2.023(8)
M−N2	2.274(2)	2.261(4)		2.188(4)	
M−N4	2.257(2)	2.248(4)		2.203(4)	
M−N6	2.184(2)	2.184(4)		2.186(4)	
M−P1			2.565(1)		2.538(2)
M−P2			2.553(1)		2.611(2)
M−Br			2.654(1)		2.612(1)
C1−C2	1.397(5)	1.407(9)	1.433(9)	1.457(8)	1.474(10)
C1−C5	1.388(6)	1.413(9)	1.433(8)	1.458(8)	1.471(10)
C2−C3	1.482(5)	1.487(9)	1.513(10)	1.401(8)	1.399(10)
C3−C4	1.493(6)	1.489(10)	1.502(12)	1.417(8)	1.430(10)
C4−C5	1.496(5)	1.492(9)	1.470(9)	1.422(8)	1.390(10)
C1−O1				1.230(7)	1.224(9)
C3−O1A[a]	1.176(7)	1.205(13)	1.185(10)		
C3−O1B[a]	1.147(6)	1.156(10)	1.11(3)		
C6−O2	1.152(3)	1.149(6)	1.131(6)	1.128(6)	1.129(8)
C7−O3	1.144(4)	1.165(7)	1.136(6)	1.124(6)	1.140(8)

[a] The cyclopentenoyl moieties are disordered with the oxygen atoms alternatively bonded to C3 or C4. Site occupation factors for O1A/O1B are 0.53(1)/0.47(1) for **3a**, 0.49(1)/0.51(1) for **4**, and 0.79(1)/0.21(1) for **8**.

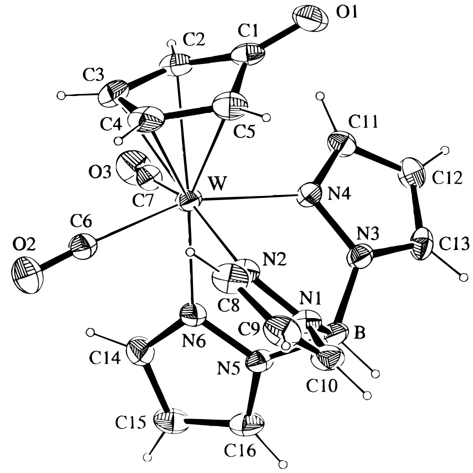


Figure 4. Structural view of [W(η^4-C_5H_4O)(CO)$_2$(HBpz$_3$)]PF$_6$ (**10**) (PF$_6^-$ omitted for clarity).

Crystal Structures of [W(η^4-C_5H_4O)(CO)$_2$(HBpz$_3$)]PF$_6$ (10) and [W(η^4-C_5H_5O)(CO)$_2$(dppm)Br]PF$_6$ (13).

Structural views of complexes **10** and **13** are shown in Figures 4 and 5. While in **10** the dienone moiety is *endo* oriented with respect to the CO ligands, complex **13** adopts the *exo* conformation. Noteworthily, the cyclopentadienone ligand of the structurally related complex [Mo(η^5-C_5H_5)(η^4-C_5H_4O)(CO)$_2$]$^+$ also adopts the *endo* orientation.[3] A main feature comprises the envelope conformation of the cyclopentadienone ring which can be subdivided into two planes, one defined by C(2), C(3),

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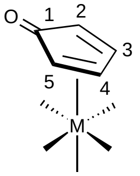
(13) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865, and references therein.

(14) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887, and references therein.

Table 9. Comparison of Bond Distances (Å) and Ring Dihedral Angles (deg) in Some η^4-Cyclopentadienone (C_5H_4O) Complexes



compound	M−C$_{2,5}$	M−C$_{3,4}$	C=C C$_{2,4}$−C$_{3,5}$	C−C C$_3$−C$_4$	C=O	dihedral angle[a]	ref
Fe(η^4-C_5H_4O)(CO)$_3$	2.108	2.072	1.416	1.463	1.137	19.9	11
[Mo(η^4-C_5H_4O)(CO)$_2$(η^5-C_5H_5)]$^+$	2.324	2.288	1.400	1.427	1.212	18.0	3
[W(η^4-C_5H_4O)(CO)$_2$(HBpz$_3$)]$^+$ (**10**)	2.362	2.252	1.394	1.430	1.230	17.7	this work
[W(η^4-C_5H_4O)(CO)$_2$(dppm)Br]$^+$ (**13**)	2.340	2.249	1.411	1.417	1.224	16.4	this work
Ru(η^4-C_5H_4O)(η^5-C_5H_5)Br	2.263	2.165	1.419	1.457	1.216	20.4	15
[Ru(η^4-C_5H_4O)(η^5-C_5H_5)(MeCN)]$^+$	2.264	2.160	1.391	1.431	1.221	18.0	16
[Ru(η^4-C_5H_4O)(η^5-C_5H_5)(AsMe$_3$)]$^+$	2.266	2.161	1.395	1.416	1.210	23.1	17

[a] Angle formed between the planes defined by C_2, C_3, C_4, C_5, and C_1, C_2, C_5, O.

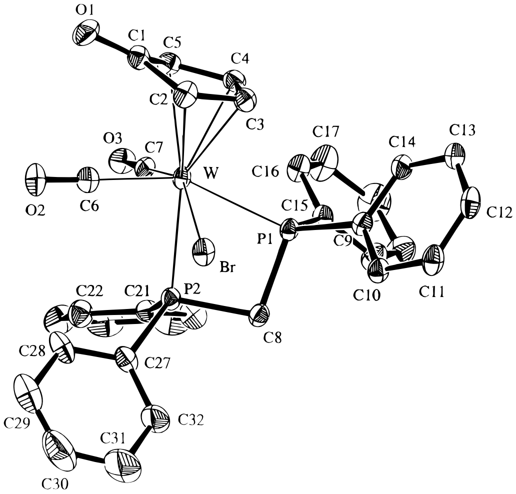


Figure 5. Structural view of [W(η^4-C_5H_4O)(CO)$_2$(dppm)Br]PF$_6$·CH$_3$CN (**13**·CH$_3$CN) (PF$_6^-$ and CH$_3$CN omitted for clarity).

C(4), and C(5) (butadiene fragment), and the other defined by C(1), C(2), O(1), and C(5). The angles between these planes are 17.5 (3) and 16.3 (4)° for **10** and **13**, respectively. The diene C−C bonds in complex **13** adopt a short−long−short pattern (C(2)−C(3) = 1.399 (10) Å, C(4)−C(5) = 1.390 (10) Å vs C(3)−C(4) = 1.430 (10) Å) as is the case for most cyclopentadienone complexes reported thus far.[2,3,15−17] The diene C−C distances in complex **10** do not exhibit this pattern but increase slightly in the order C(2)−C(3), C(3)−C(4), and C(4)−(C5) being 1.401 (8), 1.417 (8), and 1.422 (8) Å, respectively. The standard deviations, however, are comparatively high. The bond distances between W and the butadiene fragment in complexes **10** and **13** for C(3) and C(4) are shorter than for C(2) and C(5) by about 0.1 Å (see Table 8) a feature that is characteristic of η^4-cyclopentadienone complexes in general. The C(1)−O(1) distances of **10** and **13** are 1.230 (7) and 1.224 (9) Å, respectively. Selected bond lengths may be found in Table 8. For comparison, structural data of related cyclopentadienone complexes are given in Table 9.

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Supporting Information Available: Listings of hydrogen atomic coordinates, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **1a**, **3a**, **4**, **8**, **10**, and **13** (50 pages). Ordering information is given on any current masthead page.

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