Molybdenum and Tungsten Cyclopentadienone Complexes. 2. Regio- and Stereospecific Nucleophilic Addition Reactions

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The cationic complexes $[M(\eta^4\text{-}C_5H_4O)(CO)_2(HB(pz)_3)]PF_6$ (**1a**, **2**) and $[M(\eta^4\text{-}C_5H_4O)(CO)_2(bipy)Br]PF_6$ (**3**, **4**) (M = Mo, W) have been shown to react with a wide variety of carbon, nitrogen, phosphorus, and sulfur nucleophiles in a regio- and stereoselective fashion to afford functionalized η^3-cyclopentenoyl complexes in high yields. Single-crystal studies have been carried out for $[Mo(\eta^3\text{-}C_5H_4OPBu_3^n)(CO)_2(HB(pz)_3)]PF_6$ (**5a**) and $[W(\eta^3\text{-}C_5H_4O\text{-}PMe_3)(bipy)(CO)_2]PF_6$ (**8a**). The reaction of $[Mo(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)(CO)_2(HB(pz)_3)]PF_6$ (**1b**) with strong bases like MeLi, $NHEt_2$, or pyridine results in the clean deprotonation of the methyl group to afford $Mo(\eta^3\text{-}C_5H_3OCH_2)(CO)_2(HB(pz)_3)$ (**9b**). This process is reversible, and **9b** is quantitatively converted to **1b** on treatment with strong acids such as CF_3SO_3H or CF_3COOH. **9b** has been characterized by X-ray crystallography. Liberation of cyclopentenone from $Mo(\eta^3\text{-}C_5H_5O)(CO)_2(HB(pz)_3)$ was attempted. Unfortunately, the various methods of demetalation well established for the C_5H_5 analog systems proved to be unsuccessful.

Introduction

The development of new electrophilic transition-metal π-complexes participating in regio- and stereocontrolled bond formations is an attractive goal of organometallic research. With respect to diene functionalization reactions cationic cyclopentadienyl-based molybdenum diene intermediates have been explored in recent years (in one example also with cyclopentadienone as the diene[2]) and found to be very useful.[3] Other metal−ligand sets such as molybdenum tris(pyrazolyl)borate ($HB(pz)_3$), 2,2′-bipyridyl (bipy), or bis(diphenylphosphino)-methane (dppm), respectively, have received little attention.[4] Moreover, only a restricted range of nucleophiles, primarily carbon nucleophiles, have been considered. As part of our current interest in the chemistry of cyclopentadienone, we have undertaken the study of molybdenum and tungsten complexes containing $HB(pz)_3$ and bipy as the spectator ligands.[5] This study is aimed at utilizing such compounds for the regio- and stereoselective synthesis of functionalized η^3-cyclopentenoyl molybdenum and tungsten complexes as synthetic precursors for new cyclopentenones. Here we report the results of nucleophilic additions of a range of carbon, nitrogen, phosphorus, and sulfur nucleophiles to complexes of the types $[M(\eta^4\text{-}C_5H_4O)(CO)_2(HB(pz)_3)]^+$ (**1a**, **2**) and $[M(\eta^4\text{-}C_5H_4O)(CO)_2(bipy)Br]^+$ (**3**, **4**). X-ray structures of representative products are given.

Experimental Section

General Information. Manipulations were performed under an inert atmosphere of purified nitrogen by using standard Schlenk techniques and/or a glovebox at room temperature unless otherwise noted. All chemicals were standard reagent grade and used without further purification. The solvents were purified according to standard procedures.[6] The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^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. IR spectra were recorded on a Mattson RS 2 spectrometer. Microanalyses were done by the Microanalytical Laboratories, University of Vienna. $[M(\eta^4\text{-}C_5H_4O)(CO)_2(HB(pz)_3)]^+$ (**1a**, **2**), $[Mo(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)(CO)_2(HB(pz)_3)]^+$ (**1b**), and $[M(\eta^4\text{-}C_5H_4O)(CO)_2(bipy)Br]^+$ (**3**, **4**) have been synthesized according to the literature.[5] $Mo(\eta^3\text{-}C_5H_5O)(CO)_2(HB(pz)_3)$ for demetalation experiments has been prepared as previously described.[5]

Synthesis. $[Mo(\eta^3\text{-}C_5H_4OPBu_3^n)(CO)_2(HB(pz)_3)]PF_6$ (5a). A solution of **1a** (250 mg, 0.424 mmol), in CH_3CN (5 mL) was treated with PBu_3^n (0.2 mL, 0.807 mmol), and the mixture was stirred for 1 h. On addition of diethyl ether a yellow solid was formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 322 mg (96%). Anal. Calcd for $C_{28}H_{41}BF_6MoN_6O_3P_2$: C, 42.44; H, 5.22; N, 10.61. Found: C, 42.38; H, 5.18; N, 10.76. ^1H NMR (δ, acetone-d_6, 20 °C): 8.70 (d, 1H), 8.06 (d, 1H), 8.01 (d, 1H), 7.87

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(m, 3H), 6.50 (t, 1H), 6.33 (t, 2H), 5.28 (m, 1H), 5.02−4.95 (m, 2H), 3.49 (d, 1H, $^2J_{HP}$ = 12.9 Hz), 2.63 (m, 6H), 1.78 (m, 6H), 1.55 (m, 6H), 0.98 (t, 9H). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 226.1 (CO), 221.7 (CO), 194.5 (C═O), 148.3, 145.2, 143.4, 137.9, 137.7, 136.6, 107.8, 107.1, 107.0, 83.6, 73.3, 66.5, 61.1 (d, $^2J_{CP}$ = 3.1 Hz), 46.7 (d, $^1J_{CP}$ = 30.4 Hz), 24.3, 18.3, 13.5. IR (diffuse reflectance (cm^{-1})): 1994 (s, ν_{CO}), 1927 (s, ν_{CO}), 1685 (s, $\nu_{C=O}$).

[Mo(η^3-$C_5H_4OPCy_3$)$(CO)_2$(HB(pz)$_3$)]PF_6 (5b). This complex was synthesized analogously to **5a** with **1a** (250 mg, 0.424 mmol) and PCy_3 (119 mg, 0.424 mmol) as starting materials. Yield: 303 mg (82%). Anal. Calcd for $C_{34}H_{47}BF_6MoN_6O_3P_2$: C, 46.91; H, 5.44; N, 9.65. Found: C, 47.03; H, 5.40; N, 9.58. ^1H NMR (δ, acetone-d_6, 20 °C): 8.70 (d, 1H), 8.08 (d, 1H), 8.00 (d, 1H), 7.88 (m, 3H), 6.51 (t, 1H), 6.33 (t, 2H), 5.44 (m, 1H), 5.04 (m, 2H), 3.61 (d, 1H, $^2J_{HP}$ = 14.1 Hz), 3.08 (m, 3H), 2.20−1.45 (m, 30H). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 227.0 (CO), 221.3 (CO), 195.4 (C═O), 149.6, 148.3, 143.5, 138.0, 137.7, 136.6, 107.9, 107.1, 107.1, 84.3, 73.3, 66.0, 62.5 (d, $^2J_{CP}$ = 3.1 Hz), 43.2 (d, $^1J_{CP}$ = 23.9 Hz), 31.7, 30.2, 27.8, 27.4, 26.9, 26.0. IR (diffuse reflectance (cm^{-1})): 1992 (s, ν_{CO}), 1926 (s, ν_{CO}), 1683 (s, $\nu_{C=O}$).

[Mo(η^3-$C_5H_4OPPh_3$)$(CO)_2$(HB(pz)$_3$)]PF_6 (5c). This complex was synthesized analogously to **5a** with **1a** (310 mg, 0.525 mmol) and PPh_3 (140 mg, 0.534 mmol) as starting materials. Yield: 413 mg (92%). Anal. Calcd for $C_{34}H_{29}BF_6MoN_6O_3P_2$: C, 47.91; H, 3.43; N, 9.86. Found: C, 47.40; H, 3.43; N, 9.76. ^1H NMR (δ, acetone-d_6, 20 °C): 8.73 (d, 1H), 8.15−7.83 (m, 20H, HB(pz)$_3$/PPh_3), 6.50 (t, 1H), 6.26 (t, 1H), 6.23 (t, 1H), 5.01 (d, 1H, $^2J_{HP}$ = 12.0 Hz), 4.85 (m, 2H), 4.55 (m, 1H). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 226.0 (CO), 221.3 (CO), 192.4 (C═O), 149.3, 145.2, 143.2, 138.0, 137.3, 136.7, 136.2, 135.6, 131.1, 118.6, 107.9, 107.0, 107.0, 83.7, 73.1, 60.8, 49.2 (d, $^1J_{CP}$ = 29.9 Hz). IR (diffuse reflectance (cm^{-1})): 1980 (s, ν_{CO}), 1916 (s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

Mo(η^3-C_5H_4OCN)$(CO)_2$(HB(pz)$_3$) (5d). A solution of **1a** (260 mg, 0.441 mmol) in CH_3CN (5 mL) was treated with KCN (65 mg, 1.00 mmol), and the mixture was stirred for 2 h. Insoluble materials were removed by filtration, and the crude product was purified via flash chromatography (silica gel/CH_2Cl_2 as eluent). The volume of the solution was reduced to about 2 mL, and diethyl ether was added. The resulting precipitate was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 200 mg (96%). Anal. Calcd for $C_{17}H_{14}BMoN_7O_3$: C, 43.34; H, 3.00; N, 20.81. Found: C, 43.51; H, 2.98; N, 20.72. ^1H NMR (δ, acetone-d_6, 20 °C): 8.68 (d, 1H), 8.10 (d, 1H), 8.07 (d, 1H), 7.87 (m, 3H), 7.48 (t, 1H), 6.66 (t, 1H), 6.32 (t, 1H), 5.00 (m, 1H), 4.94 (m, 1H), 4.79 (m, 1H), 3.25 (s, 1H). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 224.9 (CO), 221.6 (CO), 192.1 (C═O), 148.2, 145.0, 143.3, 137.8, 137.6, 136.4, 120.0 (CN), 107.7, 106.9, 106.7, 81.2, 70.8, 64.9, 42.5. IR (diffuse reflectance (cm^{-1})): 2232 (m, ν_{CN}), 1992 (s, ν_{CO}), 1891 (s, ν_{CO}), 1687 (s, $\nu_{C=O}$).

Mo(η^3-C_5H_4OMe)$(CO)_2$(HB(pz)$_3$) (5e). **1a** (217 mg, 0.368 mmol) in 5 mL of dry tetrahydofuran was treated at −40 °C with 0.13 mL (0.390 mmol) of MeMgBr (3.0 M in diethyl ether). The mixture was stirred for 1 h without further cooling. The reaction mixture was evaporated to dryness, and the residue was purified by flash chromatography (neutral Al_2O_3/CH_2Cl_2 as eluent). The volume of the solvent was reduced to about 2 mL, and diethyl ether was added. The resulting precipitate was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 95 mg (56%). Anal. Calcd for $C_{17}H_{17}BMoN_6O_3$: C, 44.38; H, 3.72; N, 18.27. Found: C, 44.21; H, 3.66; N, 18.09. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.53 (d, 1H), 7.69 (d, 1H), 7.63−7.61 (m, 3H), 7.54 (d, 1H), 6.30 (t, 1H), 6.22 (t, 1H), 6.19 (t, 1H), 4.78 (m, 1H), 4.37 (m, 2H), 2.44 (q, 1H), 1.21 (d, 3H, Me). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 226.4 (CO), 222.2 (CO), 205.5 (C═O), 147.9, 144.0, 141.5, 136.8, 136.6, 135.3, 106.9, 106.3, 106.3, 82.6, 72.8, 71.6, 48.5, 23.4 (Me). IR (diffuse reflectance (cm^{-1})): 1974 (s, ν_{CO}), 1889 (s, ν_{CO}), 1687 (s, $\nu_{C=O}$).

Mo(η^3-C_5H_4OSPh)$(CO)_2$(HB(pz)$_3$) (5f). A solution of **1a** (245 mg, 0.415 mmol) in tetrahydrofuran (5 mL) was treated at −20 °C with LiSPh (245 mg, 0.415 mmol), and the mixture was stirred for 1 h without further cooling. The solution was evaporated to dryness and dissolved in 2 mL of CH_2Cl_2. Insoluble materials were removed by filtration, and on addition of *n*-hexane a yellow precipiate was formed, which was collected on a glass frit, washed with *n*-hexane, and dried under vacuum. Yield: 200 mg (87%). Anal. Calcd for $C_{22}H_{19}BMoN_6O_3S$: C, 47.68; H, 3.46; N, 15.16. Found: C, 47.82; H, 3.54; N, 15.01. ^1H NMR (δ, acetone-d_6, 20 °C): 8.64 (d, 1H), 8.02 (d, 1H), 7.98 (d, 1H), 7.82 (m, 3H), 7.59 (m, 2H, Ph), 7.40−7.30 (m, 3H, Ph), 6.46 (t, 1H), 6.31 (t, 1H), 6.28 (t, 1H), 4.85 (m, 1H), 4.62 (m, 1H), 4.51 (m, 1H), 3.62 (s, 1H). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 226.0 (CO), 222.5 (CO), 196.9 (C═O), 148.2, 144.8, 143.3, 137.6, 137.5, 136.3, 135.0, 133.5, 129.8, 128.2, 107.6, 106.9, 106.8, 81.8, 70.9, 69.3, 57.9. IR (diffuse reflectance (cm^{-1})): 1978 (s, ν_{CO}), 1880 (s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

Mo(η^3-$C_5H_4ONHPr^i$)$(CO)_2$(HB(pz)$_3$) (5g). To a solution of **1a** (350 mg, 0.593 mmol) in CH_3CN (5 mL) was added isopropylamine (500 mg, 9.940 mmol), and the mixture was stirred for 1 h, whereupon a yellow precipitate was formed which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 282 mg (95%). Anal. Calcd for $C_{19}H_{22}BMoN_7O_3$: C, 45.35; H, 4.41; N, 19.49. Found: C, 45.56; H, 4.55; N, 19.52. ^1H NMR (δ, $CDCl_3$, 20 °C): 8.49 (d, 1H), 7.70 (d, 1H), 7.66 (d, 1H), 7.60 (d, 2H), 7.53 (d, 1H), 6.43 (t, 1H), 6.38 (t, 1H), 6.27 (t, 1H), 4.74 (m, 1H), 4.46 (m, 1H), 4.40 (m, 1H), 3.25 (m, 1H, NC*H*(Me)$_2$), 3.14 (s, 1H), 1.14 (d, 3H, diastereotopic CH_3), 1.09 (d, 3H, diastereotopic CH_3). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 225.2 (CO), 221.7 (CO), 202.0 (C═O), 147.8, 144.2, 141.9, 137.0, 136.8, 135.5, 107.1, 106.6, 106.5, 82.4, 72.0, 70.0, 64.5 (CH_2), 48.4, 24.1 (Me), 23.7 (Me). IR (diffuse reflectance (cm^{-1})): 1971 (s, ν_{CO}), 1885 (s, ν_{CO}), 1687 (s, $\nu_{C=O}$).

Mo(η^3-$C_5H_4ONEt_2$)$(CO)_2$(HB(pz)$_3$) (5h). This complex was synthesized analogously to **5g** with **1a** (315 mg, 0.534 mmol) and diethylamine (500 mg, 6.836 mmol). Yield: 230 mg (83%). Anal. Calcd for $C_{20}H_{24}BMoN_7O_3$: C, 46.45; H, 4.68; N, 18.96. Found: C, 46.72; H, 4.54; N, 18.73. ^1H NMR (δ, acetone-d_6, 20 °C): 8.61 (d, 1H), 8.03 (d, 1H), 8.00 (d, 1H), 7.85−7.83 (m, 3H), 6.46 (t, 1H), 6.31 (t, 1H), 6.28 (t, 1H), 4.88 (m, 1H), 4.65 (m, 1H), 4.49 (m, 1H), 3.19 (s, 1H), 2.91−2.63 (m, 4H, N(CH_2Me)$_2$), 1.05 (t, 6H, Me). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 226.6 (CO), 221.3 (CO), 203.0 (C═O), 148.0, 144.7, 143.1, 137.6, 137.3, 136.2, 107.5, 106.8, 106.7, 83.8, 72.5, 69.6, 69.3 (NCH_2), 44.6, 14.2 (Me). IR (diffuse reflectance (cm^{-1})): 1980 (s, ν_{CO}), 1894(s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

[Mo(η^3-$C_5H_4ONC_5H_5$)$(CO)_2$(HB(pz)$_3$)]PF_6 (5i). This complex was synthesized analogously to **5a** using **1a** (209 mg, 0.354 mmol) and pyridine (37 mg, 0.468 mmol) as starting materials. Yield: 214 mg (90%). Anal. Calcd for $C_{21}H_{19}BF_6MoN_7O_3P$: C, 37.69; H, 2.86; N, 14.65. Found: C, 37.56; H, 2.89; N, 14.84. ^1H NMR (δ, acetonitrile-d_3, 20 °C): 8.99 (d, 2H, py), 8.65 (d, 1H, HB(pz)$_3$), 8.55 (t, 1H, py), 8.08 (t, 2H, py), 7.88−7.78 (m, 5H), 6.45 (t, 1H), 6.35 (t, 1H), 6.30 (t, 1H), 5.10 (m, 1H), 5.04 (s, 1H), 4.96 (m, 1H), 4.90 (m, 1H). $^{13}C\{^1H\}$ NMR (δ, acetonitrile-d_3, 20 °C): 223.2 (CO), 220.8 (CO), 201.4 (C═O), 148.3, 147.5, 145.3, 143.7, 143.0, 138.4, 138.3, 137.1, 129.1, 108.0, 107.3, 107.2, 82.3, 76.6, 70.4, 62.6. IR (diffuse reflectance (cm^{-1})): 1978 (s, ν_{CO}), 1903 (s, ν_{CO}), 1662 (s, $\nu_{C=O}$).

Mo(η^3-C_5H_4O(2-NH-C_5H_4N))$(CO)_2$(HB(pz)$_3$) (5j) and [Mo(η^3-C_5H_4O-5-(NC_5H_4-2-NH_2))$(CO)_2$(HB(pz)$_3$)]PF_6 (5k). Following the protocol above, treatment of **1a** (350 mg, 0.593 mmol) in acetonitrile (5 mL) with 2-aminopyridine (165 mg, 1.752 mmol) led to a mixture of **5j**,**k** in a ratio of about 1:1. Purification by flash chromatography (basic Al_2O_3/acetonitrile as eluent) afforded a pure sample of **5j**. **5k** could not be isolated in pure form. Yield: 140 mg (44%). Anal. Calcd for $C_{21}H_{19}BMoN_8O_3$: C, 46.87; H, 3.56; N, 20.82. Found: C, 46.76;

H, 3.67; N, 20.57. ^{1}H NMR (δ, acetonitrile-d_3, 20 °C): 8.60 (d, 1H), 7.91−7.74 (m, 5H, HB(pz)$_3$/2H, py), 7.20 (bs, 1H, NH), 6.96 (t, 1H, py), 6.87 (t, 1H, py), 6.43 (t, 1H), 6.38 (t, 1H), 6.27 (t, 1H), 4.80 (m, 1H), 4.67 (m, 2H), 4.15 (s, 1H). ^{13}C{^{1}H} NMR (δ, acetonitrile-d_3, 20 °C): 224.5 (CO), 222.1 (CO), 198.7 (C═O), 154.5, 148.3, 147.2, 145.2, 143.4, 138.7, 138.2, 137.1, 136.9, 114.9, 114.5, 107.9, 107.3, 107.1, 82.3, 70.1, 66.3, 61.5. IR (diffuse reflectance (cm^{-1})): 1974 (s, ν_{CO}), 1891 (s, ν_{CO}), 1672 (s, $\nu_{C=O}$). ^{1}H NMR for **5k** (δ, acetonitrile-d_3, 20 °C): 9.02 (d, 1H), 8.56 (d, 1H), 7.96−7.64 (m, 7H), 7.20 (t, 1H), 6.45−6.26 (m, 3H), 5.02 (s, 1H), 4.73−4.65 (m, 2H), 4.15 (m, 1H).

Attempted Reaction of 1a with Alkoxides. Following the protocol above, treatment of **1a** (350 mg, 0.593 mmol) in tetrahydrofuran (5 mL) with either NaOEt or LiOPh (1.1 equiv) for 2 h did not yield η^3-cyclopentenoyl complexes but afforded only intractable materials.

[W(η^3-C$_5$H$_4$OPBu$^n_3$)(CO)$_2$(HB(pz)$_3$)]PF$_6$ (6a). This complex was synthesized analogously to **5a** with **2** (260 mg, 0.384 mmol) and PBu$^n_3$ (0.3 mL, 1.210 mmol) as starting materials. Yield: 301 mg (89%). Anal. Calcd for $C_{28}H_{41}BF_6N_6O_3P_2W$: C, 38.21; H, 4.69; N, 9.55. Found: C, 38.46; H, 4.57; N, 9.98. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.73 (d, 1H), 8.14 (d, 2H), 8.10 (d, 2H), 7.92 (d, 1H), 6.50 (t, 1H), 6.36 (t, 1H), 4.77 (m, 1H), 4.68 (m, 1H), 4.43 (m, 1H), 4.00 (d, 1H, $^2J_{HP}$ = 12.1 Hz, H^4), 2.61 (m, 6H), 1.75 (m, 6H), 1.55 (m, 6H), 0.96 (t, 9H). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 218.8 (CO), 214.8 (CO), 195.6 (C═O), 149.5, 146.0, 143.9, 138.2, 137.9, 137.0, 108.5, 107.6, 107.5, 74.2, 66.1, 52.0, 47.4 (d, $^1J_{CP}$ = 30.3 Hz), 24.5 , 24.1, 13.4, 13.5. IR (diffuse reflectance (cm^{-1})): 1992 (s, ν_{CO}), 1912 (s, ν_{CO}), 1685 (s, $\nu_{C=O}$).

[W(η^3-C$_5$H$_4$OPPh$_3$)(CO)$_2$(HB(pz)$_3$)]PF$_6$ (6b). This complex was synthesized analogously to **5a** with **2** (240 mg, 0.354 mmol) and PPh$_3$ (200 mg, 0.763 mmol) as starting materials**.** Yield: 291 mg (87%). Anal. Calcd for $C_{34}H_{29}BF_6N_6O_3P_2W$: C, 43.43; H, 3.11; N, 8.94. Found: C, 43.14; H, 2.98; N, 8.75. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.76 (d, 1H), 8.14−7.75 (m, 20H, HB(pz)$_3$/Ph), 6.52 (t, 1H), 6.30 (t, 1H), 6.27 (t, 1H), 5.42 (d, 1H, $^2J_{HP}$ = 11.0 Hz), 4.55 (m, 1H), 4.38 (m, 1H), 3.01 (m, 1H). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 218.7 (CO), 214.4 (CO), 193.5 (C═O), 149.4, 146.0, 143.6, 138.2, 138.0, 137.1, 136.1, 135.6, 131.5, 118.6, 108.6, 107.6, 107.4, 74.3, 65.8, 51.6, 50.4 ($^1J_{CP}$ = 28.8 Hz). IR (diffuse reflectance (cm^{-1})): 1977 (s, ν_{CO}), 1911 (s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

W(η^3-C$_5$H$_4$OCN)(CO)$_2$(HB(pz)$_3$) (6c). This complex was synthesized analogously to **5d** with **2** (376 mg, 0.555 mmol) and KCN (170 mg, 2.571 mmol) as starting materials**.** Yield: 290 mg (94%). Anal. Calcd for $C_{17}H_{14}BN_7O_3W$: C, 36.53; H, 2.52; N, 17.54. Found: C, 36.51; H, 2.49; N, 17.60. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.52 (d, 1H), 7.76 (d, 1H), 7.68−7.66 (m. 3H), 7.60 (d, 1H), 6.35 (t, 1H), 6.30 (t, 1H), 6.27 (t, 1H), 4.37 (m, 1H), 4.18 (m, 1H), 3.97 (m, 1H), 3.74 (s, 1H). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20 °C): 216.7 (CO), 213.1 (CO), 193.1 (C═O), 149.1, 145.0, 142.4, 137.5, 137.3, 136.1, 123.8 (CN), 108.1, 107.4, 107.3, 71.7, 64.1, 54.9, 43.8. IR (diffuse reflectance (cm^{-1})): 2230 (m, ν_{CN}), 1968 (s, ν_{CO}), 1872 (s, ν_{CO}), 1686 (s, $\nu_{C=O}$).

W(η^3-C$_5$H$_4$ONEt$_2$)(CO)$_2$(HB(pz)$_3$) (6d). This complex was synthesized analogously to **5g** with **2** (240 mg, 0.354 mmol) and HNEt$_2$ (500 mg, 6.836 mmol) as the nucleophile**.** Yield: 195 mg (91%). Anal. Calcd for $C_{20}H_{24}BN_7O_3W$: C, 39.70; H, 4.00; N, 16.20. Found: C, 39.86; H, 3.95; N, 16.01. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.64 (d, 1H), 8.10 (d, 1H), 8.07 (d, 1H), 7.89−7.88 (m, 3H), 6.47 (t, 1H), 6.35 (t, 1H), 6.33 (t, 1H), 4.32−4.28 (m, 2H), 4.09 (m, 1H), 3.63 (s, 1H), 2.84−2.65 (m, 4H, Et), 1.08 (t, 6H, Et). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20 °C): 219.0 (CO), 216.1 (CO), 203.4 (C═O), 149.2, 145.4, 143.4, 137.8, 137.6, 136.6, 108.2, 107.2, 74.8, 70.5, 65.2, 61.0 (CH_2CH_3), 44.7, 14.3 (CH_2CH_3). IR (diffuse reflectance (cm^{-1})): 1956 (s, ν_{CO}), 1864 (s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

[Mo(η^3-C$_5$H$_4$OPMe$_3$)(bipy)(CO)$_2$Br]PF$_6$ (7a). To a suspension of **3** (250 mg, 0.408 mmol) in acetonitrile (5 mL) was added PMe$_3$ (200 mg, 2.817 mmol), and the reaction mixture was stirred for 3 h. Insoluble materials were removed by filtration, and the volume of the solution was reduced to about 2 mL. On addition of diethyl ether a red precipitate was slowly formed, which was collected on a glass frit, washed with diethyl ether, and dried under vacuum. Yield: 267.1 mg (95%). Anal. Calcd for $C_{20}H_{21}BrF_6MoN_2O_3P_2$: C, 34.86; H, 3.07; N, 4.06. Found: C, 34.98; H, 2.98; N, 3.94. ^{1}H NMR (δ, CD_3CN, 20 °C): 8.68 (d, 2H), 8.42 (d, 2H), 8.18 (t, 2H), 7.59 (t, 2H), 4.54 (m, 1H), 4.16 (m, 2H), 3.33 (d, 1H, $^2J_{HP}$ = 10.7 Hz), 1.77 (d, 9H, $^2J_{HP}$ = 14.2 Hz). ^{13}C{^{1}H} NMR (δ, CD_3CN, 20 °C): 223.5 (CO), 221.0 (CO), 193.7 (C═O), 154.5, 153.4, 153.2, 141.1, 127.7, 124.7, 81.9, 55.2 (d, $^1J_{CP}$ = 5.9 Hz), 50.5, 49.9, 7.3 (d, $^1J_{CP}$ = 51.9 Hz). IR (diffuse reflectance (cm^{-1})): 1990 (s, ν_{CO}), 1920 (s, ν_{CO}), 1685 (s, $\nu_{C=O}$).

[Mo(η^3-C$_5$H$_4$OPCy$_3$)(bipy)(CO)$_2$Br]PF$_6$ (7b). This complex was synthesized analogously to **7a** with **3** (260 mg, 0.424 mmol) and 123.4 mg (0.440 mmol) of PCy$_3$ as the starting materials**.** Yield: 356.1 mg (94%). Anal. Calcd for $C_{35}H_{45}BrF_6MoN_2O_3P_2$: C, 47.05; H, 3.14; N, 5.08. Found: C, 46.97; H, 3.13; N, 5.08. ^{1}H NMR (δ, CD_2Cl_2, 20 °C): 8.56 (d, 2H), 8.22 (d, 2H), 8.13 (t, 2H), 7.55 (t, 2H), 4.56 (m, 1H), 4.10 (m, 2H), 3.43 (d, $^2J_{HP}$ = 11.6 Hz), 2.65 (m, 3H), 2.00−1.24 (m, 30H). IR (diffuse reflectance (cm^{-1})): 1992 (s, ν_{CO}), 1910 (s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

[Mo(η^3-C$_5$H$_4$OPPh$_3$)(bipy)(CO)$_2$Br]PF$_6$ (7c). This complex was synthesized analogously to **7a** with **3** (260 mg, 0.424 mmol) and 111 mg (0.424 mmol) of PPh$_3$ as the starting materials**.** Yield: 148.5 mg (40%). Anal. Calcd for $C_{35}H_{27}BrF_6MoN_2O_3P_2$: C, 28.71; H, 2.81; N, 3.72. Found: C, 28.75; H, 2.94; N, 3.63. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 8.66 (d, 2H), 8.44 (d, 2H), 8.17 (t, 2H), 7.90−7.65 (m, 15H, Ph), 7.53 (t, 2H), 4.69 (d, $^2J_{HP}$ = 11.2 Hz, 1H), 4.33 (m, 1H), 4.24 (m, 1H), 3.19 (m, 1H). IR (diffuse reflectance (cm^{-1})): 1980 (s, ν_{CO}), 1905 (s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

[W(η^3-C$_5$H$_4$OPMe$_3$)(bipy)(CO)$_2$Br]PF$_6$ (8a). This complex was synthesized analogously to **7a** with **4** (240 mg, 0.342 mmol) and PMe$_3$ (200 mg, 2.817 mmol) as starting materials. Yield: 255.1 mg (96%) Anal. Calcd for $C_{20}H_{21}BrF_6N_2O_3P_2W$: C, 30.91; H, 2.72; N, 3.60. Found: C, 31.00; H, 2.75; N, 3.54. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 8.87 (d, 2H), 8.57 (d, 2H), 8.31 (t, 2H), 7.69 (t, 2H), 4.12 (m, 1H), 3.91 (m, 2H), 3.80 (m, 1H), 1.91 (d, 9H, $^2J_{HP}$ = 14.0 Hz). IR (diffuse reflectance (cm^{-1})): 1991 (s, ν_{CO}), 1902 (s, ν_{CO}), 1686 (s, $\nu_{C=O}$).

[W(η^3-C$_5$H$_4$OPCy$_3$)(bipy)(CO)$_2$Br]PF$_6$ (8b). This complex was synthesized analogously to **7a** with **4** (285 mg, 0.407 mmol) and PCy$_3$ (120.3 mg, 0.429 mmol) as starting materials. Yield: 366.3 mg (94%). Anal. Calcd for $C_{35}H_{45}BrF_6N_2O_3P_2W$: C, 42.83; H, 4.62; N, 2.85. Found: C, 42.76; H, 4.66; N, 2.93. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 8.85 (d, 2H), 8.57 (d, 2H), 8.31 (t, 2H), 7.68 (t, 2H), 4.33 (m, 1H), 4.22 (m, 1H), 3.96 (m, 1H), 3.90 (d, $^2J_{HP}$ = 11.6 Hz), 2.75 (m, 3H), 2.09−1.32 (m, 30H). IR (diffuse reflectance (cm^{-1})): 1990 (s, ν_{CO}), 1899 (s, ν_{CO}), 1680 (s, $\nu_{C=O}$).

W(η^3-C$_5$H$_4$OSMe)(bipy)(CO)$_2$Br (8c). This complex was synthesized in similar fashion to **7a** with **4** (300 mg, 0.428 mmol) and LiSMe (23.2 mg, 0.429 mmol) used as starting materials**.** The crude product was purified via flash chromatography (neutral Al_2O_3/acetonitrile as eluent). Yield: 143.8 mg (58%). Anal. Calcd for $C_{18}H_{15}BrN_2O_3SW$: C, 35.85; H, 2.51; N, 4.84. Found: C, 35.74; H, 2.56; N, 4.68. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 8.86 (d, 2H), 8.52 (d, 2H), 8.27 (t, 2H), 7.67 (t, 2H), 3.88 (m, 1H), 3.78 (m, 1H), 3.70 (m, 1H), 3.58 (s, 1H), 2.14 (s, 3H). IR (diffuse reflectance (cm^{-1})): 1978 (s, ν_{CO}), 1879 (s, ν_{CO}), 1683 (s, $\nu_{C=O}$).

W(η^3-C$_5$H$_4$OSPh)(bipy)(CO)$_2$Br (8d). This complex was synthesized analogously to **7a** with **4** (295 mg, 0.421 mmol) and LiSPh (49.1 mg, 0.423 mmol) as starting materials**.** Yield: 170.1 mg (63%). Anal. Calcd for $C_{23}H_{17}BrN_2O_3SW$: C, 41.53; H, 2.58; N, 4.21. Found: C, 41.56; H, 2.70; N, 4.54. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 8.82 (d, 2H), 8.50 (d, 2H), 8.25 (t, 2H), 7.64 (t, 2H), 7.45 (m, 2H), 7.26 (m, 3H), 4.21 (m, 1H), 3.93 (m, 1H), 3.80 (m, 2H). IR (diffuse reflectance (cm^{-1})): 1976 (s, ν_{CO}), 1876 (s, ν_{CO}), 1684 (s, $\nu_{C=O}$).

W(η^3-$C_5H_4OCH(COOEt)_2$)(bipy)$(CO)_2Br$ (8e). This complex was synthesized analogously to **7a** with **4** (310 mg, 0.442 mmol) and $LiCH(COOEt)_2$ (74.1 mg, 0.446 mmol) as starting materials in tetrahydrofuran as the solvent. Yield: 183.3 mg (60%). Anal. Calcd for $C_{24}H_{23}BrN_2O_7W$: C, 40.31; H, 3.24; N, 3.92. Found: C, 40.11; H, 3.31; N, 4.05. ^{1}H NMR (δ, CD_3NO_2, 20 °C): 8.85 (d, 2H), 8.52 (d, 2H), 8.26 (t, 2H), 7.66 (t, 2H), 4.12 (two overlapping quartets, diastereotopic CH_2, 4H), 3.88 (m, 2H), 3.49 (m, 2H), 3.32 (d, 1H, $^3J_{HH}$ = 6.7 Hz, C*H*$(COOEt)_2$), 1.21 (two overlapping triplets, diastereotopic CH_3, 6H). IR (diffuse reflectance (cm^{-1})): 1979 (s, ν_{CO}), 1889 (s, ν_{CO}), 1713 (s, ν_{COOH}), 1701(s, ν_{COOH}), 1690 (s, $\nu_{C=O}$).

[W(η^3-$C_5H_4OPPh_2CH_2CH_2NMe_2$)(bipy)$(CO)_2Br$]$PF_6$ (8f). This complex was synthesized analogously to **7a** with **4** (300 mg, 0.428 mmol) and *N*,*N*-dimethyl-2-(diphenylphosphino)-ethanamine (185 mg, 1.000 mmol) as starting materials and acetonitrile as the solvent (0.5 mL). Yield: 319.9 mg (80%). Anal. Calcd for $C_{33}H_{32}BrF_6N_3O_3P_2W$: C, 41.36; H, 3.37; N, 4.38. Found: C, 41.41; H, 3.50; N, 4.36. ^{1}H NMR (δ, CD_3NO2, 20 °C): 8.78 (d, 2H), 8.46 (d, 2H), 8.21 (t, 2H), 7.89−7.55 (m, 10H, Ph/2H bipy), 5.28 (d, 1H, $^2J_{HP}$ = 12.5 Hz), 3.97 (m, 1H), 3.67 (m, 1H), 3.43 (m, 1H), 3.24 (m, 1H), 3.02 (m, 1H), 2.60−2.32 (m, 2H), 2.15 (s, 6H). IR (diffuse reflectance (cm^{-1})): 1971 (s, ν_{CO}), 1900 (s, ν_{CO}), 1679 (s, $\nu_{C=O}$).

[Mo(η^3-C_5H_3O-2-Me-5-$PPh_2CH_2CH_2NMe_2$)$(CO)_2(HB(pz)_3)$]-PF_6 (9a). This complex was synthesized analogously to **5a** using **1b** (300 mg, 0.497 mmol) and *N*,*N*-dimethyl-2-(diphenylphosphino)ethanamine (185 mg, 1.000 mmol) as starting materials. Yield: 356 mg (91%). Anal. Calcd for $C_{33}H_{36}BF_6MoN_7O_3P_2$: C, 42.60; H, 4.60; N, 10.54. Found: C, 42.67; H, 4.63; N, 10.48. ^{1}H NMR (δ, acetone-d_6, 20 °C): 8.63 (d, 1H), 8.13−7.79 (m, 15H, $HB(pz)_3$/Ph), 6.44 (t, 1H), 6.28 (t, 2H), 4.86−4.78 (m, 3H), 3.76−3.28 (m, 2H, CH_2), 2.97 (d, 1H, $^2J_{HP}$ = 11.0 Hz), 2.74−2.49 (m, 2H, CH_2), 2.17 (s, 3H, NMe), 2.08 (s, 3H, NMe), 1.45 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (δ, acetone-d_6, 20 °C): 232.3 (CO), 222.1 (CO), 192.2 (C=O), 148.5, 147.8, 143.5, 139.5, 138.2, 137.0, 136.6, 135.9, 132.2−130.7, 118.9, 117.6, 108.1, 107.9, 107.5, 92.2, 73.3, 73.2, 54.1 ($^1J_{CP}$ = 26.8 Hz), 45.8 (N*Me*$_2$), 44.5 (N*C*H_2), 22.8 (P*C*H_2), 14.9 (Me). IR (diffuse reflectance (cm^{-1})): 1969 (s, ν_{CO}), 1902 (s, ν_{CO}), 1674 (s, $\nu_{C=O}$).

Mo(η^3-$C_5H_3OCH_2$)$(CO)_2(HB(pz)_3)$ (9b). Method 1. A 300 mg amount of **1b** (0.497 mmol) dissolved in 5 mL of CH_3CN was treated with a 5-fold excess of either pyridine, NEt_3, or $HNEt_2$, and the mixture was stirred for 2 h. The solvent was removed under vacuum, and the air-stable residue was purified via flash chromatography (silica gel/CH_2Cl_2 as eluent). The volume of the solvent was reduced to about 2 mL and *n*-hexane was added whereupon a precipitate was formed, which was collected on a glass frit, washed with *n*-hexane, and dried under vacuum. Yield: 212 mg (93%).

Method 2. A 300 mg amount of **1b** (0.497 mmol) dissolved in 5 mL of THF was treated with 1.1 equiv of MeLi (1.6 M in diethyl ether) at −78 °C. The mixture was stirred for 1 h without further cooling. The reaction mixture was evaporated to dryness, and the residue was purified as described above for method 1. Yield: 102 mg (45%). Anal. Calcd for $C_{17}H_{15}BMoN_6O_3$: C, 44.57; H, 3.30; N, 18.35. Found: C, 44.51; H, 3.28; N, 18.37. ^{1}H NMR (δ, $CDCl_3$, 20 °C): 8.64 (d, 1H), 8.07 (d, 1H), 8.05 (d, 1H), 7.95−7.83 (m, 3H), 6.46 (t, 1H), 6.33 (t, 1H), 6.30 (t, 1H), 5.42 (m, 1H), 4.90 (m, 1H), 4.80 (m, 1H), 4.76 (s, 1H, $=CH_2$), 4.68 (s, 1H, $=CH_2$). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 20 °C): 225.4 (CO), 223.5 (CO), 192.0 (C=O), 149.0, 148.0 (*C*$=CH_2$), 145.5, 144.4, 138.3, 138.2, 137.0, 108.3, 107.5, 107.5 , 101.1 ($=CH_2$), 81.3, 74.3, 72.6. IR (diffuse reflectance (cm^{-1})): 1978 (s, ν_{CO}), 1891 (s, ν_{CO}), 1672 (s, $\nu_{C=O}$).

Attempted Demetalations with Trifluoroacetic Acid. A solution of Mo(η^3-C_5H_5O)$(CO)_2(HB(pz)_3)$ (200 mg, 0.506 mmol) in $CHCl_3$ (10 mL) was treated with trifluoroacetic acid (ca. 5 equiv), and the mixture was refluxed for 24 h. It was then quenched with saturated sodium bicarbonate solution (5 mL) and extracted with CH_2Cl_2 (2 × 10 mL). Drying over sodium sulfate, filtration, and evaporation resulted in the quantitative recovery of the starting material.

Attempts of Oxidative Demetalation by I_2, $I^+CF_3COO^-$, Br_2, and $NO^+PF_6^-$. I_2. A solution of Mo(η^3-C_5H_5O)-$(CO)_2(HB(pz)_3)$ (200 mg, 0.506 mmol) in CH_2Cl_2 (10 mL) was treated with 1.1 equiv of I_2 at −78 °C. Neither at low temperature nor after warming up to room temperature and stirring for additional 2 h nor even at refluxing conditions was observed any liberation of cyclopentenone as checked by TLC.

$I^+CF_3COO^-$. A solution of $I^+CF_3COO^-$ was prepared in situ according to the literature[2] and was transferred via canula into a solution of Mo(η^3-C_5H_5O)$(CO)_2(HB(pz)_3)$ in CH_2Cl_2 (10 mL) at −78 °C and stirred for 1 h. According to TLC monitoring no reaction took place even at room temperature and stirring for additional 3 h.

Br_2. Treatment of Mo(η^3-C_5H_5O)$(CO)_2(HB(pz)_3)$ (200 mg, 0.506 mmol) in CH_2Cl_2 (10 mL) with 1.1 equiv of Br_2 at −78 °C caused complete decomposition of the starting material to several intractable materials.

$NO^+PF_6^-$. A solution of Mo(η^3-C_5H_5O)$(CO)_2(HB(pz)_3)$ (200 mg, 0.506 mmol) in either dimethoxyethane, CH_3CN, acetone, or CH_3NO_2 was treated with 1.1 equiv of solid $NO^+PF_6^-$ at 0 °C and stirred for 1 h. Again, TLC monitoring (every 5 min) did not reveal any changes in the reaction mixture.

X-ray Structure Determination for 5a, 8a, and 9b. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Philips PW 1100 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 (**8a**) 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.

Results and Discussion

Nucleophilic Addition Reactions. The electrophilicity of the cationic cyclopentadienone complexes **1a** and **2**−**4** has been surveyed by reacting them with a variety of carbon, nitrogen, oxygen, sulfur, and phosphorus nucleophiles in CH_2Cl_2 as the solvent. Only with the alkoxides NaOEt and LiOPh no clean reaction occurs with only intractable decomposition products encountered. All other nucleophiles led to functionalized η^3-cyclopentenoyl complexes **5**−**8**, respectively, in high yields (Tables 2 and 3). Complexes **1a** and **2**−**4** were treated typically with 1 equiv of the nucleophile. Only primary and secondary amines were used in excess in order to quantitatively deprotonate the initially formed quaternary ammonium salts to afford the neutral complexes **5g**, **5h**, **5j**, and **6d**. Attack at the cyclopentadienone ligand took place *anti* to the coordinated metal and exclusively α to the ketonic functional group. Confirmation of the regioselectivity of the nucleophilic addition was readily apparent from the ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic characterization of the products. Further, proof of the stereospecific *anti* addition and the conformation of the allyl moiety with respect to the CO ligands was obtained by X-ray crystallography. Structural views of complexes **5a** and **8a** are shown in Figures 1 and 2 with important bond

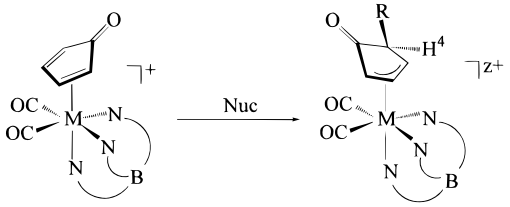
(7) Hall, S. R.; Flack, H. D.; Stuart, J. M. XTAL3.2: Integrated system of computer programs for crystal structure determination, Universities of Western Australia, Geneva (Switzerland), and Maryland, 1992.

(8) Sheldrick, G. M. SHELXL93. Program for crystal structure refinement, University of Göttingen, Germany, 1993.

Table 1. Crystallographic Data

	5a	8a	9b
formula	$C_{28}H_{41}BF_6MoN_6O_3P_2$	$C_{20}H_{21}BrF_6N_2O_3P_2W$	$C_{17}H_{15}BMoN_6O_3$
fw	792.36	777.09	458.10
cryst size, mm	0.50 × 0.55 × 0.88	0.23 × 0.25 × 0.38	0.08 × 0.10 × 0.15
space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)
a, Å	31.203(5)	8.965(2)	20.425(5)
b, Å	15.503(3)	9.631(2)	13.837(5)
c, Å	14.535(2)	15.035(3)	13.156(4)
α, deg	90	94.76(1)	90
β, deg	90	101.94(1)	90
γ, deg	90	92.26(1)	90
V, Å^3	7031(2)	1263.5(4)	3718(2
Z	8	2	8
ρ_{calc}, g cm^{-3}	1.497	2.042	1.637
T, K	297	297	298
μ, mm^{-1} (Mo Kα)	0.535	0.635	0.737
abs corr	none	analytical	none
transm factors: min/max		0.33/0.52	
θ_{max}, deg	25	25	24
index ranges	$0 \le h \le 37$	$-10 \le h \le 10$	$0 \le h \le 23$
	$0 \le k \le 18$	$0 \le k \le 11$	$0 \le k \le 15$
	$0 \le l \le 17$	$-17 \le l \le 17$	$0 \le l \le 15$
no. of rflns measd	6239	4464	2916
no. of unique rflns	6224	4464	2916
no. of rflns $F > 4\sigma(F)$	4574	4168	1917
no. of params	559	318	253
$R(F)$ ($F > 4\sigma(F)$)	0.039	0.018	0.039
$R(F)$ (all data)	0.062	0.021	0.079
$R_w(F^2)$ (all data)	0.097	0.044	0.079
diff Fourier peaks: min/max, e Å^{-3}	−0.32/0.39	−0.41/0.64	−0.26/0.24

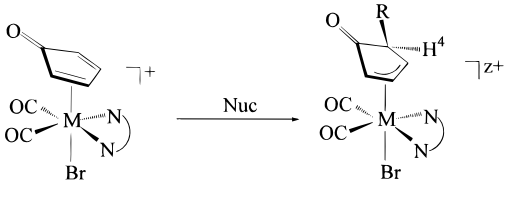
Table 2. Nucleophilic Additions to Cyclopentadienone Complexes 1a and 2



1a, 2 **5, 6**

		product			
entry	nucleophile	no.	R	yield, %	*z*
		M = Mo			
1	PBu_3	**5a**	PBu_3	96	1
2	PCy_3	**5b**	PCy_3	82	1
3	PPh_3	**5c**	PPh_3	92	1
4	KCN	**5d**	CN	96	0
5	MeMgBr	**5e**	Me	56	0
6	LiSPh	**5f**	SPh	87	0
7	NH_2Pr^i	**5g**	$NHPr^i$	95	0
8	$HNEt_2$	**5h**	NEt_2	83	0
9	NC_5H_5	**5i**	NC_5H_5	90	1
10	NH_2-NC_5H_4	**5j**	NH-NC_5H_4	44	0
		M = W			
1	PBu_3	**6a**	PBu_3	89	1
2	PPh_3	**6b**	PPh_3	87	1
3	KCN	**6c**	CN	94	0
4	$HNEt_2$	**6d**	NEt_2	91	0

Table 3. Nucleophilic Additions to Cyclopentadienone Complexes 3 and 4



3, 4 **7, 8**

		product			
entry	nucleophile	no.	R	yield, %	*z*
		M = Mo			
1	PMe_3	**7a**	PMe_3	95	1
2	PCy_3	**7b**	PCy_3	94	1
3	PPh_3	**7c**	PPh_3	40	1
		M = W			
1	PMe_3	**8a**	PMe_3	95	1
2	PCy_3	**8b**	PCy_3	94	1
3	LiSMe	**8c**	SMe	58	0
4	LiSPh	**8d**	SPh	63	0
5	$LiHC(COOMe)_2$	**8e**	$CH(COOMe)_2$	60	0
6	$PPh_2C_2H_4NMe_2$	**8f**	$PPh_2C_2H_4NMe_2$	80	1

lengths and angles reported in the captions. The ^{1}H NMR spectra of complexes **5**−**8** bear no unusual features, with the characteristic allyl resonances of the cyclopentenoyl moiety giving rise to three multiplets in the range of 5.4−3.2 ppm. The methylene proton H^4 (see Table 2) appears as a singlet and in case of the phosphine substituents as a doublet with $^2J_{HP} = 10.7-14.1$ Hz. It is worth noting that no coupling between H^4 and H^3 could be observed pointing to a dihedral angle close to 90° between these atoms. Further, the resonances of the coligands $HB(pz)_3$ and bipy are in the expected ranges. Where solubility has permitted (**5a**−**k**, **6a**−**d**, **7a**) $^{13}C\{^1H\}$ NMR spectra have also been recorded and do not contain any surprising features. Thus, the resonance of the ketonic "carbonyl" carbon was observed in the range of 205.5−192.0 ppm typical of nonconjugated ketones. In **1a** and **2**−**4**, for comparison, the resonance of the ketonic "carbonyl" carbon is in the range 176.0−172.4 ppm.[5] Although the $HB(pz)_3$ ligand might be a somewhat weaker electron donor than C_5H_5 as judged from the higher ν_{CO} in **1a** vs [Mo(η^4-C_5H_4O)(η^5-C_5H_5)$(CO)_2$]$^+$,[2,5] the electrophilicity of the cyclopentadienone ligand is rather similar in both

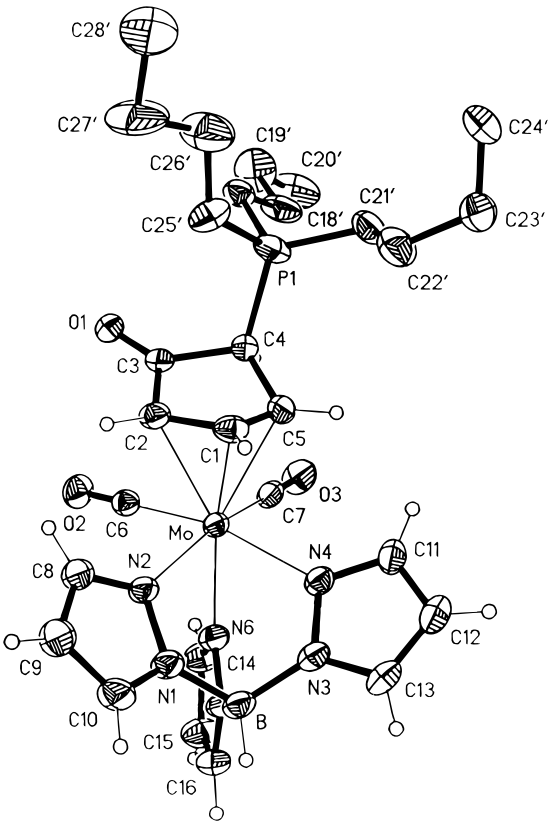


Figure 1. Structural view of $[Mo(\eta^3\text{-}C_5H_4O\text{-}PBu^n_3)(CO)_2(HB(pz)_3)]PF_6$ (**5a**). Only one of the two different Bu^n chain orientations is shown. Selected bond lengths (Å) and angles (deg): Mo−C(1) 2.182(4), Mo−C(2) 2.334(4), Mo−C(5) 2.329(4), Mo−C(6) 1.982(5), Mo−C(7) 1.969(5), Mo−N(2) 2.263(3), Mo−N(4) 2.259(3), Mo−N(6) 2.187(4), C(1)−C(2) 1.411(6), C(2)−C(3) 1.457(6), C(3)−C(4) 1.536(6), C(4)−C(5) 1.524(6), C(1)−C(5) 1.415(6), C(3)−O(1) 1.215(5), C(4)−P(1) 1.832(4), N(6)−Mo−C(6) 87.1(2), N(6)−Mo−C(7) 86.0(2), C(6)−Mo−C(7) 84.4(2), N(2)−Mo−N(4) 84.4(1), N(2)−Mo−N(6) 80.5(1).

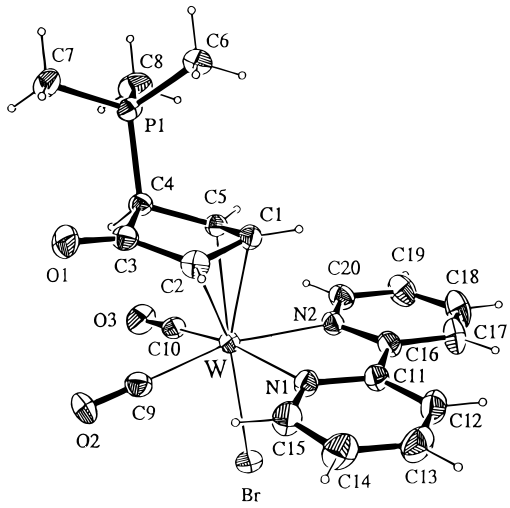


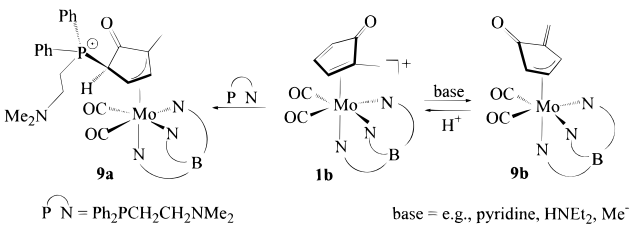
Figure 2. Structural view of $[W(\eta^3\text{-}C_5H_4OPMe_3)(bipy)(CO)_2]PF_6$ (**8a**). Selected bond lengths (Å) and angles (deg): W−C(1) 2.162(3), W−C(2) 2.325(3), W−C(5) 2.290(3), W−C(9) 1.998(3), W−C(10) 1.976(3), W−N(1) 2.216(3), W−N(2) 2.222(3), W−Br 2.582(1), C(1)−C(2) 1.433(4), C(2)−C(3) 1.464(5), C(3)−C(4) 1.543(4), C(4)−C(5) 1.532(4), C(1)−C(5) 1.425(5), C(3)−O(1) 1.211(4), C(4)−P(1) 1.811(3), N(1)−W−N(2) 73.3(1), C(9)−W−Br 86.0(1), C(10)−W−Br 84.5(1), C(9)−W−C(10) 81.3(1), N(1)−W−Br 82.7(1), N(2)−W−Br 81.6(1).

complexes. Both are excellent scaffolds for the regio- and stereoselective synthesis of functionalized η^3-cyclopentenoyl complexes.

The use of heteronucleophiles like amines or other strongly basic nucleophiles is uncommon for functionalizations since most diene ligands investigated include aliphatic hydrogens undergoing facile deprotonation rather than nucleophilic addition.[3d,4c] In the case of cyclopentadienone a wider range of nucleophiles can be used since no aliphatic hydrogen is present. On the other hand, 2-methylcyclopentadienone as a ligand is readily deprotonated by strong bases (see below).

Reactions of $Mo(\eta^4\text{-}C_5H_3O\text{-}2\text{-}Me)(CO)_2(HB(pz)_3)$ (1b) with Strong Nucleophiles. The reaction of **1b** with strong bases like Me^- (introduced as the lithium salt), $NHEt_2$, NEt_3, or pyridine results in the clean deprotonation of the methyl group to afford **9b** in up to 93% isolated yield (Scheme 1). This process is reversible, and **9b** is quantitatively converted to **1b** on treatment with strong acids such as CF_3SO_3H or CF_3COOH. Hence, the exocyclic methylene group exhibits nucleophilic behavior. **9b** has been characterized by a combination of elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The ^1H NMR spectrum exhibits two characteristic singlets assigned to the methylene protons at 4.76 and 4.68 ppm. The structure of **9b** has been

Scheme 1



confirmed by X-ray crystallography (Figure 3). By contrast, **1b** reacts with the bifunctional nucleophile $PPh_2CH_2CH_2NMe_2$ solely to produce the η^3-cyclopentenoyl compound **9a** where the phosphine donor is attached to the cyclopentenoyl moiety as established by ^1H NMR spectroscopy. The methylene proton gives rise to a doublet centered at 2.97 ppm ($^2J_{HP} = 11.0$ Hz) due to coupling with ^{31}P of the adjacent phosphine moiety. Since no deprotonation has been observed, it is suggested that nucleophilic attack at the α-carbon atom is more facile than the deprotonation of CH_3 by the more basic nitrogen donor site of $PPh_2CH_2CH_2NMe_2$ under this reaction conditions.

Attempted Demetalation Reactions. After the ability of complexes **1**−**4** to function as a synthetic equivalent of an α electrophilic cyclopentadienone was established, liberation of a cyclopentenone was attempted from $Mo(\eta^3\text{-}C_5H_5O)(CO)_2(HB(pz)_3)$. Unfortunately, the various methods of demetalation well established for the C_5H_5 analog systems proved to be unsuccessful. Thus, on protonation of $Mo(\eta^3\text{-}C_5H_5O)(CO)_2(HB(pz)_3)$ with trifluoroacetic acid in $CHCl_3$ at reflux the starting material was regained. The attempt of oxidative decomplexation of $Mo(\eta^3\text{-}C_5H_5O)(CO)_2(HB(pz)_3)$ by means of I_2, $I^+CF_3COO^-$, and Br_2 was just as unsuccessful. While with I_2 and $I^+CF_3COO^-$ no reaction took place at all, reaction of $Mo(\eta^3\text{-}C_5H_5O)(CO)_2(HB(pz)_3)$ with Br_2 gave several intractable mate-

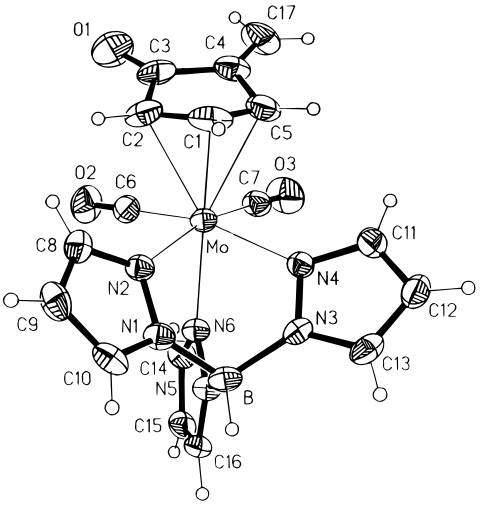


Figure 3. Structural view of Mo(η^3-$C_5H_3OCH_2$)$(CO)_2$(HB-$(pz)_3$) (**9b**). Selected bond lengths (Å) and angles (deg): Mo−C(1) 2.194(5), Mo−C(2) 2.344(6), Mo−C(5) 2.372(5), Mo−C(6) 1.969(6), Mo−C(7) 1.969(5), Mo−N(2) 2.282(4), Mo−N(4) 2.252(4), Mo−N(6) 2.185(4), C(1)−C(2) 1.400(8), C(2)−C(3) 1.460(7), C(3)−C(4) 1.478(9), C(4)−C(5) 1.467(8), C(4)−C(17) 1.282(7), C(1)−C(5) 1.415(8), C(3)−O(1) 1.254(7), N(6)−Mo−C(6) 84.1(2), N(6)−Mo−C(7) 88.1(2), C(6)−Mo−C(7) 82.8(2), N(2)−Mo−N(4) 82.5(2), N(2)−Mo−N(6) 80.1-(1).

trials. Finally, activation of Mo(η^3-C_5H_5O)$(CO)_2$ (HB-$(pz)_3$) by CO → NO replacement also failed.

Although $HB(pz)_3$ complexes behave similarly to their C_5H_5 analogs with respect to functionalization reactions of coordinated dienes, several differences in the reactivity patterns are particularly noteworthy with regard to practical applications. First, the steric bulk of the HB-$(pz)_3$ ligand obviously disfavors the availability of higher coordination numbers. As to this, compare the high cone angle of the $HB(pz)_3$ ligand close to 180° with about 100° calculated for C_5H_5.[9] Second, the $Mo(CO)_2$(HB-$(pz)_3$) fragment is strongly hybridized to bind to one additional group for a six-coordinate structure. By contrast, the diffuse electron cloud of the C_5H_5 ligand is ineffective in promoting strongly directional frontier orbitals of the $Mo(CO)_2(\eta^5$-$C_5H_5)$ fragment. Both effects, relief of steric congestion and orbital hybridization, favor the formation of six- rather than seven-coordinate species. Consequently, demetalation reactions proceeding via a seven-coordinate transition state (e.g., associative displacement of CO by NO^+) or resulting in the formation of a seven-coordinate species (e.g., oxidative addition of I_2 or Br_2, electrophilic attack of I^+) are unlikely to occur. As a matter of fact, seven-coordinate molybdenum complexes containing $HB(pz)_3$ as the coligand are rare and restricted to sterically little demanding ligands such as X = H, Cl, Br, and I in Mo(HB-$(pz)_3$)$(CO)_3$X.[10] For X = Me and Ph, spontaneous rearrangement takes place to give the quasi six-coordinate η^2-acyl complexes Mo$(HB(pz)_3)(CO)_2(\eta^2$-COX).[11] Such facile alkyl migrations are not observed in analogous C_5H_5 chemistry.[12]

Crystal Structures of [Mo(η^3-C_5H_4O-5-PBu_3^n)-$(CO)_2$(HB$(pz)_3$)]PF_6 (5a), [W(η^3-C_5H_4O-5-PMe_3)(bipy)-$(CO)_2$Br]PF_6 (8a), and Mo(η^3-$C_5H_3OCH_2$)$(CO)_2$(HB-$(pz)_3$) (9b). Structural views of complexes **5a**, **8a**, and **9b** are shown in Figures 1−3. Selected bond lengths of complexes **5a**, **8a**, and **9b** are given in the captions. These molecules can 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 complexes **5a** and **9b** the two carbonyls (C(6)−O(2), C(7)−O(3)) and two of the nitrogen atoms (N(2), N(4) of the $HB(pz)_3$ ligand) and for complex **8a** the two carbonyls (C(9)−O(2), C(10)−O(3)) and the two nitrogen atoms (N(1) and N(2)). The η^3-cyclopentenoyl ligand and the third coordinating nitrogen (N(6)) of $HB(pz)_3$ and the halogen (Br), respectively, lie trans to one another in apical positions above and below the equatorial plane. In the solid state, complexes **5a**, **8a**, and **9b** are found to adopt exclusively the *exo* conformation with respect to the orientation of the allyl moiety. The cyclopentenoyl moieties of **5a**, **8a**, and **9b** are distinctly bent and can be subdivided by two planes, one defined by C(1), C(2), and C(5) (allyl fragment) and the other defined by C(2), C(3), C(4), and C(5). The angle between this plane is 26.7(5), 28.0(4), and 23.1-(4)°, respectively. The M−CO and C−O distances are both within the range reported for other molybdenum and tungsten carbonyl complexes. No structural features in complexes **5a**, **8a**, and **9b** indicate unusual deviations or distortions.

Conclusions. [M(η^4-C_5H_4O)$(CO)_2$(HB$(pz)_3$)]PF_6 (**1a**, **2**) and [M(η^4-C_5H_4O)$(CO)_2$(bipy)Br]PF_6 (**3**, **4**) (M = Mo, W) react with a wide variety of carbon, nitrogen, phosphorus, and sulfur nucleophiles in a regio- and stereoselective fashion to functionalized η^3-cyclopentenoyl complexes in high yields. Unfortunately, decomplexation of the form functionalized cyclopentenones by common methods involving intermediate seven-coordinate species failed. Apparently, steric as well as electronic effects would promote six-coordination in the $HB(pz)_3$ complexes in contrast to their C_5H_5 analogues.

Acknowledgment. Financial support by the "Jubiläumsfond der österreichischen Nationalbank" is gratefully acknowledged (Project 5305).

Supporting Information Available: Listings of atomic coordinates and *U* values, anisotropic temperature factors, complete bond lengths and angles, and least-squares planes for complexes **5a**, **8a**, and **9b** (33 pages). Ordering information is given on any current masthead page.

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