# (2-(Dimethylamino)ethyl)cyclopentadienyl Group VI Metal Carbonyl Anions and Divalent Tin(IV) Derivatives

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*Received October 12, 2004*

*Summary: Salts of (2-(dimethylamino)ethyl)cyclopentadienyl ($Cp^N$) group VI metal carbonyl anions ($[M(CO)_3(\eta^5\text{-}Cp^N)]^-$ (M = Cr, Mo, W)), important reagents for studies involving $Cp^N$, have been characterized by X-ray crystallography. These anions (M′ = Mo, W) react with $R_3SnCl$ (R = Ph, cyclohexyl) to provide structurally characterized tin(IV) derivatives.*

## Introduction

The introduction of a donor-functionalized side chain into a cyclopentadienyl transition-metal compound typically modulates complex reactivity relative to that of the parent cyclopentadienyl species.[1] The (2-(dimethylamino)ethyl)cyclopentadienyl ligand ($Cp^N$) has been employed to enhance metal complex solubility in protic solvents,[2] stabilize electron-deficient metal centers,[3] promote ligand exchange with low-valent metals,[4] and assist in catalysis.[5] It has also been utilized in intramolecular Lewis acid−base adducts in which the tethered dimethylamino group coordinates to an electron-deficient ligand.[4,6]

Metal carbonyl anions containing $Cp^N$ are reagents for these studies. The anions $[NiCO(\eta^5\text{-}Cp^N)]^-$ [6a] and $[Mo(CO)_3(\eta^5\text{-}Cp^N)]^-$ [3b] have been synthesized, identified by infrared spectra, and used in situ. However, to date, no anions of the general formula $[M(CO)_x(Cp^N)]^-$ have been isolated or fully characterized. We have synthesized and characterized $[PPN][M(CO)_3(\eta^5\text{-}Cp^N)]$ (M = Cr, Mo, W) in solution and the solid state.

Tetraorganotin compounds that are pentacoordinate by virtue of intramolecular tin−amine dative bonding[7] exhibit enhanced reactivity due to Sn−R bond elongation trans to the dative amine. Hypervalent tin compounds are often exceptionally reactive toward redistribution and Stille coupling reactions.[8] Early examples of pentacoordinate tetraorganotin compounds featured bidentate C,N ligands where intramolecular Sn−N binding is enforced by ligand rigidity.[9] Subsequent reports demonstrated that more flexible C,N chelating ligands provide tetraorgano compounds with Sn−N interactions.[10,11] Although $M{-}SnR_3$ bonds are ubiquitous,[12] the possibility of intramolecular amine coordination to $SnR_3$ ligands has been poorly explored. We have examined reactions of $[M'(CO)_3(\eta^5\text{-}Cp^N)]^-$ (M′ = Mo, W) with triorganotin halides to investigate the potential utility of $Cp^N$ to obtain intramolecular amine-stabilized $SnR_3$ complexes.

## Results and Discussion

Reactions of $M(CO)_6$ and $NaCp^N$ followed by metathesis with PPNCl afforded $[PPN][M(CO)_3(\eta^5\text{-}Cp^N)]$ (Scheme 1). The $\nu$(CO) infrared spectra of $Na[M(CO)_3(\eta^5\text{-}Cp^N)]$ in ethereal solvents (Table S1) indicate $C_s$ ion pairs analogous to $Na[M(CO)_3(\eta^5\text{-}Cp)]$.[13] The two $\nu$(CO) IR absorptions of **1**−**3** indicate $C_{3v}$ $M(CO)_3$ units un-

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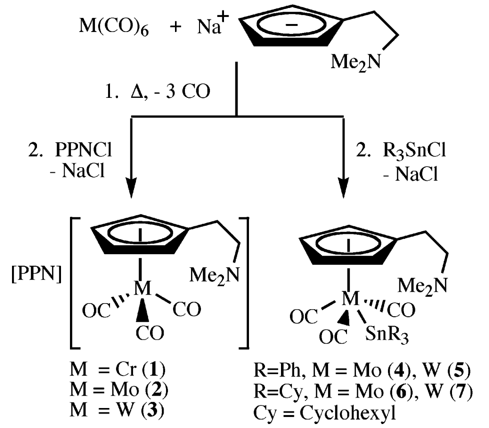
10.1021/om0492101 CCC: $30.25

**Scheme 1**



perturbed by PPN$^+$ and the amine in solution. The $^{13}$CO chemical shifts of **1**−**3** are nearly identical with those of [M(CO)$_3$($\eta^5$-Cp)]$^-$ (Table S2).[14]

**Structural Characterization of [PPN][M(CO)$_3$($\eta^5$-Cp$^N$)].** Salts **1**−**3** contain the first crystallographically characterized triad of [M(CO)$_3$(C$_5$H$_4$R)]$^-$ complexes. The three-legged piano-stool structures of **1** and **3** are shown in Figures 1 and 2, respectively; **2** is displayed in Figure S1 (Supporting Information).[15] The amines of **1**−**3** are not engaged in any interactions with PPN$^+$ or M(CO)$_3$ units. In **1** and **2**, the $\eta^5$-Cp$^N$ ring is oriented such that methylene carbon C(6) is roughly opposite the CO defined by C(12). This permits the 2-(dimethylamino)ethyl substituent to occupy space between the other two CO ligands. The $\eta^5$-Cp$^N$ ring is oriented differently in **3**; C(6) is almost directly above the CO defined by C(10). Important average structural parameters for **1** (Cr−C(O), 1.813(3) Å; C−O, 1.177(5) Å; Cr−C(dienyl), 2.220(9) Å; (O)C−Cr−C(O), 88.4(7)°; Cr−C−O, 178.4(3)°) are statistically identical with those of [CpCr(NC-$^t$Bu)$_4$][Cr(CO)$_3$($\eta^5$-Cp)].[16] The distance between an $\eta^5$-Cp and a Cr(CO)$_3$ fragment appears independent of cyclopentadienyl substitution, as the average Cr−C(dienyl) distance in **1** is statistically indistinguishable from that of [PPN][Cr(CO)$_3$($\eta^5$-C$_5$Ph$_5$)],[17] [PPh$_4$][Cr(CO)$_3$($\eta^5$-C$_5$H$_4$CHO)],[18] and Cr(CO)$_3$($\eta^5$-C$_5$H$_4$C(CH$_3$)$_2$PEt$_3$).[19] Important average structural parameters for **2** (Mo−C(O), 1.926(2) Å; C−O, 1.172(2) Å; Mo−C(dienyl), 2.381(7) Å; (O)C−Mo−C(O), 86.2(8)°; Mo−C−O, 179.0(6)°) are statistically indistinguishable from those of [PPN][Mo(CO)$_3$($\eta^5$-Cp)].[20] Both **1** and **2** feature slight M−C(1) elongation due to influence of the pendant amine. The Cr−C(1) distance in **1** is significantly longer ($\sim 4\sigma$) than the average Cr−C(2−5) distance (2.216(5) Å), while the Mo−C(1) distance of **2** (2.394(3) Å) is approximately $5\sigma$ longer than the average Mo−C(2,5) length (2.378(3) Å). The small absolute differences between these distances ($\sim$0.02 Å) do not rule out consideration of **1** and **2** as $\eta^5$-Cp$^N$ complexes. Important average lengths and angles of **3** (W−C(O), 1.926(6) Å; C−O, 1.18(1) Å; W−C(dienyl), 2.38(1) Å; (O)C−W−C(O), 88(2)°; W−C−O, 177.8(8)°) are statistically identical with the corresponding parameters of **2**. Although **3** is an $\eta^5$-Cp$^N$ complex, its M−C(dienyl) distances are irregular relative to those in **2**. The W−C(1) and W−C(5) distances are nearly $7\sigma$ longer than W−C(3), although the absolute difference is small ($\sim$0.03 Å). This minor distortion may be related to an alternate position of the pendant group, as rotation about the C(6)−C(7) bond is much more pronounced in **3** relative to **2** and **1**. The C1−C6−C7−N1 torsion angle in **3** is −156.5(3)°, while this angle in **2** is −70.0(4)°. Disordered solvent of crystallization (most likely 2 THF molecules per unit cell; see the Supporting Information) may influence the orientation of the amine in **3**.

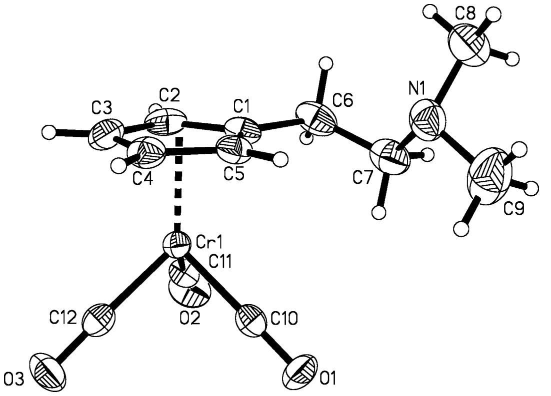


**Figure 1.** Molecular structure of the anion of **1** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Cr−C(1) = 2.235(3), Cr−C(2) = 2.214(3), Cr−C(3) = 2.211(3), Cr−C(4) = 2.218(3), Cr−C(5) = 2.222(3), Cr−C(10) = 1.810(3), Cr−C(11) = 1.815(3), Cr−C(12) = 1.815(3), C(10)−O(1) = 1.175(3), C(11)−O(2) = 1.174(3), C(12)−O(3) = 1.183(3); C(10)−Cr−C(12) = 87.90(12), C(10)−Cr−C(11) = 88.07(12), C(12)−Cr−C(11) = 89.25(12), O(1)−C(10)−Cr = 178.6(2), O(2)−C(11)−Cr = 178.6(3), O(3)−C(12)−Cr = 178.0(2).

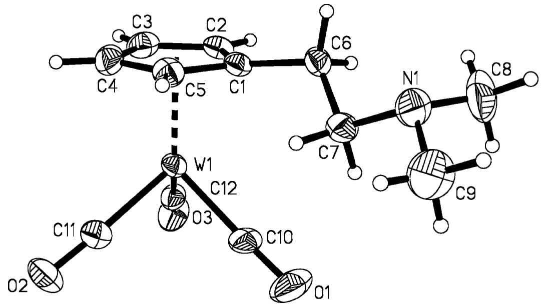


**Figure 2.** Molecular structure of the anion of **3** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): W−C(1) = 2.390(4), W−C(2) = 2.374(4), W−C(3) = 2.363(4), W−C(4) = 2.374(4), W−C(5) = 2.389(4), W−C(10) = 1.928(4), W−C(11) = 1.931(4), W−C(12) = 1.919(4), C(10)−O(1) = 1.174(5), C(11)−O(2) = 1.174(5), C(12)−O(3) = 1.191(4); C(10)−W−C(12) = 86.02(17), C(10)−W−C(11) = 89.43(18), C(12)−W−C(11) = 88.64(17), O(1)−C(10)−W = 177.5(5), O(2)−C(11)−W = 177.1(4), O(3)−C(12)−W = 178.7(4).

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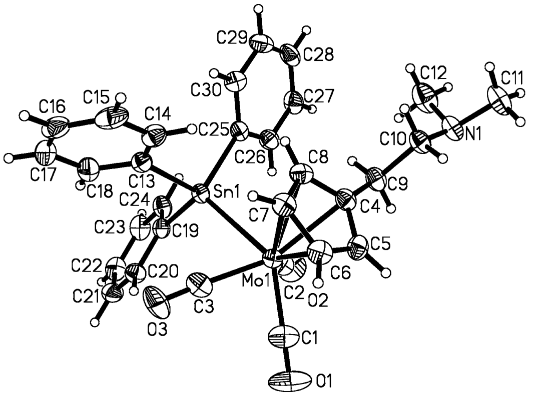

**Figure 3.** Molecular structure of **4** (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo−Sn = 2.8152(3), Mo−C(1) = 1.989(3), Mo−C(2) = 1.985(3), Mo−C(3) = 1.972(3), Mo−C(4) = 2.357(2), Mo−C(5) = 2.316(2), Mo−C(6) = 2.312(2), Mo−C(7) = 2.342(2), Mo−C(8) = 2.356(2); C(1)−Mo−Sn = 130.31(9), C(3)−Mo−C(2) = 107.40(11), C(3)−Mo−Sn = 70.97(8), C(2)−Mo−Sn = 72.74(8), C(3)−Mo−C(1) = 79.68(12), C(2)−Mo−C(1) = 79.29(11).

**Tin(IV) Derivatives.** Reactions of in situ Na[M′$(CO)_3(\eta^5\text{-}Cp^N)$] (M′ = Mo, W) and $R_3SnCl$ afforded M′$(SnR_3)(CO)_3(\eta^5\text{-}Cp^N)$ (Scheme 1). The solubility of these substances in hydrocarbons is significantly higher than that of their Cp analogues.[21] Isolation of M′$(SnMe_3)(CO)_3(\eta^5\text{-}Cp^N)$ was unsuccessful, since the melting points of these exceedingly pentane soluble derivatives are <−20 °C. The ν(CO) IR spectra of **4**−**7** are diagnostic of four-legged piano-stool $CpM(CO)_3L$ structures. These spectra for **4** and **5** are nearly identical with those of M′$(SnPh_3)(CO)_3(\eta^5\text{-}Cp)$.[22]

The spectral data of **6** and **7** provide additional points of reference to gauge stannylene donor ability. The ligands SnAr (Ar = $C_6H_3$-2,6-$R_2$ (R = $C_6H_2$-2,4,6-$Me_3$, $C_6H_2$-2,4,6-$Pr^i{}_3$)) of M′$(SnAr)(CO)_3(\eta^5\text{-}Cp)$ were deemed better donors than $SnMe_3$ on the basis of IR and $^1H$ NMR spectral comparisons to M′$(SnMe_3)(CO)_3(\eta^5\text{-}Cp)$.[23] Infrared data of **6** and **7** suggest that SnAr ligands are stronger donors than $SnCy_3$ (Table S3). This difference is not well-defined on the basis of $^{13}C$ NMR; the carbonyl carbons of **6** and **7** are deshielded similarly to those of the Mo and W stannylenes. A dramatic upfield shift of the metallostannylene Cp hydrogen resonances is attributed to strong SnAr donation.[23] These absorptions are more than 1 ppm upfield from those of **6** and **7**.

**Structural Characterization of M′$(SnPh_3)(CO)_3(\eta^5\text{-}Cp^N)$.** The isostructural compounds **4** and **5** were characterized by X-ray crystallography. The molecular structures of **4** and **5** are displayed in Figures 3 and S2 (Supporting Information), respectively. The geometric parameters of **4** and **5** satisfy the requirements for $CpM(CO)_3L$ four-legged piano-stool structures.[24] In **4** and **5**, the amine is oriented away from nearly tetrahedral and unperturbed $SnPh_3$ ligands. The lack of constraints on the amine is not conducive to an intramolecular N−Sn interaction.

The nearly identical M′−Sn lengths of **4** and **5** (2.8215(4) Å) are similar to those of $[PPN][W(SnPh_3)(CO)_5]$[25] and $\{p\text{-}[(CO)_3MoC_5H_4C(O)]_2C_6H_4\}\{(Ph_2Sn)_2S\}$.[26] The metallostannylenes M′$(SnC_6H_3\text{-}2,6\text{-}Mes_2)(CO)_3(\eta^5\text{-}Cp)$ (M′ = Mo (**8**), W (**9**)) exhibit slightly elongated M−Sn distances.[23] The average M−C(dienyl) lengths of **4** and **5** are uniform (2.34(2) Å) and statistically indistinguishable from those of **8** (2.348(5) Å) and **9** (2.346(9) Å), but the M−C(dienyl) lengths of **4** and **5** are more irregular. Specifically, the average M−C(4,7,8) distances (**4**, 2.352(8) Å; **5**, 2.352(12) Å) are statistically longer than the average M−C(5,6) lengths (**4**, 2.314(3) Å; **5**, 2.314(8) Å). The $\eta^5$-$Cp^N$ groups of **4** and **5** engage in minor tilting due to the influence of $SnPh_3$ and the pendant group. Greater M−C(dienyl) uniformity in **8** and **9** is consistent with longer metal−tin bond lengths.

The $SnPh_3$ ligands of **4** and **5** are modestly distorted from tetrahedral geometries. The *ipso*-C−Sn−*ipso*-C angles range from 105.60(9) to 108.06(8)° in **4** and 105.82(14) to 107.98(14)° in **5**. The slight compression in these angles accommodates C(19)−Sn−M′ angles of 116.15(6) and 115.87(10)° in **4** and **5**, respectively. It is reasonable to attribute this larger angle to steric hindrance between the phenyl ring defined by C(19) and the CO defined by C(3). However, rationalization of $SnPh_3$ ligand geometries based solely on intramolecular considerations is tenuous. The $SnPh_3$ of $[W(SnPh_3)CO)_5]^-$ is considerably distorted, with *ipso*-C−Sn−*ipso*-C angles of 98.6(2), 98.8(2), and 104.2(2)°.[25] The flat phenyl rings appear to render the $SnPh_3$ ligand geometry rather susceptible to crystal-packing forces.

The flexibility of the $Cp^N$ amine is too great to permit N−Sn dative bonding to these $SnR_3$ ligands. Less sterically hindered, more Lewis acidic ligands are required to entice adduct formation. An examination of reactions of $[M(CO)_3(\eta^5\text{-}Cp)]^-$ and related anions with $R_2SnX_2$, $RSnX_3$, $SnX_4$, and other electrophiles is underway.

## Experimental Section

**General Procedures.** All operations were performed under an atmosphere of 99.5% argon purified by passage through a column of activated Aceto Corp. catalyst R3-11 and 10 Å molecular sieves. Standard Schlenk techniques were employed with double-manifold vacuum lines.[27] Solids were handled in a glovebox. Solvents were purified by standard procedures. Literature procedures were employed to prepare $NaCp^N$.[28] $M(CO)_6$ (M = Cr, Mo, W) and $R_3SnCl$ (R = Ph, Cy) were used as received (Aldrich). PPNCl (Aldrich) was recrystallized from $H_2O$ and dried. Solution IR spectra were acquired on a Nicolet Magna 550 FTIR spectrometer with samples sealed in 0.1 mm gastight NaCl cells. NMR samples were sealed under argon into 5 mm tubes and analyzed on a Varian Gemini 300 MHz FT-NMR spectrometer at ambient temperature. $^1H$ and $^{13}C$

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chemical shifts are reported in parts per million ($\delta$) and are given with reference to residual $^1$H and $^{13}$C solvent references relative to TMS. Melting points (uncorrected) were determined under argon in sealed capillary tubes on a Laboratory Devices Mel-Temp apparatus. Microanalyses were carried out by H. Malissa and G. Reuter Analytische Laboratorien, Lindlar, Germany.

Similar procedures were conducted to synthesize **1**–**3** and **4**–**7**, respectively. Representative procedures for **1** and **4** are provided below. Complete experimental details for **2**, **3**, and **5**–**7** are given in the Supporting Information.

**[PPN][Cr(CO)$_3$($\eta^5$-Cp$^N$)] (1).** $CH_3CN$ (80 mL) was added to $Cr(CO)_6$ (0.345 g, 1.57 mmol) and NaCp$^N$ (0.300 g, 1.88 mmol). The yellow solution was refluxed for 64 h. The $CH_3CN$ was removed in vacuo, and THF (80 mL) was added. The suspension was filtered into PPNCl (0.991 g, 1.73 mmol) and stirred for 3 h prior to filtration through alumina. The THF was removed in vacuo until ~5 mL remained. A yellow solid precipitated upon addition of $Et_2O$ (80 mL). The solid was isolated via filtration, washed with $Et_2O$ (4 × 15 mL), and dried in vacuo. Recrystallization (THF/$Et_2O$) provided yellow, moderately air-sensitive microcrystals (0.567 g, 45%). Anal. Calcd for $C_{48}H_{44}CrN_2O_3P_2$: C, 71.10; H, 5.47; N, 3.45. Found: C, 70.91, H, 5.51; N, 3.55. Mp: 132 °C dec. IR (THF): $\nu$(CO) 1890 (m), 1776 (s) cm$^{-1}$. IR ($CH_3CN$): $\nu$(CO) 1889 (s), 1771 (s) cm$^{-1}$. IR (Nujol): $\nu$(CO) 1886 (m), 1755 (s, br) cm$^{-1}$. $^1$H NMR ($CD_3CN$, 300 MHz): $\delta$ 7.62–7.34 (m, 30H, PPN), 4.24 (app t, $J$ = 2.1 Hz, 2H, Cp), 4.17 (app t, $J$ = 2.1 Hz, 2H, Cp), 2.22 (m, 4H, $CH_2CH_2$), 2.03 (s, 6H, $CH_3$). $^{13}$C{$^1$H} NMR ($CD_3CN$, 75 MHz): $\delta$ 247.0 (s, CO).

**[PPN][Mo(CO)$_3$($\eta^5$-Cp$^N$)] (2).** Anal. Calcd for $C_{48}H_{44}MoN_2O_3P_2$: C, 67.45; H, 5.19; N, 3.28. Found: C, 67.28, H, 5.25; N, 3.37. Mp: 138 °C dec. IR (THF): $\nu$(CO) 1894 (s), 1779 (s) cm$^{-1}$. IR ($CH_3CN$): $\nu$(CO) 1893 (s), 1775 (s) cm$^{-1}$. IR (Nujol): $\nu$(CO) 1894 (s), 1771 (s, br) cm$^{-1}$. $^1$H NMR ($CD_3CN$, 300 MHz): $\delta$ 7.60–7.34 (m, 30H, PPN), 4.91 (app t, $J$ = 2.1 Hz, 2H, Cp), 4.81 (app t, $J$ = 2.1 Hz, 2H, Cp), 2.26 (m, 4H, $CH_2CH_2$), 2.04 (s, 6H, $CH_3$). $^{13}$C{$^1$H} NMR ($CD_3CN$, 75 MHz): $\delta$ 237.3 (s, CO).

**[PPN][W(CO)$_3$($\eta^5$-Cp$^N$)] (3).** Anal. Calcd for $C_{48}H_{44}WN_2O_3P_2$: C, 61.15; H, 4.70; N, 2.97. Found: C, 59.18, H, 4.83; N, 2.98. Mp: 133 °C dec. IR (DME): $\nu$(CO) 1888 (s), 1774 (s) cm$^{-1}$. IR (THF): $\nu$(CO) 1888 (s), 1774 (s) cm$^{-1}$. IR (Nujol): $\nu$(CO) 1887 (s), 1767 (s) cm$^{-1}$. $^1$H NMR ($CD_3CN$, 300 MHz): $\delta$ 7.70–7.42 (m, 30H, PPN), 5.03 (app t, $J$ = 2.1 Hz, 2H, Cp), 4.93 (app t, $J$ = 2.1 Hz, 2H, Cp), 2.43–2.24 (m, 4H, $CH_2CH_2$), 2.14 (s, 6H, $CH_3$). $^{13}$C{$^1$H} NMR ($CD_3CN$, 75 MHz): $\delta$ 228.1 (s, CO, ($^{183}$W–$^{13}$C satellites 229.42, 226.80, $^1J_{WC}$ = 198 Hz)).

**Mo(SnPh$_3$)(CO)$_3$($\eta^5$-Cp$^N$) (4).** THF (80 mL) was added to $Mo(CO)_6$ (0.829 g, 3.14 mmol) and NaCp$^N$ (0.600 g, 3.77 mmol). The yellow solution was refluxed for 15 h. Addition of $Ph_3SnCl$ (1.21 g, 3.14 mmol) in THF (30 mL) resulted in a pale yellow suspension. The [Mo(CO)$_3$($\eta^5$-Cp$^N$)]$^-$ was consumed within 30 min. The suspension was filtered through alumina. THF was removed in vacuo, revealing a yellow, oily residue. The product was extracted with pentane (5 × 70 mL); each colorless extract was filtered. Pentane was removed in vacuo from the combined extracts until a yellow solid had precipitated. The suspension (~75 mL) was cooled and filtered at −50 °C. The pale yellow, moderately air-sensitive microcrystals (1.423 g, 68%) were washed with pentane (−50 °C, 5 × 15 mL) and dried in vacuo. Anal. Calcd for $C_{30}H_{29}O_3NSnMo$: C, 54.09; H, 4.39; N, 2.10. Found: C, 54.12, H, 4.49; N, 2.23. Mp: 101–102 °C dec. IR (THF): $\nu$(CO) 1997 (s), 1925 (m, sh), 1902 (s) cm$^{-1}$. IR ($CH_2Cl_2$): $\nu$(CO) 2000 (s), 1928 (m, sh), 1899 (s) cm$^{-1}$. IR (pentane): $\nu$(CO) 2003 (s), 1935 (m), 1912 (s) cm$^{-1}$. IR (Nujol): $\nu$(CO) 1990 (m), 1922 (m, sh), 1893 (s) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 300 MHz): $\delta$ 7.68–7.44 (m, 6H, ortho, $SnPh_3$), 7.42–7.26 (m, 9H, meta/para, $SnPh_3$), 5.42 (app t, $J$ = 2.1 Hz, 2H, Cp), 5.18 (app t, $J$ = 2.1 Hz, 2H, Cp), 2.31 (m, 4H, $CH_2CH_2$), 2.14 (s, 6H, $CH_3$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 75.5 MHz): $\delta$ 230.5 (s, CO ($^{117,119}$Sn-$^{13}$C satellites (merged) 230.72, 230.35, $^2J_{SnC}$ = 27.9 Hz)), 225.6 (s, CO ($^{117,119}$Sn–$^{13}$C satellites 226.60, 226.56, 224.72, 224.68, $^2J_{SnC}$ = 142 Hz)).

**W(SnPh$_3$)(CO)$_3$($\eta^5$-Cp$^N$) (5).** Anal. Calcd for $C_{30}H_{29}NO_3SnW$: C, 47.78; H, 3.88; N, 1.86. Found: C, 47.74, H, 3.99; N, 1.92. Mp: 106–107 °C dec. IR (DME): $\nu$(CO) 1992 (s), 1917 (m, sh), 1895 (s) cm$^{-1}$. IR (THF): $\nu$(CO) 1992 (s), 1916 (m, sh), 1894 (s) cm$^{-1}$. IR (pentane): $\nu$(CO) 2000 (s), 1927 (m), 1906 (s) cm$^{-1}$. IR (Nujol): $\nu$(CO) 1980 (s), 1913 (s, sh), 1885 (s) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 300 MHz): $\delta$ 7.56–7.34 (m, 6H, ortho, $SnPh_3$), 7.32–7.16 (m, 9H, meta/para, $SnPh_3$), 5.38 (app t, $J$ = 2.1 Hz, 2H, Cp), 5.15 (app t, $J$ = 2.1 Hz, 2H, Cp), 2.30–2.16 (m, 4H, $CH_2CH_2$), 2.02 (s, 6H, $CH_3$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 75 MHz): $\delta$ 218.8 (s, CO, ($^{117,119}$Sn–$^{13}$C satellites (merged) 218.98, 218.63, $^2J_{SnC}$ = 26.4 Hz)), 215.1 (s, CO, ($^{117,119}$Sn–$^{13}$C satellites 216.12, 216.01, 214.42, 214.11, $^2J_{SnC}$ = 136 Hz)).

**Mo(SnCy$_3$)(CO)$_3$($\eta^5$-Cp$^N$) (6).** Anal. Calcd for $C_{30}H_{47}O_3NSnMo$: C, 52.65; H, 6.92; N, 2.05. Found: C, 52.78, H, 6.93; N, 2.09. Mp: 109–110 °C dec. IR (THF): $\nu$(CO) 1982 (s), 1907 (m, sh), 1886 (s) cm$^{-1}$. IR (Nujol): $\nu$(CO) 1970 (s), 1892 (s, br) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 300 MHz): $\delta$ 5.41 (app t, $J$ = 2.1 Hz, 2H, Cp), 5.32 (app t, $J$ = 2.1 Hz, 2H, Cp), 2.53–2.35 (m, 4H, $CH_2CH_2$), 2.21 (s, 6H, $CH_3$), 2.02–1.19 (m, 33H, $SnCy_3$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 75.5 MHz): $\delta$ 232.4 (s, br, CO), 226.3 (s, br, CO).

**W(SnCy$_3$)(CO)$_3$($\eta^5$-Cp$^N$) (7).** Anal. Calcd for $C_{30}H_{47}O_3NSnW$: C, 46.66; H, 6.13; N, 1.81. Found: C, 46.49, H, 6.01; N, 1.88. Mp: 113–114 °C dec. IR (DME): $\nu$(CO) 1979 (s), 1900 (m, sh), 1880 (s) cm$^{-1}$. IR (pentane): $\nu$(CO) 1987 (s), 1911 (m), 1891 (s) cm$^{-1}$. IR (Nujol): $\nu$(CO) 1983 (m, sh), 1966 (s), 1903 (s), 1886 (s, sh) cm$^{-1}$. $^1$H NMR ($CD_2Cl_2$, 300 MHz): $\delta$ 5.49 (app t, $J$ = 2.1, 2H, Cp), 5.42 (app t, $J$ = 2.1 Hz, 2H, Cp), 2.56 (t, $J$ = 7.20 Hz, 2H, $CH_2N$), 2.39 (t, $J$ = 7.20 Hz, 2H, $CH_2CH_2N$), 2.21 (s, 6H, $CH_3$), 2.03–1.16 (m, 33H, $SnCy_3$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 75 MHz): $\delta$ 220.7 (s, CO), 216.2 (s, CO).

**X-ray Crystallography.** X-ray-quality crystals of **1**–**3** were obtained by diffusion of $Et_2O$ into a THF solution of each salt. Crystals of **4** were obtained from a supersaturated THF solution. Crystals of **5** were obtained by evaporation of a THF solution. All manipulations with the crystals of **1**–**4** were conducted in a $N_2$-filled glovebag. Crystals of **1** and **2** were selected from the mother liquor; those of **3** and **4** had been dried in vacuo. A crystal of **5** was selected in air.

**Acknowledgment.** The donors of Petroleum Research Fund, administered by the American Chemical Society (ACS PRF 39928-GB3), and an award from Research Corp. (CC5932) supported this research. We are grateful for the generosity of these agencies and Macalester College. We are indebted to William W. Brennessel (Crystallographic Laboratory). P.J.F. thanks Prof. John E. Ellis for his support and encouragement over the years.

**Supporting Information Available:** Text giving additional experimental details, $^{13}$C NMR spectral data for **1**–**7**, and tables giving spectroscopic data and crystallographic data as well as data collection, solution, and refinement information for **1**–**5**; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0492101