Cycloheptadienyl Complexes of the Group 6 Metals

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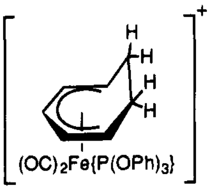
The syntheses of cycloheptadienyl complexes of chromium and molybdenum are described. Addition of potassium triethylborohydride to [(η^6-C_7H_8)M(CO)$_3$] (M = Cr or Mo) gave the salts K[(η^5-C_7H_9)M(CO)$_3$] (M = Cr or Mo), which reacted with Me_3SnCl and Ph_3SnCl to form [(η^5-C_7H_9)M(CO)$_3$SnR$_3$] (M = Cr or Mo, R = Me, Ph). Treatment of K[(η^5-C_7H_9)M(CO)$_3$] with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) gave [(η^5-C_7H_9)M(CO)$_2$(NO)] (M = Cr or Mo).

Introduction

The η^5-cycloheptadienyl ligand (η^5-C_7H_9) has been used in organic synthesis for the stereospecific functionalization of seven-membered rings,[1] as well as in the study of novel insertion reactions.[2,3] Noteworthy is the work of Pearson and co-workers[1] on derivatives of [Fe(CO)$_2$L(η^5-C_7H_9)]$^+$, (L = CO or P(OPh)$_3$) (**1**), as well as that of Williams et al.[2] with [Fe(CO)$_2$(η^5-C_7H_9)]$^-$-derived species. The manganese complexes [Mn(CO)$_3$(η^5-C_7H_8R)] (**2**) have been studied by us[3] and others,[4] and we have demonstrated the intramolecular coupling of a carbene ligand with the dienyl ring.[3] To explore the generality of this coupling reaction, we are investigating other cycloheptadienyl species and have found these to be somewhat rare. For example, the group 6 metal complexes [M(CO)$_3$L(η^5-C_7H_9)] and [M(CO)$_2$(NO)(η^5-C_7H_9)] (M = Cr, Mo; L = 1e donor) have not been prepared despite their similarity to the well-studied cyclopentadienyl species [CpM(CO)$_3$L][5a] (M = Cr, Mo; L = H,[5a] L = CpM(CO)$_3$,[5a] L = M′R$_3$, {M′ = Ge, Sn, Pb; R = Me, Ph}[5b]) and [CpM(CO)$_2$(NO)].[5a] At present, the only cycloheptadienyl complexes of any group 6 metal are those formed by the protonation of [M(CO)$_3$(η^6-C_7H_8)] (M = Mo {**4b**} or W) in the presence of CO, CN^t-Bu, or PPh$_3$ (Scheme 1)[6,7] or by the oxidative addition of HCl to **4b**.[6b] An electrochemical reduction of [W(CO)$_3$(η^6-C_7H_8)] in the presence of proton donors has also been reported. The presumed product [W(CO)$_3$(η^5-C_7H_9)]$^-$ was characterized via its reaction with MeI which gave [WMe(CO)$_3$(η^5-C_7H_9)].[6c]



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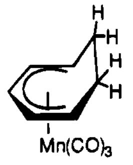

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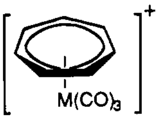
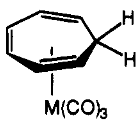


3a M = Cr
3b M = Mo



4a M = Cr
4b M = Mo

The lack of cycloheptadienylchromium and -molybdenum species is due in part to the stability of cycloheptatrienylium (**3**) and cycloheptatriene (**4**) group 6 complexes.[5a] Thus, most synthetic approaches to the dienyl ligand give **3** or **4** (Scheme 2), especially for chromium. For example, reaction of [(η^6-C_7H_8)Cr(CO)$_3$] **4a** with NO$^+$ or H$^+$ gives mostly decomposition plus small amounts of **3a**. The desired substitution or addition products are not formed.[8] Similar trends are seen for the synthesis of cyclohexadienyl Cr or Mo complexes, where only the highly substituted η-arenetricarbonylchromium complexes substitute NO$^+$ for CO.[9] In fact, the simple complex [(η^5-C_6H_7)Cr(CO)$_2$(NO)] has never been made.

Herein we report the synthesis of cycloheptadienyl derivatives of Cr and Mo in excellent yields via the addition of hydride to **4a,b** followed by either R$_3$SnCl (R = Me, Ph) or Diazald. The cyclohexadienyl analogs of the tin complexes described herein have recently been synthesized via hydride addition to (η-arene)Cr(CO)$_3$.[10]

Results and Discussion

Tricarbonyl(cycloheptadienyl)chromates and -molybdates. The dropwise addition of potassium triethylborohydride to dry diethyl ether solutions of [(η^6-C_7H_8)M(CO)$_3$] (**4a**, M = Cr; **4b**, M = Mo) at −78 °C

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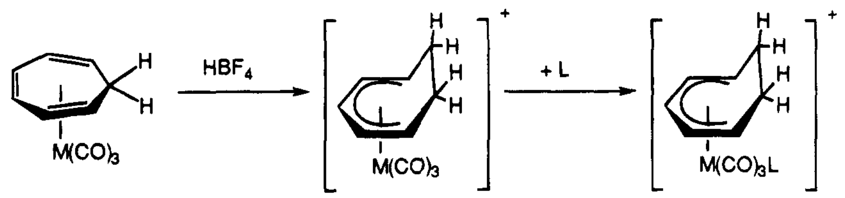
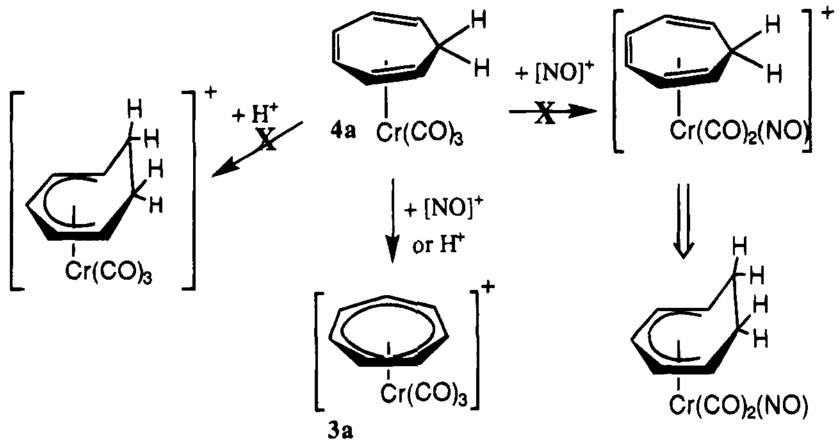
Scheme 1[a]

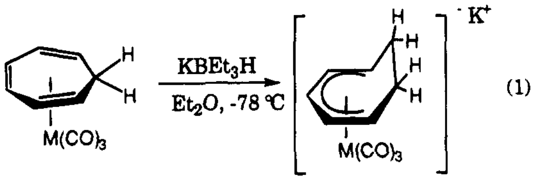


[a] M = Mo, W.

Scheme 2 Failed Routes to Cycloheptadienyl Cr Species



causes a gradual color change from red to yellow and formation of $[(\eta^5\text{-}C_7H_9)M(CO)_3]^-$ (**5a**, M = Cr; **5b**, M = Mo) (eq 1). The anions **5a,b** are highly air and temperature sensitive and convert readily to **4a,b** upon warming to room temperature. All attempts at isolating **5a,b** including metathesis with $[N(PPh_3)_2]Cl$, failed.



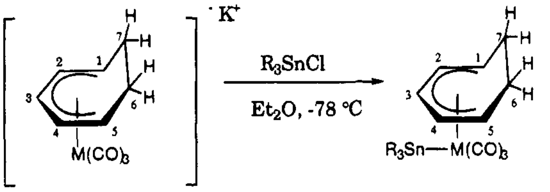
(1)

4a M = Cr
4b M = Mo

5a M = Cr
5b M = Mo

Complex **5a** was characterized by IR and ^{1}H and ^{13}C NMR spectroscopy (Table 1). The IR spectrum indicates three carbonyl ligands are present in the complex with absorbance bands indicative of an anionic species. The NMR spectra were measured at −80 °C and show signals consistent with an η^5-coordinated dienyl ring. In the proton NMR spectrum, five signals are observed in a 1:2:2:2:2 ratio from low field to high field. Three of the resonances between δ 3.3 and 5.0 are assigned to H(3), H(2,4), and H(1,5), and the remaining two signals between δ 1 and 2 are assigned to H(6,7) and H(6′,7′), respectively. In contrast, the ^{1}H NMR spectrum of the parent species **4a** shows a 2:2:2:1:1. The low-temperature ^{13}C{^{1}H} NMR spectrum confirmed the presence of the η^5-dienyl ring and shows five signals. Three are observed between δ 74 and 100, one of which, assigned to C(3), was half the intensity of the other two which were assigned as C(2,4) and C(1,5). The signal at higher field (δ 34) was assigned to C(6,7) and that at δ 244 to the CO ligands. Complex **5b** shows similar IR spectral data and reactivity to **5a**; however, definitive NMR data were not obtained due to its extreme sensitivity and contamination with traces of **4b**.

Trialkyltin Complexes. The anions **5a,b** react with R_3SnCl (R = Me, Ph) to give the new complexes **6a–d** (eq 2). Addition of an equimolar amount of the tin reagent to diethyl ether solutions of **5a,b** at −78 °C gives orange (**6a**) or yellowish orange (**6b–d**) solutions of tricarbonyl(trialkylstannyl)(η^5-cycloheptadienyl)chromium(II) and molybdenum(II) (**6a–d**).



(2)

5a M = Cr
5b M = Mo

6a M = Cr, R = Me
6b M = Cr, R = Ph
6c M = Mo, R = Me
6d M = Mo, R = Ph

The bimetallic complexes were isolated in excellent yields as orange or yellow solids and were characterized by IR and ^{1}H and ^{13}C NMR spectroscopy (Table 1). Complex **6b** was fully characterized by elemental analysis. The ^{1}H NMR spectra of **6a–d** are similar to that of **5a**, with, in the case of **6a**, three resonances between δ 3.5 and 5.1, in a 1:2:2 ratio typical of a η^5-coordinated dienyl ring. Two additional signals at ca. δ 1.2 (d) and 2.2 (m) are assigned to *exo*-H(6), H(7), and *endo*-H(6)′, H(7)′ respectively, based upon their chemical shifts and multiplicities. A singlet signal at high field (δ 0.40, 9H) shows two satellite peaks[11] and is assigned to the $SnMe_3$ group. The coupling constants ($^2J_{^{119}Sn-H}$, $^2J_{^{117}Sn-H}$) are 43.8 Hz and are similar to those found in the cyclopentadienyl analog ($^2J_{^{119}Sn-H} = 41.8$ Hz; $^2J_{^{117}Sn-H} = 46.0$ Hz).[11] The ^{13}C{^{1}H} NMR data for **6a** is consistent with the proton NMR spectrum and shows signals indicative

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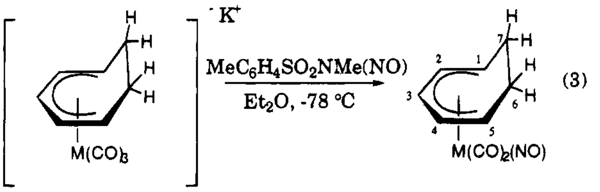
Table 1. ^{1}H and ^{13}C{^{1}H} NMR Spectral Data

complex	$\delta(^1H)^b$	$\delta(^{13}C)^{b,c}$
5a	1.37 (2H, d, H_6, H_7), 1.64 (2H, m, $H_{6'}$, $H_{7'}$), 3.37 (2H, t, H_1, H_5), 4.83 (2H, t, H_2, H_4), 4.99 (1H, t, H_3)^d	34.4 (C6, C7), 74.2 (C1, C5), 87.9 (C3), 99.9 (C2, C4), 244.1 (CO)^d
6a	0.49 (9H, t, $J_{^{119}Sn-H} = J_{^{117}Sn-H} = 43.8$ Hz, Me), 1.35 (2H, d, $J =$ 9.4 Hz, H_6, H_7), 2.08 (2H, m, $H_{6'}$, $H_{7'}$), 3.61 (2H, t, H_1, H_5), 3.99 (2H, t, $J = 7.0$ Hz, H_2, H_4), 5.08 (1H, t, H_3)	−5.9 (Me), 33.4 (C6, C7), 89.2 (C1, C5), 95.3 (C3), 96.2 (C2, C4), 231.7 (CO)
6b	1.27 (2H, d, H_6, H_7), 2.02 (2H, m, $H_{6'}$, $H_{7'}$), 3.59 (2H, t, H_1, H_5), 4.11 (2H, t, H_2, H_4), 5.85 (1H, t, H_3), 7.12 (3H, Ph), 7.57 (6H, Ph), 7.80 (6H, Ph)	33.3 (C6, C7), 91.2 (C1, C5), 95.2 (C3), 96.5 (C2, C4), 128.9 (Ph), 136.9 (Ph), 137.2 (Ph), 137.6 (Ph), 231.8 (CO)
6c	0.42 (9H, t, $J_{^{119}Sn-H} = J_{^{117}Sn-H} = 46.1$ Hz, Me), 1.50 (2H, d, $J =$ 8.6 Hz, H_6, H_7), 1.90 (2H, m, $H_{6'}$, $H_{7'}$), 3.86 (2H, t, $J =$ 3.2 Hz, H_1, H_5), 4.40 (2H, t, $J = 4.3$ Hz, H_2, H_4), 5.25 (1H, t, $J = 5.9$ Hz, H_3)	−6.1 (Me), 34.6 (C6, C7), 87.4 (C1, C5), 95.8 (C3), 100.0 (C2, C4), 221.3 (CO)
6d	1.36 (2H, d, $J = 9.0$ Hz, H_6, H_7), 1.78 (2H, m, $H_{6'}$, $H_{7'}$), 3.82 (2H, t, H_1, H_5), 4.43 (2H, t, $J = 5.9$ Hz, H_2, H_4), 5.75 (1H, t, H_3), 6.89 (3H, Ph), 7.49 (6H, Ph), 7.76 (6H, Ph)	34.5 (C6, C7), 89.0 (C1, C5), 96.5 (C3), 100.0 (C2, C4), 129.0 (Ph), 129.3 (Ph), 137.2 (Ph), 221.4 (CO)
7a	1.24 (2H, d, $J = 9.0$ Hz, H_6, H_7), 1.69 (2H, m, $H_{6'}$, $H_{7'}$), 3.45 (2H, t, H_1, H_5), 4.65 (2H, t, $J = 8.6$ Hz, H_2, H_4), 5.13 (1H, t, $J = 5.1$ Hz, H_3)	32.6 (C6, C7), 84.2 (C1, C5), 97.2 (C3), 105.5 (C2, C4), 221.3 (CO)
7a	0.72 (1H, dd, H_6 or H_7), 0.98 (1H, dd, H_7 or H_6), 1.07 (1H, dd, $H_{6'}$ or $H_{7'}$), 1.47 (1H, dd, $H_{7'}$ or $H_{6'}$), 2.64 (1H, dd, H_1 or H_5), 3.89 (1H, dd, H_5 or H_1), 4.37 (1H, dd, H_2 or H_4), 5.02 (1H, dd, H_4 or H_2), 5.34 (1H, dd, H3)^e	31.3 (C6 or C7), 32.3 (C7 or C6), 79.0 (C1 or C5), 90.1 (C5 or C1), 98.1 (C3), 103.3 (C2 or C4), 107.7 (C4 or C2), 225.9, 240.1 (CO)^e
7b	1.76 (2H, d, H_6, H_7), 2.16 (2H, s brd, $H_{6'}$, $H_{7'}$), 4.03 (2H, s brd, H_1, H_5), 5.32 (2H, s brd, H_2, H_4), 5.95 (1H, t, H_3)^f	32.4 (C6, C7), 84.7 (C1, C5), 97.1 (C3), 105.4 (C2, C4), 232 (CO)^f

[a] Labeling refers to eqs 1−4. [b] In C_6D_6 at 20 °C unless otherwise stated. [c] ^{1}H-decoupled spectra. [d] THF-d_8. [e] In acetone-d_6 at −60 °C. [f] In $CDCl_3$.

of a symmetric dienyl ring: three resonances between δ 88 and 96 {C(2,4), C(3), and C(1,5)}; a methyl group signal at δ −5.9, again with two sets of tin satellites ($^1J_{^{119}Sn-C}$ = 254 Hz; $^1J_{^{117}Sn-H}$ = 257 Hz). Only one carbonyl signal (δ 231) is observed which indicates that **6a** is either symmetric or highly fluxional. Complex **6c** has NMR and IR spectra similar to **6a** with typical tin−^{1}H and tin−^{13}C couplings (Table 1). The NMR spectra for **6b,d** were similar to those of **6a,c** except that the H(3) signal for **6b,d** is about 1 ppm downfield of that in **6a,c**. The IR spectra of the bimetallic species show three absorptions in the carbonyl stretching region distinctly different from those of the parent cycloheptadienyl anions **5a,b** and the cycloheptatriene complexes **4a,b**. The Ph_3Sn species, **6b,d**, are thermally and moderately air stable; however, the trimethyltin derivatives, **6a,c**, are sensitive to air and decompose within a few days at room temperature under a nitrogen atmosphere.

Nitrosyl Complexes. The anions **5a,b** react with equimolar amounts of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) in diethyl ether at −78 °C to give orange dicarbonylnitrosyl(η^5-cycloheptadienyl)chromium(0) and -molybdenum(0) (**7a,b**) (eq 3).



(3)

5a M = Cr
5b M = Mo

7a M = Cr
7b M = Mo

Complex **7a** was isolated in 73% yield (from **4a**) as an orange crystalline solid and was fully characterized by elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy (Table 1). At room temperature, the proton NMR spectrum shows four triplets and one doublet at δ 5.12 (H_3), 4.65 ($H_{2,4}$), 3.45 ($H_{1,5}$), 1.69 ($H_{6',7'}$), and δ 1.23 ($H_{6,7}$), respectively, due to the cycloheptadienyl ring protons. The H(1,5) signal is very broad and suggests a fluxional molecule. A variable-temperature NMR study was performed and the following observed. As the temperature is lowered to 268 K, the H(1,5) signal broadens, as does that for H(2,4). At 248 K, H(1,5) give rise to two separate but broad signals as do H(2,4) and H(6,7). At even lower temperatures, the new signals sharpen, and at 213 K, the spectrum consists of nine unique cycloheptadienyl ring proton signals consistent in a static molecule of C_1 symmetry. These data indicate that at room temperature the $Cr(CO)_2(NO)$ group rotates relative to the cycloheptadienyl ring averaging the signals for H(1) and H(5) as well as those for H(2) and H(4). At lower temperatures the rotation is slowed or stopped, and only one of the two rotamer types **A** or **B/C** (Figure 1) is observed. Rotamer **A** has C_s symmetry and would give rise to spectra with only three dienyl carbon or proton signals. Thus, we propose that the racemic mixture **B/C** is the low-temperature structure of **7a**.

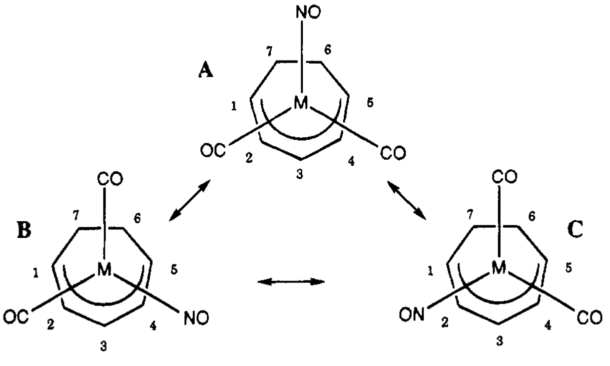


Figure 1. Possible rotamers for **7a**.

The room-temperature ^{13}C{^{1}H} spectrum of **7a** shows three signals between δ 84 and 105 {C(1,5), C(3), and C(2,4)} and one signal at δ 233.4 assigned to the carbonyl ligand. At lower temperatures, the same phenomenon as in the proton NMR is observed. Both signals for C(2,4) and C(1,5) begin to split at 268 K with complete decoalescence at 213 K. At this temperature two carbonyl signals and five dienyl sp^2 and two sp^3 carbon signals are observed. These data are again consistent with the dynamic process shown in Figure 1.

Similar dynamic NMR studies have been reported for a number of [(dienyl)M(CO)$_2$X] species.[12] For example, the proton NMR spectra of the cyclohexadienyl complexes [M(CO)$_2$(NO)(C$_6$H$_6$Ph)] (M = Mn, Re) show a total of six proton resonances at 198 K, compared to four signals at room temperature.[12] These authors attributed this behavior to the interconversion of similar rotamers and determined the preferred rotamer to be that in which the NO ligand eclipses C(2) as in **B**/**C** above.

The infrared spectral data for **7a,b** show a typical NO stretch at around 1700 cm^{-1} and two carbonyl absorptions to higher wavenumber. The molybdenum complex **7b** was isolated in 60% yield (from **4b**) as a yellow oil and was characterized by ^{1}H and ^{13}C NMR and IR spectroscopy. The spectroscopic data for **7b** is similar to that for **7a**, but no low-temperature studies were performed. Nevertheless, the broad signals in both room temperature spectra suggest that a similar dynamic process occurs for **7b**.

Conclusions

We have demonstrated the synthesis of a series of new (trialkylstannyl)tricarbonyl(cycloheptadienyl) and dicarbonyl(nitrosyl)(cycloheptadienyl) complexes of chromium and molybdenum. Addition of KBEt$_3$H to [M(CO)$_3$(η^6-C$_7$H$_8$)] (M = Cr, Mo) led to the anionic cycloheptadienyl species [M(CO)$_3$(η^5-C$_7$H$_9$)]$^-$ (M = Cr, Mo), which are highly air and temperature sensitive. The anions can be alkylated with R$_3$SnCl (R = Me, Ph) to form [(R$_3$Sn)M(CO)$_3$(η^5-C$_7$H$_9$] (M = Cr, Mo; R = Me, Ph). The substitution of NO$^+$ for CO in the anions [M(CO)$_3$(η^5-C$_7$H$_9$)]$^-$ gave [M(CO)$_2$(NO)(η^5-C$_7$H$_9$)] complexes. A variable-temperature NMR study of [Cr(CO)$_2$(NO)(η^5-C$_7$H$_9$)] was also performed which confirmed the low-temperature structure to be that in which the NO ligand eclipses the C(2) carbon of the dienyl ring. The analogous tungsten complexes [W(CO)$_2$(NO)(η^5-C$_7$H$_9$)] and [(R$_3$Sn)W(CO)$_3$(η^5-C$_7$H$_9$] (R = Me, Ph), although not reported here should also be accessible using the synthetic procedure described, particularly in light of the prior report on [W(CO)$_3$(η^5C$_7$H$_9$)]$^-$.[6c] Further chemistry of these new cycloheptadienyl complexes is currently under investigation.

Experimental Section

General Considerations. The preparation, purification and reactions of all complexes described were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. Manipulations of air-sensitive solids were performed inside a Braun MB 150 inert atmosphere glovebox containing a nitrogen atmosphere. Solvents were dried over Na/benzophenone (toluene, benzene, THF, diethyl ether), CaH$_2$ (*n*-hexane, *n*-pentane, CH$_2$Cl$_2$) or K$_2$CO$_3$ (acetone) and were freshly distilled prior to use. The 1.0 M solutions of potassium triethylborohydride and chlorotrimethyltin and the reagents chlorotriphenyltin, Diazald, tricarbonyl(cycloheptatriene)chromium(0) (**4a**) were used as supplied by the Aldrich Chemical Co. (Milwaukee, WI). Infrared spectra were recorded on a Nicolet 5ZDX FT instrument operated in the transmittance mode, and all NMR spectra were recorded on a Varian VXR-400S NMR Fourier transform spectrometer. Microanalyses were carried out by Robertson Microlit Laboratories (Madison, NJ). Chromatography was performed on Alumina (150 mesh, standard grade, activated, neutral, purchased from Aldrich) or silica gel (230–425 mesh, purchased from Fisher Scientific). Tricarbonyl(cycloheptatriene)molybdenum(0) was prepared using the literature procedure.[13]

General Procedure for the Preparation of Chromium and Molybdenum Cycloheptadienyl Complexes. (a) Tricarbonyl(η^5-cycloheptadienyl)chromate(0) (5a) and -molybdate(0) (5b). Potassium triethylborohydride (1.5 equiv of a 1.0 M solution in THF) was added dropwise by syringe to a stirred red solution of **4a** or **4b** (0.7–4.0 mmol) in diethyl ether (20–50 mL) at −78 °C. The resulting yellow suspensions were stirred for a further 20 min at −78 °C after which the IR spectra showed the anions **5a,b** as the only carbonyl containing species present. These anions could not be isolated due to decomposition at room temperature. K[(η^5-C$_7$H$_9$)Cr(CO)$_3$] (**5a**): yield 95% (based on IR spectrum); ν_{max} (CO)/cm^{-1} 1888, 1794, and 1758 (Et$_2$O). K[(η^5-C$_7$H$_9$)Mo(CO)$_3$] (**5b**): yield 95%; ν_{max} (CO)/cm^{-1} 1895, 1799, and 1743 (Et$_2$O).

(b) Tricarbonyl(trialkylstannyl)(η^5-cycloheptadienyl)chromium(II) and -molybdenum(II) (6a–d). Solutions of the anions **5a,b** were prepared as described in part (a) above and R$_3$SnCl (1.5 equiv; R = Me, 1.0 M solution in CH$_2$Cl$_2$; R = Ph, pure solid) was added at −78 °C. The solution quickly turned orange, and the mixture was allowed to slowly warm up to room temperature (ca. 90 min). Filtration through Celite (5 cm × 2.5 cm) and evaporation to dryness in vacuo gave the products as yellow solids. Multiple recrystallizations from *n*-hexane or CH$_2$Cl$_2$/*n*-hexane gave pure products.

Characterization of 5a by Low-Temperature NMR Spectroscopy. A dried sample of **4a** (0.050 g, 0.22 mmol) was dissolved in THF-*d*$_8$ (1 mL) inside the glovebox and filtered through Celite (1 cm) into a 5-mm NMR tube and sealed. The sample was frozen in liquid nitrogen, and potassium triethylborohydride (1.25 equivalents of a 1.0 M THF solution) was added by syringe. The frozen sample was quickly inserted into the precooled (−80 °C) NMR instrument, and the spectra were measured.

Preparation of [(η^5-C$_7$H$_9$)(Me$_3$Sn)Cr(CO)$_3$] (6a). Chlorotrimethyltin (1.3 mL of a 1.0 M solution, 1.3 mmol) was added to a stirred yellow suspension of **5a**, prepared as described earlier from **4a** (0.200 g, 0.88 mmol) and KBEt$_3$H (1.3 mmol), in diethyl ether (20 mL) at −78 °C. The resulting turbid orange solution was filtered through Celite and the solvent removed in vacuo. Extraction of the residue with *n*-hexane (50 mL) and evaporation to dryness gave **6a** as an orange powder. The product is both air and temperature sensitive but can be stored for up to 1 week under a nitrogen atmosphere in a freezer (−10 °C): yield (based on **4a**) 0.327 g, 95%; ν_{max} (CO)/cm^{-1} (hex), 1989 (vs), 1932 (s), and 1886 (vs).

Preparation of [(η^5-C$_7$H$_9$)(Ph$_3$Sn)Cr(CO)$_3$] (6b). Ph$_3$SnCl (0.635 g, 1.65 mmol) was added to a stirred yellow solution of **5a**, prepared as described earlier from **4a** (0.250 g, 1.10 mmol) and KBEt$_3$H (1.65 mmol), in diethyl ether (20 mL) at −78 °C. The resulting turbid yellow solution was filtered through Celite and the solvent removed in vacuo. Recrystallization of the residue from CH$_2$Cl$_2$/*n*-hexane gave **6b** as a yellow powder: yield (based on **4a**) 0.616 g, 97%; ν_{max} (CO)/cm^{-1} (hex), 1992 (vs), 1942 (s), and 1895 (vs). Anal. Calcd for C$_{28}$H$_{24}$CrSnO$_3$: C, 58.03; H, 4.15. Found: C, 57.98; H, 4.11.

Preparation of [(η^5-C$_7$H$_9$)(Me$_3$Sn)Mo(CO)$_3$] (6c). Chlorotrimethyltin (1.65 mmol) was added to a stirred yellow solution of **5b**, prepared as described earlier from **4b** (0.300 g, 1.10 mmol) and KBEt$_3$H (1.65 mmol), in diethyl ether (30 mL) at −78 °C. The resulting yellowish orange turbid solution was

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[12] Pike, R. D.; Alvosus, T. J.; Hallows, W. H.; Lennhoff, N. S.; Ryann, W. J.; Sweigart, D. A.; Bushweller, C. H.; Dimeglio, C. M.; Brown, J. H. *Organometallics* **1992**, *11*, 2841 and references therein.

[13] Eisch, J. J.; King, R. B. *Organomet. Synth.* **1965**, *1*, 125.

filtered through Celite and the solvent removed in vacuo. Extraction of the residue with *n*-hexane (50 mL) and evaporation to dryness gave **6c** as a bright yellow powder. Like **6a**, the product is both air and temperature sensitive but can be stored for up to 1 week under a nitrogen atmosphere in a freezer (−10 °C): yield (based on **4b**) 0.448 g, 93%; ν_{max} (CO)/cm^{-1} (hex) 2008 (vs), 1945 (s), and 1901 (vs).

Preparation of [(η^5-C_7H_9)(Ph_3Sn)Mo(CO)$_3$] (6d). Ph_3SnCl (0.424 g, 1.10 mmol) was added to a stirred yellow solution of **5b**, prepared as described earlier from **4b** (0.200 g, 0.74 mmol) and $KBEt_3H$ (1.10 mmol), in diethyl ether (20 mL) at −78 °C. The resulting turbid solution was filtered through Celite and the solvent removed in vacuo. Recrystallization of the residue from CH_2Cl_2/*n*-hexane gave **6d** as a yellow powder. Repeated attempts at obtaining satisfactory analyses failed due to presumed contamination with unreacted Ph_3SnCl: crude yield (based on **4b**) 0.449 g, 98%; ν_{max} (CO)/cm^{-1} (hex), 2013 (vs), 1956 (s), and 1911 (vs).

Preparation of Dicarbonylnitrosyl(η^5-cycloheptadienyl)chromium(0) [(η^5-C_7H_9)Cr(CO)$_2$(NO)] (7a). *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide, (Diazald) (0.278 g, 1.3 mmol) was added to a stirred yellow suspension of **5a**, prepared from **4a** (0.200 g, 0.88 mmol) and $KBEt_3H$ (1.3 mmol), in diethyl ether (20 mL) at −78 °C. The mixture was allowed to slowly warm to room temperature (90 min). The turbid red solution was then filtered through Celite and evaporated to dryness. The residue was chromatographed on alumina (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), eluting with *n*-hexane to give complex **7a** as an orange oil (the product elutes from the column before any unreacted **4a**). Recrystallization from *n*-pentane at −60 °C gave the product as an orange powder: yield from **4a** 0.148 g, 73%; ν_{max} (CO)/cm^{-1} (hex), 2023 (vs), 1973 (vs), and 1702 (vs). Anal. Calcd for $C_9H_9CrNO_3$: C, 46.75; H, 3.90; N, 6.06. Found: C, 46.73; H, 3.87; N, 6.01.

Preparation of [(η^5-C_7H_9)Mo(CO)$_2$(NO)] (7b). *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) (0.353 g, 1.65 mmol) was added to a stirred yellow solution of **5b**, prepared from **4b** (0.300 g, 1.1 mmol) and $KBEt_3H$ (1.65 mmol), in diethyl ether (30 mL) at −78 °C. Workup as for **7a** above gave **7b** as a yellow oil: yield from **4b** 0.182 g, 60%; ν_{max} (CO)/cm^{-1} (hex), 2022 (vs), 1973 (vs), and 1702 (vs).

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