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Cyclohexa- and Cycloheptadienyl Complexes of the Group 6 Metals

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The syntheses of a range of cyclohexadienyl- and cycloheptadienylchromium complexes are presented. Addition of nucleophiles to [(η-C$_6$H$_6$)Cr(CO)$_3$] and [(η^6-C$_7$H$_8$)Cr(CO)$_3$] followed by treatment with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) gave [(η^5-C$_6$H$_6$R)Cr(CO)$_2$(NO)] (**3a**, R = H; **3b**, R = $\overline{\mathrm{C(Me)S(CH_2)_3S}}$; **3c**, R = CHPh$_2$) and [($\eta^5$-C$_7H_8$R)Cr(CO)$_2$(NO)] (**9b**, R = $\overline{\mathrm{C(Me)S(CH_2)_3S}}$; **9c**, R = CHPh$_2$), respectively. Reaction of **3b** with phenyllithium followed by treatment with electrophiles [R′$_3$O]$^+$ (R′ = Me, Et) gave the carbene complexes [(η^5-C$_6$H$_6$R)(CO)(NO)Cr=C(OR′)Ph] (**5a,b**). Abstraction of hydride from **3a** and **9a** (R = H) gave the highly sensitive cations [(η-C$_6$H$_6$)Cr(CO)$_2$(NO)]$^+$ (**6**) and [(η^6-C$_7$H$_8$)Cr(CO)$_2$(NO)]$^+$ (**11**), respectively. The preparation of the triarylstannyl complexes [(η^5-C$_7$H$_8$R)M(CO)$_3$(SnPh$_3$)] (**10a**, M = Cr, R = $\overline{\mathrm{C(Me)S(CH_2)_3S}}$; **10b**, M = Cr, R = CHPh$_2$; **10c**, M = W, R = H) is presented. The X-ray crystal structure of [(η^5-C$_7$H$_9$)W(CO)$_3$(SnPh$_3$)]·0.5CH$_2$Cl$_2$ (**10c**) is reported and shows two different rotamers of **10c** as well as a single molecule of CH$_2$Cl$_2$ in the asymmetric unit.

Introduction

Complexes containing the η^5-cyclohexadienyl (η^5-C$_6$H$_7$) and η^5-cycloheptadienyl ligand (η^5-C$_7$H$_9$) have been reported for most transition metals and widely studied due to their application toward the stereospecific functionalization of six- and seven-membered rings.[1] In the case of cyclohexadienyl derivatives, the complexes [Fe(CO)$_3$(η^5-C$_6$H$_7$)]$^+$, and to a lesser extent [Mn(CO)$_3$(η^5-C$_6$H$_7$)], have attracted considerable attention, in part due to their ease of fabrication from [Fe(CO)$_3$(η^4-C$_6$H$_8$)] and [Mn(CO)$_3$(η-C$_6$H$_6$)]$^+$, respectively. In contrast, stable isolable η^5-cyclohexadienyl derivatives of chromium are rare, and with the exception of [Cr(CO)$_3$(SnPh$_3$)(η^5-C$_6$H$_6$R)] {R = H[2] and ($\overline{\mathrm{C(Me)S(CH_2)_3S}}$)[3] }, none have been prepared, even though the generation of cyclohexadienylchromates via nucleophilic addition to (η-arene)tricarbonylchromium(0) is well-known.[4] One surprising absence from the literature is the simple species [Cr(CO)$_2$(NO)(η^5-C$_6$H$_7$)]. This complex, reported herein for the first time, is closely related to the manganese and iron species mentioned above and is isoelectronic and isostructural with the cations [Mn(CO)$_2$(NO)(η^5-C$_6$H$_6$R)]$^+$ (R = Me, Ph) studied by Sweigart and coworkers.[5] These latter complexes were generated by the addition of [NO][BF$_4$] to [Mn(CO)$_3$(η^5-C$_6$H$_6$R)]; however, the reaction of [NO][BF$_4$] with chromium arene or cyclohexadienyl complexes has proved unsuccessful for the preparation of nitrosyl derivatives for all but the permethylated (η-arene)tricarbonylchromium species.[6]

A similar absence of cycloheptadienyl complexes of chromium exists, and we have recently reported routes to previously inaccessible group 6 cycloheptadienyl species by reaction of tricarbonyl(η^6-cycloheptatriene)chromium(0) and -molybdenum(0) with potassium triethylborohydride followed by treatment with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) or organotin chlorides (Scheme 1).[7] We now report the syntheses of a range of related chromium cyclohexadienyl complexes, including [Cr(CO)$_2$(NO)(η^5-C$_6$H$_7$)], using a similar methodology, as well as the preparation of functionalized cycloheptadienyl(nitrosyl)chromium and cycloheptadienyl(triphenylstannyl)metal group 6 complexes. We also present evidence for new carbene complexes of the (cyclohexadienyl)chromium manifold, as well as the hitherto unknown cations [Cr(CO)$_2$(NO)(η-C$_6$H$_6$)]$^+$ and [Cr(CO)$_2$(NO)(η^6-C$_7$H$_8$)]$^+$ via reaction of cyclohexa- and cycloheptadienyl Cr(CO)$_2$(NO) species with [CPh$_3$][PF$_6$].

Results and Discussion

Cyclohexadienyl−Nitrosyl Complexes. The anions [(η^5-C$_6$H$_6$R)Cr(CO)$_3$]$^-$ (**2a**,[2] R = H; **2b**,[3] R = $\overline{\mathrm{C(Me)S(CH_2)_3S}}$; **2c**,[4b] R = CHPh$_2$) react with equimolar amounts of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald)

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(1) See for example: (a) Pearson, A. J. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, p 637. (b) Pearson, A. J. In *Comprehensive Organic Synthesis*; Semmelhack, M. F., Ed.; Pergamon Press: Oxford, U.K., 1991; Vol. 4, p 663.

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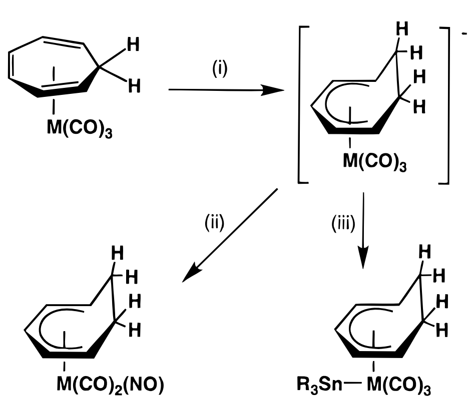
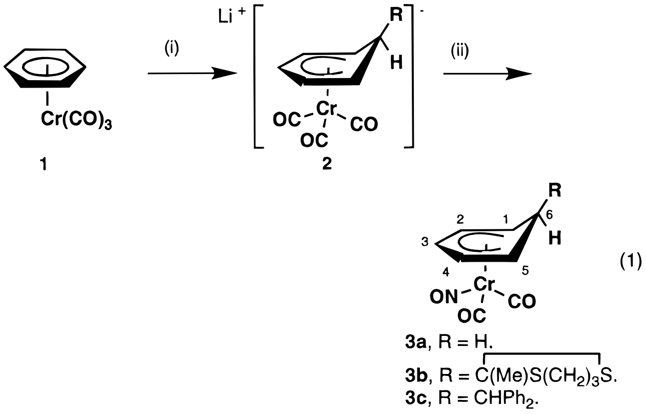
Scheme 1. Synthesis of Group 6 Cycloheptadienyl Derivatives[a]



[a] M = Cr, Mo; (i) KBHEt$_3$; (ii) Diazald; (iii) R$_3$SnCl, R = Me, Ph.

in tetrahydrofuran (THF) at −78 °C to give orange dicarbonyl(nitrosyl)(η^5-cyclohexadienyl)chromium(0) complexes (**3a**−**c**) (eq 1). These complexes can be separated



1 2

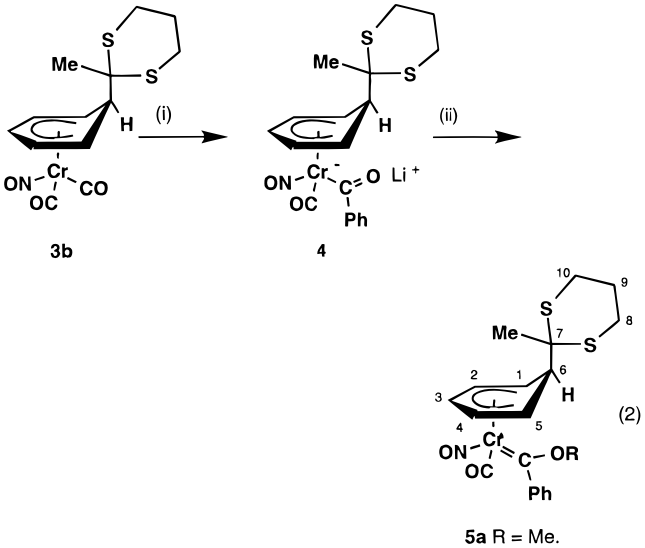
3a, R = H.
3b, R = $\overline{C(Me)S(CH_2)_3S}$.
3c, R = CHPh$_2$.

(i) Li[BHEt$_3$] or Li[$\overline{C(Me)S(CH_2)_3S}$] or Li[CHPh$_2$]; (ii) Diazald.

from unreacted [(η-C$_6$H$_6$)Cr(CO)$_3$] (**1**) using column chromatography on alumina with *n*-hexane as eluant. The pure crystalline solids are moderately stable in air, readily soluble in hexanes, and are isolated in moderate (**3a**) to excellent (**3b,c**) yields. The complexes were fully characterized by elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy (Table 1) and show the expected carbonyl and nitrosyl stretching vibrations in their IR spectra (e.g. **3a**: ν_{max}(CO) 2022, 1966, ν_{max}(NO) 1703 cm^{-1}). The ^{1}H and ^{13}C NMR data are consistent with a dynamic structure in which the Cr(CO)$_2$(NO) group rotates rapidly with respect to the dienyl moiety. This leads to the simple spectra reported in Table 1, in which the signals for H(1) and H(5) are averaged to a single sharp signal. No low-temperature studies were performed to probe this process, and this fluxionality is typical of such species as reported for the seven-membered-ring analog [(η^5-C$_7$H$_9$)Cr(CO)$_2$(NO)] (**9a**)[7] and the isostructural [(η^5-C$_6$H$_6$Ph)M(CO)$_2$(NO)]$^+$ (M = Mn, Re).[8]

Cyclohexadienyl−Carbene Complexes. The reactions of cyclohexadienyl complexes with nucleophiles have been widely studied and usually result in η^4-diene complexes if the dienyl species is cationic such as [(η^5-C$_6$H$_7$)Fe(CO)$_3$]$^{+\,1}$ or [(η^5-C$_6$H$_6$R)Mn(CO)$_2$(NO)]$^+$.[5] Similarly, under certain conditions the neutral complex [(η^5-C$_6$H$_7$)Mn(CO)$_3$] has been shown to add carbanions[9] or hydride[10] to the C$_6$ ring. In our laboratory, we have demonstrated that phenyllithium adds to the carbonyl carbon of [(η^5-C$_6$H$_7$)Mn(CO)$_3$] to give an acylmetalate, which can be converted to either $\eta^{3\text{-CH}}$-cyclohexenyl complexes by reaction with HBF$_4$·Et$_2$O or to carbene complexes by treatment with appropriate electrophiles (Scheme 2).[11]

Complex **3b** also reacts with phenyllithium to form acyl and carbene complexes (eq 2). Thus, addition of



3b **4**

5a R = Me.
5b R = Et.

(i) PhLi; (ii) [R$_3$O][BF$_4$]

phenyllithium to **3b** at −78 °C in diethyl ether gave a bright orange colored solution of the acylmetalate **4**. Complex **4** is both air and temperature sensitive and was identified only by IR spectroscopy and through its subsequent reaction with [R$_3$O][BF$_4$]. The IR spectrum in diethyl ether shows well-defined signals for the carbonyl and nitrosyl ligands at 1926 and 1563 cm^{-1}, respectively, consistent with an anionic complex, although the acyl stretch could not be observed due to solvent absorptions. Subsequent addition of [Me$_3$O][BF$_4$] or [Et$_3$O][BF$_4$] to CH$_2$Cl$_2$ solutions of **4**, respectively, gave carbene complexes **5a,b**, which were characterized using elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy (Table 1). Each shows a distinctive signal at ca. δ 345 in the ^{13}C NMR spectrum assigned to the carbene carbon and six unique signals for the cyclohexadienyl ring as expected with the presence of the asymmetric Cr(CO)(NO)(C{OR}Ph) unit. Complexes **5a,b** represent unusual examples of chiral transition-metal−carbene complexes, and the chirality of the metal center is manifested in the ^{1}H NMR spectrum of **5b** by two diastereotopic methylene hydrogens at δ 4.71 and 4.85 assigned to the ethoxy group. Compounds **5a,b** are isostructural with the manganese species shown in

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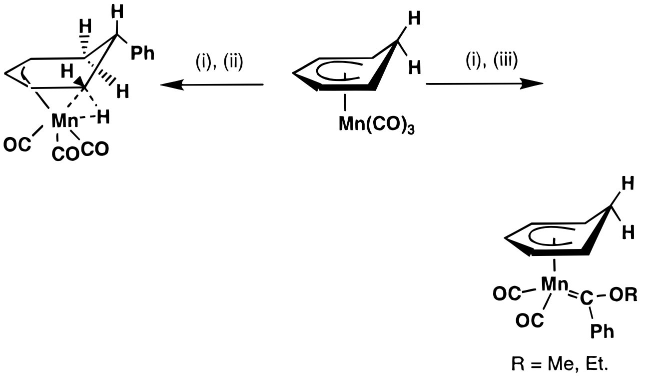
Table 1. ^{1}H and ^{13}C{^{1}H} NMR Spectral Data for Cyclohexadienyl Derivatives[a]

complex	$\delta(^{1}H)$	$\delta(^{13}C)^b$
3a	1.99 (1H, d, H_6), 2.38 (1H, m, $H_{6'}$), 3.15 (2H, dd, H_1, H_5), 5.06 (2H, t, H_2, H_4), 5.92 (1H, t, H_3)	24.1 (C6), 56.7 (C1, C5), 86.2 (C3), 104.5 (C2, C4), 233.7 (CO)
3b	1.15 (3H, s, Me), 1.85 (1H, m, H_9), 1.96 (1H, m, $H_{9'}$), 2.64 (2H, m, H_8, H_{10}), 2.73 (2H, m, $H_{8'}$, $H_{10'}$), 2.92 (1H, dd, H_6), 3.71 (2H, dd, $H_{1,5}$), 5.27 (2H, dd, $H_{2,4}$), 5.71 (1H, dd, H_3)	24.0 (Me), 25.1 (C9), 25.9 (C8,10), 39.8 (C6), 55.7 (C7), 63.1 (C1,5), 85.4 (C3), 104.4 (C2,4), 232.9 (CO)
3c	2.88 (1H, m, H_6), 3.05 (1H, d, C*H*Ph$_2$), 3.27 (2H, t brd, $H_{1,5}$), 5.01 (2H, t, $H_{2,4}$), 5.86 (1H, t, H_3), 7.0−7.25 (10H, m, Ph)	37.9 (C6), 61.9 (C7), 62.2, 62.5 (C1,5), 87.4 (C3), 102.1 (C2,4), 126.2, 126.5, 126.6, 127.9, 128.2, 128.6, 140.3, 143.4 (Ph), 232.9 (CO)
5a	1.08 (3H, s, Me_7), 1.90 (2H, m, H_9,$H_{9'}$), 2.5−2.6 (4H, m, H_8, $H_{8'}$, H_{10}, $H_{10'}$), 3.07 (1H, s brd, H_6), 3.41 (1H, s brd, H_1 or H_5), 3.80 (1H, s brd, H_1 or H_5), 4.45 (3H, s, O*Me*), 4.90 (1H, s brd, H_2 or H_4), 5.04 (1H, s brd, H_2 or H_4), 5.40 (1H, s brd, H_3), 7.10 (2H, s, Ph), 7.25 (3H, m, Ph)	23.5 (C9), 25.4 (C8), 25.8 (C10), 25.9 (Me7), 39.2 (C6), 56.1 (C7), 66.6 (O*Me*), 69.5 (C1 or C5), 70.7 (C1 or C5), 84.5 (C3), 109.2 (C2 or C4), 111.8 (C2 or C4), 125.0 (Ph), 127.8 (Ph), 129.3 (Ph), 152.1 (ipso Ph), 235.7 (CO), 345.5 (Cr=C)
5b	1.10 (3H, s, Me_7), 1.59 (3H, t, CH_2*Me*), 1.80 (1H, m, H_9), 1.85 (1H, m, $H_{9'}$), 2.5−2.65 (4H, m, H_8, $H_{8'}$, H_{10}, $H_{10'}$), 3.06 (1H, t, H_6), 3.44 (1H, brd, H_1 or H_5), 3.80 (1H, brd, H_1 or H_5), 4.71 (1H, m, C*H*$_2$Me), 4.85 (1H, m, C*H*$_2$Me), 4.95 (1H, t, H_2 or H_4), 5.04 (1H, t, H_2 or H_4), 5.42 (1H, t, H_3), 7.17 (2H, d, Ph), 7.28 (3H, m, Ph)	15.5 (OCH_2*Me*), 23.5, 25.1, 25.4, 25.6 (Me7, C8, C9, C10), 38.9 (C6), 55.8 (C7), 68.8 (C1 or C5), 70.0 (C1 or C5), 75.0 (O*C*H$_2$Me), 84.0 (C3), 108.5 (C2 or C4), 111.3 (C2 or C4), 124.5 (Ph), 127.3 (Ph), 128.3 (Ph), 151.6 (*ipso* Ph), 235.0 (CO), 343.2 (Cr=*C*)

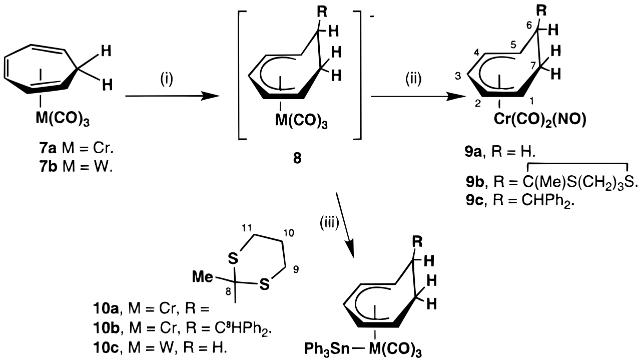
[a] Labeling refers to eqs 1 and 2; in $CDCl_3$. [b] ^{1}H-decoupled spectra.

Scheme 2[a]



[a] (i) PhLi; (ii) $HBF_4{\cdot}Et_2O$; (iii) $[R_3O]^+$.

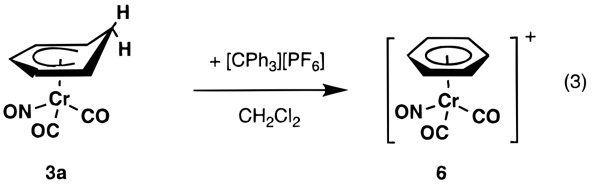
Scheme 3[a]



[a] (i) $K[BHEt_3]$ or $Li[\overline{C(Me)S(CH_2)_3S}]$ or $Li[CHPh_2]$; (ii) Diazald; (iii) Ph_3SnCl.

Scheme 2 and have remarkably similar ^{13}C NMR data. The major difference is a shift downfield for the signals of **5a,b** (e.g. Cr=*C*, δ 345, compared to Mn=*C*, δ 335), indicating the more electrophilic nature of the Cr(CO)(NO) fragment compared to the $Mn(CO)_2$ moiety. In contrast to the manganese system, the reaction of the acylmetalate **4** with proton sources gave no tractable products.

Complex **3a** reacts with triphenylcarbenium hexafluorophosphate to form a highly air sensitive cation $[(\eta\text{-}C_6H_6)Cr(CO)_2(NO)]^+$ (**6**, eq 3). Complex **6** is only sparingly soluble in CH_2Cl_2 and precipitates as a yellow solid from the reaction solution. It could be identified only from its IR spectrum {ν_{max}(CO) (CH_2Cl_2) 2084 (w), 2035 (w), ν_{max}(NO) 1774 (w) cm^{-1}}. Attempts to obtain solution NMR spectra of **6** in acetone, acetonitrile, or nitromethane lead to rapid decomposition as observed by the immediate formation of a deep red solutions with NMR resonances due to benzene and undefined metal−carbonyl-containing compounds, most probably solvated $Cr(CO)_2(NO)$ species. Samples of **6** are extremely air sensitive, and a satisfactory elemental analysis could not be obtained. Despite its simplicity and the fact that it is isostructural and isoelectronic with both $[(\eta\text{-}C_6H_6)Mn(CO)_3]^+$ and $[(\eta\text{-}C_6H_6)Cr(CO)_3]$ (**1**), complex **6** has not been reported elsewhere and typical synthetic approaches, such as treatment of **1** with $[NO][PF_6]$, have failed.[6]



3a **6** (3)

Cycloheptadienyl Complexes. As described earlier, treatment of tricarbonyl−η^6-cycloheptatriene complexes of group 6 metals with potassium triethylborohydride allows access to cycloheptadienyl derivatives either as the anions $[(\eta^5\text{-}C_7H_9)M(CO)_3]^-$ (M = Cr, Mo), the nitrosyl species $[(\eta^5\text{-}C_7H_9)M(CO)_2(NO)]$, or the organostannyl compounds $[(\eta^5\text{-}C_7H_9)M(CO)_3SnR_3]$ (Scheme 1).[7] Likewise, $[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$ (**7a**) reacts with nucleophiles to give anions $[(\eta^5\text{-}C_7H_8R)Cr(CO)_3]^-$ (**8**), which in turn react with equimolar amounts of Diazald to form $[(\eta^5\text{-}C_7H_8R)Cr(CO)_2(NO)]$ (**9b**, R = $\overline{C(Me)S(CH_2)_3S}$; **9c**, R = $CHPh_2$; Scheme 3). The products are crystalline solids and were fully characterized by elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy (Table 2). The ^{1}H and ^{13}C NMR data are again consistent with the fluxional process reported for **3a** and **9a**[7] although no detailed variable-temperature NMR spectral measurements were taken. The anions **8** also react with chlorotriphenyltin to yield the heterobimetallic complexes $[(\eta^5\text{-}C_7H_8R)Cr(CO)_3SnPh_3]$ (**10a,b**) which were similarly characterized (Scheme 3, Table 2).

The related complex $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ (**7b**) also undergoes a tandem reaction with potassium triethyl-

Table 2. ^{1}H and ^{13}C{1H} NMR Spectral Data for Cycloheptadienyl Derivatives[a]

complex	δ(^{1}H)	δ(^{13}C)[b]
9b	1.27 (1H, t, H_7), 1.39 (3H, s, Me), 1.92 (2H, m, H_{10}, $H_{10'}$), 2.11 (1H, m, $H_{7'}$), 2.79 (3H, m, H_9, $H_{9'}$, H_{11}), 2.91 (1H, m, $H_{11'}$), 3.37 (1H, t, H_6), 3.80 (1H, brd, H_1 or H_5), 4.1 (1H, brd, H_1 or H_5), 5.40 (2H, brd, H_2, H_4), 5.99 (1H, t, H_3)	24.0, 25.0, 26.4, 26.6, 27.5 (Me, C7, C9, C10, C11), 53.5 (C8), 57.9 (C6), 76.3 (brd, C1 or C5), 82.4 (brd, C1 or C5), 98.9 (C3), 105.6 (C2 or C4), 106.6 (C2 or C4), 232.8 (CO)[c]
9c	0.85 (1H, s brd, H_7), 1.69 (1H, s brd, $H_{7'}$), 3.12 (1H, d, H_8), 3.45 (1H, s brd, H_6), 3.73 (2H, s brd, $H_{1,5}$), 4.94 (1H, s brd, H_2 or H_4), 5.33 (1H, s brd, H_2 or H_4), 5.87 (1H, s brd, H_3), 7.1 (6H, m, Ph), 7.2 (4H, m, Ph)	32.8 (C7), 55.0 (C6), 62.5 (C8), 77.6 (brd, C1 or C5), 88.1 (brd, C1 or C5), 99.0 (C3), 104.6 (C2 or C4), 106.1 (C2 or C4), 126.6, 126.7, 127.3, 128.3, 128.8, 129.0 (Ph), 143.5, 144.5 (*ipso* Ph), 232.1 (brd, CO)
10a	1.24 (1H, s brd, H_7), 1.35 (3H, s, Me), 1.91 (2H, s brd, H_{10}, $H_{10'}$), 2.26 (1H, s brd, $H_{7'}$), 2.82 (3H, s brd, H_9, $H_{9'}$, H_{11}), 2.95 (1H, s brd, $H_{11'}$), 3.82 (1H, s brd, H_6), 3.94, 4.20 (2H, s brd, H_1, H_5), 4.34, 4.48 (2H, s brd, H_2, H_4), 6.12 (1H, s brd, H_3), 7.2−7.6 (15H, m, Ph)	24.3, 25.0, 26.6, 27.7, 28.0 (Me, C7, C9, C10, C11), 53.3 (C8), 59.4 (C6), 76.5, 82.2 (C1, C5), 88.5 (C3), 96.4, 96.8 (C2, C4), 128.9, 137.0, 141.7 (Ph), 231.0 (CO)
10b	0.87 (1H, m, H_7), 1.90 (1H, m, $H_{7'}$), 3.12 (1H, d, H_8), 3.81 (1H, t, H_1), 3.99 (1H, m, H_5), 4.02 (1H, m, H_4), 4.13 (1H, m, H_6), 4.49 (1H, m, H_2), 6.13 (1H, t, H_3), 7.28−7.67 (25H, m, Ph)	32.9 (C7), 56.8 (C6), 62.8 (C8), 84.8 (C1), 94.4 (C5), 95.3 (C3), 96.8 (C4), 97 (C2), 126.7−144.6 (Ph), 231 (CO)
10c	2.04 (2H, s brd, H_6, H_7), 2.14 (2H, s brd, $H_{6'}$, $H_{7'}$), 4.41 (2H, s brd, H_1, H_5), 4.97 (2H, t, H_2, H_4), 6.21 (1H, t, H_3), 7.32 (Ph), 7.57 (Ph)	34.8 (C6, C7), 83.1 (C1, C5), 97.8 (C2, C3, C4), 128.2, 136.9, 142.1 (Ph), 230.6 (CO)

[a] Labeling refers to Scheme 3; in $CDCl_3$. [b] ^{1}H-decoupled spectra. [c] Measured at −50 °C.

Table 3. Crystal Data for Compound 10c

formula	$C_{28}H_{24}O_3SnW\cdot{}^1/_2CH_2Cl_2$
fw	753.53
space group	$P\bar{1}$ (No. 2)
a, Å	9.382(5)
b, Å	16.387(7)
c, Å	17.782(7)
α, deg	76.82(3)
β, deg	87.34(5)
γ, deg	86.70(4)
V, Å^3	2656(3)
Z	4
D(calc), g cm^{-3}	1.884
μ(Mo Kα), cm^{-1}	54
radiation	Mo Kα (*λ* = 0.710 73 Å)
R(F), %[a]	6.13
$R_w(F)$, %[a]	7.07

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w(F) = \sum(w^{1/2}(|F_o| - |F_c|))/w^{1/2}(|F_o|)$.

borohydride and chlorotriphenyltin to form tricarbonylcycloheptadienyl(triphenylstannyl)tungsten(II) (**10c**) (Scheme 3). This species has been spectroscopically characterized (Table 2) and shows similar data to the Cr and Mo derivatives presented herein and earlier.[7] Furthermore, an X-ray crystallographic study was performed on **10c**·$0.5CH_2Cl_2$, (Tables 3 and 4; Figure 1), which reveals some unusual and interesting features of its solid-state structure. The asymmetric unit contains two molecules of **10c** and a single molecule of methylene chloride, leading to the $[(\eta^5\text{-}C_7H_9)W(CO)_3(SnPh_3)]\cdot0.5CH_2Cl_2$ formulation. Moreover the two molecules of **10c** are different rotamers, the first of which has the triphenyltin ligand beneath the dienyl portion of the seven-membered ring, with the second (labeled A in Figure 1) having the $SnPh_3$ moiety beneath the methylene groups. A clearer representation of the two rotamers is shown in Figure 2, and with the exception of this feature, they are structurally similar showing no significant differences in bond lengths and angles. Two related structures have been determined. in which a cyclodienyl ligand is coordinated to a $Cr(CO)_3(SnPh_3)$ group. In each of these cases, $[Cr(CO)_3(SnPh_3)(\eta^5\text{-}C_6H_6R)]$ ($R = \overline{C(Me)S(CH_2)_3S}$)[3] and $[Cr(CO)_3(SnPh_3)(\eta^5\text{-}C_{12}H_8O)]$,[2] the tin atom lies beneath the dienyl moiety. The room-temperature solution NMR and IR data for **10c** show no unusual features, suggesting there is rotation about the W−dienyl vector that interconverts the two rotamers.

Table 4. Selected Bond Distances and Angles for 10c

(a) Bond Distances (Å)

W(1)−Sn	2.813(2)	W(1A)−Sn(A)	2.821(2)
W(1)−C(1)	2.35(2)	W(1A)−C(1A)	2.33(2)
W(1)−C(2)	2.31(1)	W(1A)−C(2A)	2.33(2)
W(1)−C(3)	2.42(1)	W(1A)−C(3A)	2.41(2)
W(1)−C(6)	2.34(2)	W(1A)−C(6A)	2.35(2)
W(1)−C(7)	2.34(2)	W(1A)−C(7A)	2.32(2)
W(1)−C(8)	1.96(2)	W(1A)−C(8A)	2.04(2)
W(1)−C(9)	2.01(2)	W(1A)−C(9A)	1.96(2)
W(1)−C(10)	1.99(2)	W(1A)−C(10A)	1.96(3)
Sn−C(11)	2.16(1)	Sn(A)−C(11A)	2.17(1)
Sn−C(17)	2.16(1)	Sn(A)−C(17A)	2.13(1)
Sn−C(23)	2.16(2)	Sn(A)−C(23A)	2.18(1)
C(8)−O(1)	1.18(3)	C(8A)−O(1A)	1.09(2)
C(9)−O(2)	1.12(2)	C(9A)−O(2A)	1.15(2)
C(10)−O(3)	1.14(2)	C(10A)−O(3A)	1.15(3)
C(1)−C(2)	1.41(3)	C(1A)−C(2A)	1.47(3)
C(1)−C(7)	1.44(2)	C(1A)−C(7A)	1.39(3)
C(2)−C(3)	1.42(2)	C(2A)−C(3A)	1.39(3)
C(3)−C(4)	1.49(3)	C(3A)−C(4A)	1.48(4)
C(4)−C(5)	1.47(3)	C(4A)−C(5A)	1.41(4)
C(5)−C(6)	1.54(3)	C(5A)−C(6A)	1.51(4)
C(6)−C(7)	1.38(3)	C(6A)−C(7A)	1.41(4)
Cl(1)−C(29)	1.71(2)	Cl(2)−C(29)	1.66(2)

(b) Bond Angles (deg)

W(1)−C(8)−O(1)	178(2)	W(1A)−C(8A)−O(1A)	172(2)
W(1)−C(9)−O(2)	177(2)	W(1A)−C(9A)−O(2A)	179(2)
W(1)−C(10)−O(3)	173(1)	W(1A)−C(10A)−O(3A)	177(2)
C(1)−W(1)−C(3)	62.8(6)	C(1A)−W(1A)−C(3A)	63.8(8)
C(1)−W(1)−C(6)	64.1(6)	C(1A)−W(1A)−C(6A)	63.1(8)
C(2)−W(1)−C(6)	79.7(6)	C(2A)−W(1A)−C(6A)	79.0(7)
C(3)−W(1)−C(6)	71.0(6)	C(3A)−W(1A)−C(6A)	71.3(8)
C(2)−W(1)−C(7)	65.0(6)	C(2A)−W(1A)−C(7A)	65.8(8)
C(3)−W(1)−C(7)	77.2(6)	C(3A)−W(1A)−C(7A)	79.0(8)
C(8)−W(1)−C(9)	80.7(7)	C(8A)−W(1A)−C(9A)	103.9(8)
C(8)−W(1)−C(10)	81.3(7)	C(8A)−W(1A)−C(10A)	80.2(8)
C(9)−W(1)−C(10)	102.5(8)	C(9A)−W(1A)−C(10A)	80.2(9)
C(11)−Sn−C(17)	102.2(6)	C(11A)−Sn(A)−C(17A)	101.5(6)
C(11)−Sn−C(23)	106.9(6)	C(11A)−Sn(A)−C(23A)	107.5(6)
C(17)−Sn−C(23)	104.8(6)	C(17A)−Sn(A)−C(23A)	103.3(5)
W(1)−Sn−C(11)	109.9(4)	W(1A)−Sn(A)−C(11A)	111.4(4)
W(1)−Sn−C(17)	117.1(4)	W(1A)−Sn(A)−C(17A)	116.1(5)
W(1)−Sn−C(23)	114.9(4)	W(1A)−Sn(A)−C(23A)	114.9(4)
C(2)−C(1)−C(7)	123(2)	C(2A)−C(1A)−C(7A)	124(2)
C(1)−C(2)−C(3)	123(2)	C(1A)−C(2A)−C(3A)	123(2)
C(2)−C(3)−C(4)	122(2)	C(2A)−C(3A)−C(4A)	127(2)
C(3)−C(4)−C(5)	117(2)	C(3A)−C(4A)−C(5A)	116(2)
C(4)−C(5)−C(6)	111(2)	C(4A)−C(5A)−C(6A)	118(2)
C(5)−C(6)−C(7)	128(2)	C(5A)−C(6A)−C(7A)	125(2)
C(6)−C(7)−C(1)	117(1)	C(6A)−C(7A)−C(1A)	120(2)
Cl(1)−C(29)−Cl(2)	114(2)		

In contrast to the cyclohexadienyl species **3b**, none of the cycloheptadienyl complexes **9a**−**c** could be con-

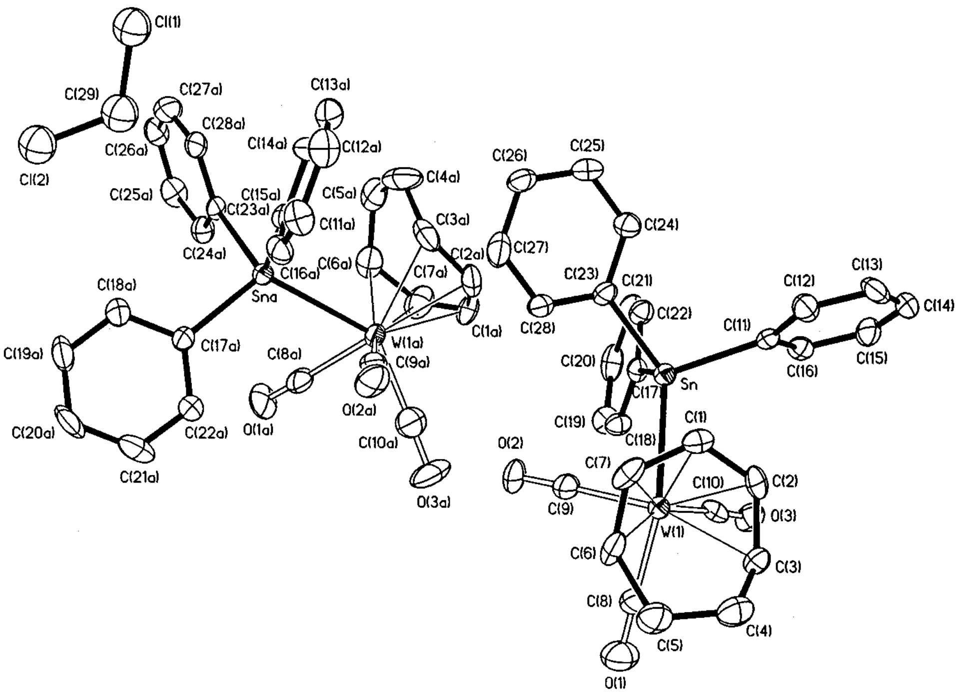


Figure 1. Molecular structure of **10c**·$^1/_2CH_2Cl_2$, showing both rotamers of **10c** and the methylene chloride of crystallization.

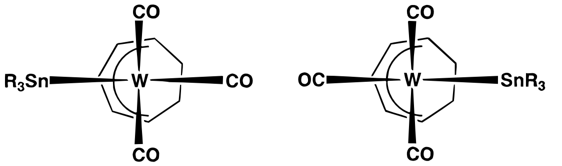
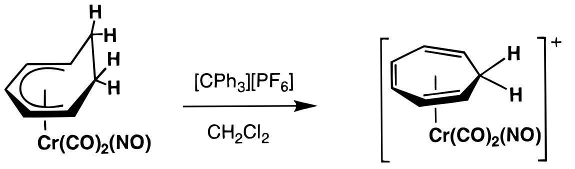


Figure 2. Rotamers of **10c** present in the X-ray crystal structure.

verted to carbene derivatives. Reaction of **9a**−**c** with phenyllithium resulted in the formation of an acylmetalate, as observed by IR spectroscopy [ν_{max}(CO) (ether), 1933, ν_{max}(NO) 1557 cm^{-1}], but upon treatment with electrophiles such as [Me_3O][BF_4] or Me_3SiCl, no tractable carbene complexes nor products derived from carbene species could be detected. This contrasts with the related manganese complexes [(η^5-C_7H_8R)Mn(CO)$_3$] in which interesting carbene−cycloheptadienyl adducts were formed from a migratory insertion of the carbene ligand into the Mn−dienyl bond.[12]

As was found for the cyclohexadienyl species **3a**, the cycloheptadienyl complex [(η^5-C_7H_9)Cr(CO)$_2$(NO)] (**9a**) undergoes hydride abstraction with [CPh_3][PF_6] to form the highly sensitive cation [(η^6-C_7H_8)Cr(CO)$_2$(NO)]$^+$ (**11**) (eq 4). Complex **11** also precipitates as a yellow solid



9a **11** (4)

from CH_2Cl_2 and like **3a** could only be identified from its IR spectrum, [ν_{max}(CO) (CH_2Cl_2), 2086 (w), 2061 (w), ν_{max}(NO) 1772 (w) cm^{-1}]. Attempts to obtain solution NMR spectra of **11** in polar solvents also resulted in deep red solutions consistent with decomposition of the complex. As previously described,[7] other potential routes to **11** give cycloheptatrienyl species, and thus, the reaction in eq 4 is the only one allowing actual isolation of **11**. Unfortunately both **6** and **11** are insoluble in all but the most polar media, in which they decompose, and unlike **1** or **7a** are not likely to be useful synthons.

Conclusions

We have demonstrated the synthesis of a series of new cyclohexa- and cycloheptadienyl complexes of chromium and tungsten. Tandem addition of nucleophiles and Diazald to [(η-C_6H_6)Cr(CO)$_3$] gave the first examples of dicarbonyl(nitrosyl)cyclohexadienylmetal complexes of chromium, which can be converted to chiral carbene complexes using a standard Fischer carbene synthesis.[13] Similarly, [M(CO)$_3$(η^6-C_7H_8)] (M = Cr, W) compounds react with nucleophiles and then Diazald or chlorotriphenyltin to give the analogous Cr(CO)$_2$(NO) or M(CO)$_3$-($SnPh_3$) cycloheptadienyl complexes, respectively. The tungsten complex [(Ph_3Sn)W(CO)$_3$(η^5-C_7H_9)] (**10c**) has been characterized by an X-ray diffraction study as its dichloromethane solvate. The structure is unusual in that two different molecules of **10c** and a single molecule of CH_2Cl_2 are present in the asymmetric unit. The two molecules of **10c** are different rotamers with respect to the orientation of the W(CO)$_3$($SnPh_3$) group. The reaction of the nitrosyl complexes [(η^5-C_6H_7)Cr(CO)$_2$(NO)] and [(η^5-C_7H_9)Cr(CO)$_2$(NO)] with [CPh_3]$^+$ leads to the previously inaccessible and highly sensitive [(η-C_6H_6)-Cr(CO)$_2$(NO)]$^+$ and [(η^6-C_7H_8)Cr(CO)$_2$(NO)]$^+$ cations.

Given the extensive chemistry of Cr(CO)$_3$(η-arene) complexes with nucleophiles,[4a] a variety of new and potentially useful dienyl complexes of chromium are accessible, either through the reaction of **1** or **7a** complexes with other carbanions or, alternatively, via

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[12] (a) Wang, C.; Sheridan, J. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3603. (b) Wang, C.; Lang, M.; Sheridan, J. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 3236.

[13] Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445.

nucleophilic addition to cations **6** and **11**. These reactions and further chemistry of the new dienyl complexes are currently under investigation.

Experimental Section

General Methods. 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_2Cl_2), or K_2CO_3 (acetone) and were freshly distilled prior to use. The 1.0 M solution of potassium triethylborohydride and the reagents chlorotriphenyltin, Diazald, and tricarbonyl(cycloheptatriene)chromium(0) (**7a**) were used as supplied by the Aldrich Chemical Co. (Milwaukee, WI). Triethyl- and trimethyloxonium salts were purchased from Alfa (Ward Hill, MA). 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). (Benzene)tricarbonylchromium(0) (**1**),[14] tricarbonyl(cycloheptatriene)tungsten(0) (**7b**),[15] and dicarbonyl(nitrosyl)cycloheptadienylchromium(0) (**9a**)[7] were prepared using the literature procedures.

3a. Lithium triethylborohydride (2 mL of a 1.0 M solution in THF, 2 mmol) was added dropwise to a stirred solution of (η-benzene)tricarbonylchromium(0) (**1**, 0.400 g, 1.87 mmol) in THF (40 mL) at room temperature followed by refluxing for 1 h. The mixture was cooled to −78 °C, and solid *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) (0.557 g, 2.6 mmol) was added. After being warmed to room temperature slowly (ca. 2 h), the turbid red solution was filtered through Celite. Removal of the solvent in vacuo and chromatography of the residue on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting with *n*-hexane gave analytically pure **3a** as an orange powder following removal of solvent in vacuo. Yield: 0.280 g, 42%. **3a:** ν_{max}(CO)/cm^{-1} (hex) 2022 (vs), 1966 (vs); ν_{max}(NO)/cm^{-1} 1703 (vs). Anal. Calcd for $C_8H_7CrNO_3$: C, 44.24; H, 3.23; N, 6.45. Found: C, 44.50; H, 3.26; N, 6.24.

3b. *n*-Butyllithium (0.48 mL of a 2.5 M solution in hexane) was added to a stirred solution of 2-methyl-1,3-dithiane (0.160 g, 1.19 mmol) in THF (10 mL) at −78 °C and then stirred at 0 °C for 1.5 h. The resulting solution of 2-lithio-2-methyl-1,3-dithiane was recooled to −78 °C and solid (η-benzene)tricarbonylchromium(0) (**1**, 0.200 g, 0.935 mmol) added. After being stirred for 0.5 h at 0 °C this mixture was recooled to −78 °C and solid *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) (0.332 g, 1.55 mmol) was added. Following slow warming to room temperature (ca. 2 h), the turbid red solution was filtered through Celite. Removal the solvent in vacuo and chromatography of the residue on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting with *n*-hexane gave pure **3b** as an orange powder following removal of solvent in vacuo. Yield: 0.322 g, 98%. **3b:** ν_{max}(CO)/cm^{-1} (hex) 2022 (vs), 1967(vs); ν_{max}(NO)/cm^{-1} 1708 (vs). Anal. Calcd for $C_{13}H_{15}CrNS_2O_3$: C, 44.70; H, 4.30; N, 4.01. Found: C, 44.83; H, 4.43; N, 3.86.

3c. *n*-Butyllithium (0.48 mL of a 2.5 M solution in hexane) was added to a stirred solution of diphenylmethane (0.3 mL, 1.78 mmol) in THF (14 mL) at −78 °C followed by stirring 1.5 h at 0 °C. The mixture was warmed to room temperature, and solid tricarbonyl(η-benzene)chromium(0) (**1**, 0.196 g, 0.916 mmol) was added. The solution was refluxed for 1.5 h and cooled to room temperature, solid *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) (0.70 g, 3.25 mmol) was added, and the solution was stirred for a further 2 h. The deep yellow solution was filtered through Celite, the solvent removed in vacuo and the residue chromatographed on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL) and eluting with *n*-hexane gave **3c** as an orange powder after evaporation of the solvents. Yield: 0.250 g, 70%. **3c:** ν_{max}(CO)/cm^{-1} (hex) 2021 (vs), 1967 (vs); ν_{max}(NO)/cm^{-1} 1704 (vs).

5a. Phenyllithium (0.34 mmol) in diethyl ether (10 mL) was added dropwise to a cooled (−78 °C) stirred solution of **3b** (0.100 g, 0.287 mmol) in diethyl ether (40 mL) over 15 min. The solution was allowed to warm to −40 °C over 2 h, during which time the yellow color gradually turned bright orange. Removal of the solvent in vacuo at 0 °C gave an orange oil which was dissolved in cold (0 °C) CH_2Cl_2 (50 mL), and excess $[Me_3O][BF_4]$ (0.127 g, 0.86 mmol) was added. Stirring for 1 h at 0 °C gave a dark red solution which was filtered through Celite. Removal the solvent in vacuo and chromatography of the residue on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting with 1:1 *n*-hexane/CH_2Cl_2 followed by CH_2Cl_2 gave **5a** as an orange powder following removal of solvent in vacuo. Yield: 0.070 g, 55%. **5a:** ν_{max}(CO)/cm^{-1} (CH_2Cl_2) 1967 (vs); ν_{max}(NO)/cm^{-1} 1654 (vs).

5b. Phenyllithium (1.1 mmol) in diethyl ether (10 mL) was added dropwise to a cooled (−78 °C) stirred solution of **3b** (0.320 g, 0.917 mmol) in diethyl ether (80 mL) over 15 min. The solution was allowed to warm to −40 °C over 2 h, during which time the yellow color gradually turned bright orange. Removal of the solvent in vacuo at 0 °C gave an orange oil which was dissolved in cold (0 °C) CH_2Cl_2 (50 mL), and excess $[Et_3O][BF_4]$ (3.0 mL of a 1.0 M CH_2Cl_2 solution) was added. Stirring for 1 h at 0 °C gave a dark red solution which was filtered through Celite. Removal the solvent in vacuo and chromatography of the residue on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting with 1:1 *n*-hexane/CH_2Cl_2 followed by CH_2Cl_2 gave pure **5b** as an orange powder following removal of solvent in vacuo. Yield: 0.372 g, 89%. **5b:** ν_{max}(CO)/cm^{-1} (hex) 1971 (vs); ν_{max}(NO)/cm^{-1} 1665 (vs). Anal. Calcd for $C_{21}H_{25}CrNS_2O_3$: C, 55.38; H, 5.49; N, 3.08. Found: C, 55.18; H, 5.56; N, 2.99.

6. Triphenylcarbenium hexafluorophosphate (0.089 g, 0.23 mmol) was added to a cooled (−78 °C) stirred solution of **3a** (0.05 g, 0.23 mmol) in CH_2Cl_2 (10 mL). The solution was allowed to warm to room temperature over 30 min, during which time a yellow precipitate formed. Removal of the mother liquor by cannula, washing with diethyl ether, and drying in vacuo gave **6** as a yellow powder. Yield: 0.045 g, 54%. **6:** ν_{max}(CO)/cm^{-1} (CH_2Cl_2) 2084 (w), 2035 (w); ν_{max}(NO)/cm^{-1} 1774 (w). The complex decomposes in air and polar solvents such as acetone, acetonitrile, and nitromethane and is only sparingly soluble in dichloromethane.

9b. *n*-Butyllithium (1.44 mL of a 2.5 M solution in hexane, 3.57 mmol) was added to a stirred solution of 2-methyl-1,3-dithiane (0.479 g, 3.57 mmol) in THF (10 mL) at −78 °C followed by stirring at 0 °C for 1.5 h. The mixture was cooled to −78 °C, and solid tricarbonyl(η^6-cycloheptatriene)chromium(0) (**7a**, 0.58 g, 2.54 mmol) was added. After being stirred for 0.5 h at 0 °C, this mixture was recooled to −78 °C and solid *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) (0.85 g, 1.2 equiv, 4.65 mmol) was added. After being slowly warmed to room temperature (ca. 2 h), the turbid red solution was filtered through Celite. Removal the solvent in vacuo and chromatography of the residue on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting with *n*-hexane gave pure **9b** as an orange powder after evaporation of the solvents. Yield: 0.654 g, 71%. **9b:** ν_{max}(CO)/cm^{-1} (hex) 2022 (vs), 1972 (vs), ν_{max}(NO)/cm^{-1} 1703 (vs). Anal. Calcd for $C_{14}H_{17}CrNS_2O_3$: C, 46.28; H, 4.68; N, 3.86. Found: C, 46.16; H, 4.86; N, 3.80.

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[14] *Inorg. Synth.* **1978**, *19*, 154.
[15] King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

9c. *n*-Butyllithium (0.48 mL of a 2.5 M solution in hexane) was added to a stirred solution of diphenylmethane (0.200 g, 1.19 mmol) in THF (10 mL) at −78 °C followed by stirring 1.5 h at 0 °C. The mixture was cooled to −78 °C, and solid tricarbonyl(η^6-cycloheptatriene)chromium(0) (**7a**, 0.195 g, 0.855 mmol) was added followed by stirring 0.5 h at 0 °C. This mixture was then recooled to −78 °C, and solid *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) (0.332 g, 1.55 mmol) was added. After being slowly warmed to room temperature (ca. 2 h), the turbid red solution was filtered through Celite. Removal the solvent in vacuo and chromatography of the residue on an alumina column (30 cm × 2.5 cm), loading with CH_2Cl_2 (2 mL), and eluting with *n*-hexane gave pure **9c** as an orange powder after evaporation of the solvents. Yield: 0.213 g, 63%. **9c:** ν_{max}(CO)/cm^{-1} (hex) 2022 (vs), 1973 (vs), ν_{max}(NO)/cm^{-1} 1702 (vs). Anal. Calcd for $C_{22}H_{19}CrNO_3$: C, 66.50; H, 4.79; N, 3.53. Found: C, 66.25; H, 4.79; N, 3.52.

10a. *n*-Butyllithium (0.48 mL of a 2.5 M solution in hexane) was added to a stirred solution of 2-methyl-1,3-dithiane (0.160 g, 1.19 mmol) in THF (10 mL) at −78 °C followed by stirring at 0 °C for 1.5 h. The mixture was cooled to −78 °C, and solid tricarbonyl(η^6-cycloheptatriene)chromium(0) (**7a**, 0.21 g, 0.921 mmol) was added. After being stirred for 0.5 h at 0 °C, this mixture was recooled to −78 °C and Ph_3SnCl (0.69 g, 1.5 equiv, 1.79 mmol) was added. After the mixture was slowly warmed to room temperature (ca. 2 h), the yellow solution was filtered through Celite. The solvent was removed in vacuo and the yellow residue washed with cold pentane. Dissolution in THF (2 mL) followed by precipitation with hexane (10 mL) and cooling to −20 °C gave the product **10a** as a yellow solid. Yield: 0.66 g, 92%. **10a:** ν_{max}(CO)/cm^{-1} (hex) 1983 (vs), 1932 (vs), 1887 (vs). Anal. Calcd for $C_{33}H_{32}CrSnS_2O_3$: C, 55.71; H, 4.53. Found: C, 56.13; H, 4.51.

10b. *n*-Butyllithium (0.48 mL of a 2.5 M solution in hexane) was added to a stirred solution of diphenylmethane (0.200 g, 1.19 mmol) in THF (10 mL) at −78 °C followed by stirring at 0 °C for 1.5 h. The mixture was cooled to −78 °C, and solid tricarbonyl(η^6-cycloheptatriene)chromium(0) (**7a**, 0.21 g, 0.921 mmol) was added. After being stirred for 0.5 h at 0 °C, this mixture was recooled to −78 °C and Ph_3SnCl (0.69 g, 1.5 equiv, 1.79 mmol) was added. After the mixture was slowly warmed to room temperature (ca. 2 h), the yellow solution was filtered through Celite. The solvent was removed in vacuo and the yellow residue washed with cold pentane. Dissolution in THF (2 mL) followed by precipitation with hexane (10 mL) and cooling to −20 °C gave the product **10b** as a yellow solid. Yield: 0.606 g, 88%. **10b:** ν_{max}(CO)/cm^{-1} (pentane) 1991 (vs), 1941 (vs), 1897 (vs). Anal. Calcd for $C_{41}H_{33}CrSnO_3$: C, 66.15; H, 4.44. Found: C, 65.90; H, 4.57.

10c. Potassium triethylborohydride (0.34 mL of a 1.0 M solution in THF, 0.34 mmol) was added dropwise by syringe to a stirred solution of $[W(CO)_3(\eta^6\text{-}C_7H_8)]$ (**7b**, 0.10 g, 0.28 mmol) in THF (10 mL) followed by stirring for a further 20 min at −78 °C. Solid Ph_3SnCl (0.184 g, 0.48 mmol) was added to the suspension. After being warmed to room temperature (ca. 2 h), the turbid red solution was filtered through Celite. Removal of the solvent in vacuo and extraction of the residue with *n*-hexane/CH_2Cl_2 (1:3) gave **10c** as a yellow powder after evaporation of the solvents. Yield: 0.187 g, 94%. **10c:** ν_{max}(CO)/cm^{-1} (hex) 2011 (vs), 1962 (vs), 1907 (vs). Anal. Calcd for $C_{28}H_{24}WSnO_3\cdot 0.5CH_2Cl_2$: C, 45.42; H, 3.34. Found: C, 45.42; H, 3.42.

11. Triphenylcarbenium hexafluorophosphate (0.039 g, 0.10 mmol) was added to a cooled (−78 °C) stirred solution of **9a** (0.023 g, 0.10 mmol) in CH_2Cl_2 (7 mL). The solution was allowed to warm to room temperature over 30 min, during which time a yellow precipitate formed. Removal of the mother liquor by cannula, washing with diethyl ether, and drying in vacuo gave **11** as a yellow powder. Yield: 0.020 g, 54%. **11:** ν_{max}(CO)/cm^{-1} (CH_2Cl_2) 2086 (w), 2061 (w); ν_{max}(NO)/cm^{-1} 1772 (w). Like **6**, complex **11** decomposes in air and polar solvents such as acetone, acetonitrile, and nitromethane and is sparingly soluble in dichloromethane.

X-ray Diffraction Study. Crystallographic data are collected in Table 3. A clear yellow parallelepiped (0.76 × 0.72 × 0.60 mm) of **10c** was mounted on a glass fiber with epoxy. Twenty-four automatically centered reflections ($7.4 < \theta < 19.7°$) were used to refine the cell parameters using graphite-monochromated Mo Kα (0.710 73 Å) radiation on a Siemens P4 diffractometer. Data were collected using the $\theta-2\theta$ mode with θ scan width = 1.0° + Kα separation, θ scan speed 10−60° min^{-1}; 10 012 reflections were measured ($1.5 < \theta < 25°$, $\pm h,\pm k,+l$), of which 9382 were unique (merging $R = 0.058$) after absorption correction (face-indexed numerical) (max, min transmission factors = 0.1166, 0.0253) giving 6383 with $F > 4\sigma(F)$. The selected crystal had a linear absorption coefficient μ(Mo Kα) = 54.0 cm^{-1}. Patterson maps were used to find the W and Sn atoms in each of the two molecules in the asymmetric unit, followed by difference maps to find all other non-hydrogen atoms. One molecule of CH_2Cl_2 was found per asymmetric unit. Full-matrix least-squares refinement was employed with all non-hydrogen atoms anisotropic and hydrogens in calculated positions and riding on the atoms to which they are bound, with U_{iso} for the methine H's (0.0523 Å^2), U_{iso} for the methylene H's (0.1250 Å^2) and U_{iso} for the phenyl H's (0.0638 Å^2). All the atoms of the methylene chloride of crystallization were given fixed values of 0.10 for their isotropic temperature factors. The weighting scheme $w = 1/[\sigma^2(F) + 0.0005F^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. Final R and R' values are 0.0613 and 0.0707, respectively, goodness of fit = 1.57, maximum $\Delta/\sigma = 0.116$, largest difference peak = 3.67, and largest difference hole = −4.18 e Å^3. Data collection, cell refinement, data reduction, structure solution, structure refinement, molecular graphics, and preparation of material for publication used SHELXTL/PC.[16,17]

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Supporting Information Available: Complete tables of X-ray structural data, including positional and *U* parameters, anisotropic thermal parameters, and bond lengths and angles for **10c** (8 pages). This material is available on the Internet, is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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