6434 *J. Am. Chem. Soc.* **1993**, *115*, 6434–6435

Synthesis of Tricarbonyl(η^5-cyclohexadienyl)chromium Complexes *via* Nucleophilic Addition of Hydride on (η^6-Arene)tricarbonylchromium Complexes

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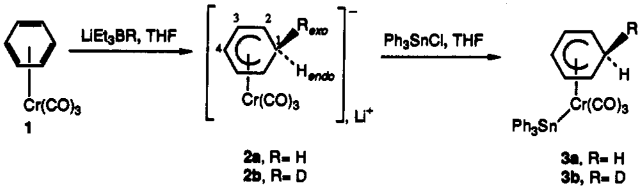
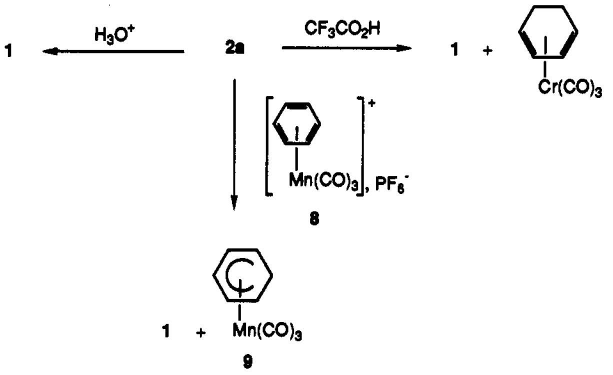
Received February 16, 1993

(η^6-Arene)tricarbonylchromium complexes have significant applications in organic synthesis. We have recently described their important role in the asymmetrical formation of (η^6-benzaldehyde)tricarbonylchromium complexes[1] as well as their role in a new method of cleavage of aromatic carbon–oxygen,[2a] carbon–halogen,[2b] and carbon–nitrogen[2c,d] bonds of alkoxy, halogeno, and dimethylamino (η^6-arene)tricarbonylchromium complexes. In these cases, the hypothetical formation of an anionic η^5-cyclohexadienyl intermediate has been involved to explain the *exo* addition of the hydride anion to the complexed arene ligand and the formation of the observed products *via ipso*,[3] *cine*,[4] and *tele-meta*[5] nucleophilic aromatic substitution reactions. Herein, we report the synthesis and the structural characterization of three cyclohexadienyl derivatives which have been obtained after addition of $LiEt_3BR$ on (η^6-benzene)tricarbonylchromium (R = H, D) and (η^6-dibenzofuran)tricarbonylchromium (R = H) complexes, clearly establishing the reaction mechanism of hydride on such complexes.

Scheme I



Scheme II



Treatment of (η^6-benzene)tricarbonylchromium (**1**) with $LiEt_3BR$ (R = H, D) (1 equiv) in THF (67 °C, 30 min) gives the lithium salt of the anionic (η^5-cyclohexadienyl)tricarbonylchromium complex **2a** (R = H) and **2b** (R = D) (97% yield) (Scheme I).

After removal of THF under reduced pressure, complexes **2a** and **2b** are recrystallized with benzene in a nitrogen drybox to give amorphous yellow powders. ^1H and ^{13}C NMR data of complex **2a**[6] are similar to those described for (η^5-cyclohexadienyl)$M(CO)_3$ complexes[7,8] (M = Cr, W–Me, Fe^+, Mn). The ^1H NMR spectrum of complex **2a** in THF-d_8 shows expected signals at 5.43 (H_4), 4.74 ($H_{3,5}$), 2.85 (H_{1endo}), 2.58 (H_{1exo}), and 2.53 ppm ($H_{2,6}$) whose multiplicities can be readily interpreted. The H_{1exo} resonance appears as a doublet which results from a ^1J(11 Hz) geminal coupling with H_{1endo}. The latter one appears as a doublet of a triplet, which results from combined ^1J(11 Hz) and ^3J(6 Hz) couplings of H_{1endo} respectively with H_{1exo} and $H_{2,6}$. IR spectroscopy of complex **2a** in THF shows three large absorption bands confirming the loss of local C_3 symmetry of the $Cr(CO)_3$ moiety.[6] Complex **1** is recovered by treatment of a THF solution of complex **2a** with acidic water. However, treatment of a THF-d_8 solution of complex **2a** in a sealed NMR tube by CF_3CO_2H at −78 °C leads to a deep red solution which turns rapidly to orange-yellow when warmed to room temperature. The ^1H NMR spectrum indicates some recovery of complex **1** but also the formation of an η^4-cyclohexadiene complex whose signals are in agreement with published data[9] (Scheme II).

Reaction of complexes **2a** and **2b** with triphenyltinchloride (1.1 equiv., THF, −78 °C, 1 h) yields the bimetallic neutral

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(6) Complex **2a**: IR (THF) ν(CO) 1710, 1800, 1880; ^1H NMR (200 MHz, THF = d_8) δ 2.53 (t, $H_{2,6}$, ^3J = 6 Hz), 2.58 (d, H_{1exo}, ^1J = 11 Hz), 2.85 (dt, H_{1endo}, ^1J = 11 Hz, ^3J = (6 Hz), 4.74 (t, $H_{3,5}$, ^3J = 6 Hz), 5.43 (t, H_4, ^3J = 6 Hz); ^{13}C NMR (50 MHz, THF-d_8) δ 27.3 (C_1), 46.3 ($C_{2,6}$), 76.4 (C_4), 98.7 ($C_{3,5}$), 244.2 (CO). Complex **3a**: mp 160 °C dec; IR (THF) ν(CO) 1880, 1935, 1965; ^1H NMR (200 MHz, C_6D_6) δ 1.60 (d, H_{1exo}, ^1J = 13 Hz), 2.43 (dt, H_{1endo}, ^1J = 13 Hz, ^3J = 6 Hz), 2.60 (t, $H_{2,6}$, ^3J = 6 Hz), 3.72 (t, $H_{3,5}$, ^3J = 5 Hz), 6.06 (t, H_4, ^3J = 5 Hz), 7.10–7.86 (m, $Sn(C_6H_5)_3$); ^{13}C NMR (50 MHz, C_6D_6) δ 26.1 (C_1), 60.1 ($C_{2,6}$), 85.3 (C_4), 95.3 ($C_{3,5}$), 129.1 (d, $C_{4'}$, $^4J_{C-Sn}$ = 5 Hz), 130.0 (d, $C_{3',5'}$, ^3J = 58 Hz), 137.2 (d, $C_{2',6'}$, ^2J = 34 Hz), 139.5 (d, $C_{1'}$, ^1J = 323 Hz), 231.8 (CO); ^{119}Sn NMR (93 MHz, C_6D_6) δ 74.7(m). Anal. Calcd for $C_{27}H_{22}CrO_3Sn$: C, 52.53; H, 4.05; Cr, 8.05; Sn, 16.16. Found: C, 52.17; H, 3.91; Cr, 7.94; Sn, 16.29. Complex **3b**: ^1H NMR (200 MHz, C_6D_6) δ 2.35 (t, H_{1endo}, ^3J = 6 Hz), 2.56 (t, $H_{2,6}$, ^3J = 6 Hz), 3.70 (t, $H_{3,5}$, ^3J = 5 Hz), 6.04 (t, H_4, ^3J = 5 Hz), 7.10–7.90 (m, $Sn(C_6H_5)_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.8 (t, C_1, $^1J_{C-D}$ = 20 Hz), 59.8 ($C_{2,6}$), 85.5 (C_4), 95.3 ($C_{3,5}$), 128.0–142.0 ($C_{1'-6'}$), 231.3 (CO). Anal. Calcd for $C_{27}H_{21}DCrO_3Sn$: C, 57.28; H + $^1/_2$D, 3.92. Found: C, 57.32; H + $^1/_2$D, 3.91. Complex **5**: IR (THF) ν(CO) 1725, 1820, 1900; ^1H NMR (200 MHz, THF-d_8) δ 2.63 (t, H_2, ^3J = 6 Hz), 2.76 (d, H_{1exo}, ^1J = 11 Hz), 3.59 (m, H_{1endo}), 4.57 (t, H_3, ^3J = 5 Hz), 5.63 (d, H_4, ^3J = 5 Hz), 7.20–6.69 (m, H_{6-9}). Complex **6**: IR ($CHCl_3$) ν(OH) 3560, ν(CO) 1905, 1975; ^1H NMR ($(CD_3)_2CO$) δ 5.70 (m, $H_{2,4,6}$), 6.06 (m, $H_{3,5}$), 6.88–7.44 (m, $H_{2',3',4',5'}$), 9.15 (OH). Anal. Calcd for $C_{15}H_{10}CrO_4$: C, 58.82; H, 3.26. Found: C, 58.68; H, 3.31. Complex **7**: IR (THF) ν(CO) 1885, 1925, 1965; ^1H NMR (200 MHz, $CDCl_3$) δ 2.80 (d, H_{1exo}, ^1J = 14 Hz), 3.42 (t, H_2, ^3J = 7 Hz), 3.88 (t, H_3, ^3J = 5 Hz), 4.06 (dd, H_{1endo}, ^1J = 14 Hz, ^3J = 6 Hz), 6.71 (d, H_4, ^3J = 5 Hz), 7.27 (m, H_{6-9}), 7.37–7.65 ($H_{2'-6'}$); ^{13}C NMR (50 MHz, $CDCl_3$, rt) δ 27.9 (C_1), 60.8 (C_2), 66.7 (C_4), 89.7 (C_3), 111.2–127.7 (C_{6-9}), 127.9 (C_{9a}), 128.4–142.8 ($C_{1'-6'}$-$C_{4a,1a}$), 156.7 (C_{5a}), 231.0 (m, CO). Anal. Calcd for $C_{33}H_{24}CrO_4Sn$: Cr, 7.86; Sn, 18.95. Found: Cr, 7.79; Sn, 18.86.

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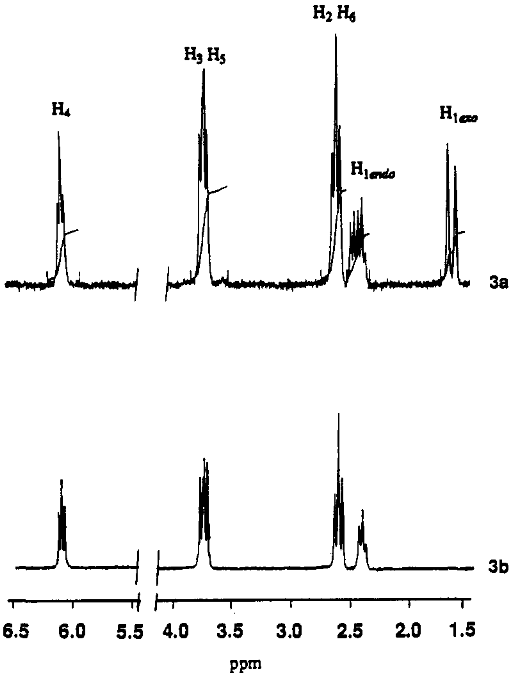
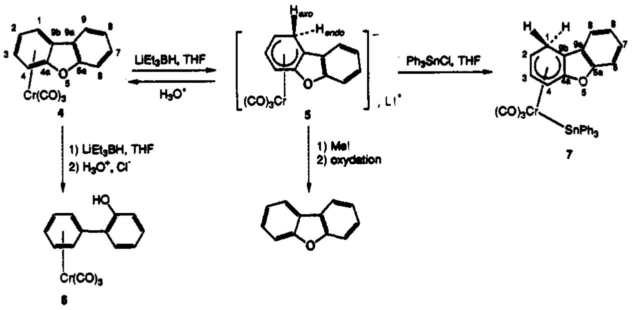


Figure 1. ^1H NMR spectra for complexes **3a** and **3b** in C_6D_6.

Scheme III



complexes **3a** and **3b** (53% yield) containing a covalent Cr–Sn bond[10] (Scheme I). The ^{119}Sn NMR spectrum of complex **3a**[6] indicates a broad signal at 74.7 ppm, in good agreement with literature data,[11] and the ^1H NMR spectrum of this complex shows a 0.83-ppm difference in chemical shifts between the H_{exo} and H_{endo} resonances in C_6D_6. Complex **3b** ^1H and ^{13}C NMR data (Figure 1) confirm that the nucleophilic addition occurred on the *exo* side of the complexed arene: indeed the H_{1exo} resonance at 1.60 ppm is absent and the C_1 resonance at 25.8 ppm is a triplet with a $^1J_{C-D} = 20$ Hz.[6]

Treatment of (η^6-dibenzofuran)tricarbonylchromium **4** with $LiEt_3BH$ (1 equiv) in THF yields the anionic adduct **5** (67 °C, 0.5 h, 55% yield) as a yellow amorphous powder[6] (Scheme III). The same reaction carried out with $LiEt_3BH$ (2 equiv) at 67 °C for 48 h affords, after hydrolysis, the biphenyl derivative **6**[6] which results from the cleavage of the C_{Ar}–O bond *via* an *ipso* S_NAr reaction (75% yield). Free dibenzofuran is recovered by treating complex **5** with methyl iodide, indicating that the anionic intermediate **5** cannot be trapped by this electrophile. However, treatment of complex **5** with triphenyltin chloride (1.1 equiv, THF, −78 °C, 1 h) gives complex **7** (Scheme III).

The ^1H NMR spectrum of complex **7**[6] in $CDCl_3$ shows the H_4 resonance at 6.71 ppm at a very low field compared to the data

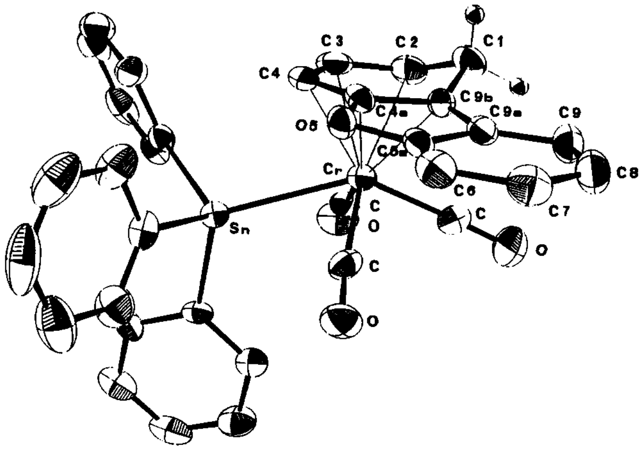


Figure 2. ORTEP diagram of compound **7**.

obtained for complexes **3a** and **3b** and a 1.3-ppm difference of chemical shifts between H_{exo} and H_{endo} resonances. The ^{13}C NMR spectrum of complex **7**[6] shows a large unresolved signal in the carbonyl resonance zone.[6] Those surprising effects are probably due to a high barrier to rotation of the bulky $(CO)_3Cr–SnPh_3$ moiety around the axis of the η^5-disubstituted cyclohexadienyl ligand. The structure of complex **7** has been confirmed by X-ray crystallographic measurements (Figure 2) and allows us to ascertain that hydride addition on complex **4** has occured only at the C-1 meta position with respect to the oxygen atom.

It is worth noting that formation of complex **5** sheds light on the mechanism of hydride addition to complex **4**. Indeed this meta addition product **5** is formed under reversible conditions, and it undergoes at a longer reaction time an isomerization that ultimately leads to C–O bond *ipso* cleavage and formation of complex **6**. This reversibility explains the recovery of complex **1** by treatment of complex **2a** with acidic water and the formation of free dibenzofuran by treatment of complex **5** with methyl iodide followed by oxidation. The reaction of such electrophiles (H_3O^+, Me^+) gives the corresponding starting materials after the abstraction of the *exo*-added nucleophile (e.g., the hydride) as it has been well described for stabilized carbanions.[7b] Moreover, a further evidence of the reversible behavior of the hydride addition is given while opposing stoichiometrically complex **2a** to cationic (η^6-benzene)tricarbonylmanganese complex **8**.[12] A mixture of complex **1** and neutral tricarbonyl(η^5-cyclohexadienyl)manganese complex **9**[8c] is obtained as a result of an hydride transfer from anionic complex **2a** toward the very electrophilic cationic complex **8**.

In conclusion, we have described the first anionic tricarbonyl(η^5-cyclohexadienyl)chromium complexes obtained after addition of hydride (or deuteride) to the ring of benzene and dibenzofuran complexes. In the case of the (η^6-dibenzofuran)tricarbonylchromium complex, the mechanism of opening the furan five-membered ring by a hydride has been unambiguously established and can be explained by a reversible addition of the hydride to the chromium complex.

Supplementary Material Available: Listing of complete crystallographic data of compound **7**, ^1H NMR spectral data of **2a**, **3a**, **3b**, **5**, **6**, and **7**, ^{13}C NMR spectral data of **3a**, **3b**, and **7**, ^{119}Sn NMR spectral data of **3a**, and full experimental procedures with analytical data (24 pages); listing of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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