bridging carbonyl band appears only upon the addition of solvent; thus a distinction is made between two types of adsorbed $RuCo_3(CO)_{12}^-$. After the addition of solvent the infrared spectrum is indistinguishable from that observed in solution for this reason it is referred to as solvated. Addition of solvent alone, however, does not extract any metal carbonyls; thus the surface species is described as adsorbed.

The reappearance of the bridging bands upon addition of THF may be consistent with poisoning of the Lewis base sites. This last explanation is often invoked for surface metal carbonyls,[1b,24] and often there is good evidence for this interaction.[1b,25] However, in the present case we do not find bands below 1600 cm^{-1} which can be assigned to such an interaction. Also, it is difficult to imagine how all three of the bridging carbonyls in $RuCo_3(CO)_{12}^-$ could interact simultaneously with the surface. An alternative explanation is that an alternative isomeric form of $RuCo_3(CO)_{12}^-$ which has no bridging CO's is stabilized on the surface. Such isomers for $M_4(CO)_{12}$ systems have been discussed recently by Lauher.[26]

In the reactions represented by eq 1 above it is clear that predominantly $RuCo_3(CO)_{12}^-$(ads, solv) is formed as the major product following the addition of THF. The stoichiometry of the transformation, however, is not clear. Other products, B in eq 1, must be formed. Broad peaks are observed in the infrared spectrum (Figure 2) consistent with other products but are not assigned. The reaction of A with THF to yield 2 on the surface is described as a disproportionation since the other possible reduction pathway utilizing CO as the reductant must generate CO_2, and this is not observed either in the gas phase or on the surface as carbonate.

The species represented by A in this scheme is characterized by the following facts: (1) It is formed with the apparent stoichiometry $RuCo_2(CO)_{10}$. (2) It decomposes in the presence of PPNCl to give predominantly $Co(CO)_4^-$. (3) It is converted predominantly to $RuCo_3(CO)_{12}^-$(ads, sol) upon addition of THF. (4) Its infrared spectrum is very simple consisting of only two terminal bands. Without being able to model this species with a known molecular analogue, we propose the assignment to be $RuCo_2(CO)_{10}$(ads) in which a surface hydroxyl group occupies a bridging position between the two cobalt atoms.

Registry No. 1, 78456-89-0; $HRuCo_3(CO)_{12}$, 24013-40-9.

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Synthetic Applications of Trialkylaluminum Reagents: Alkylation and Reduction of Transition-Metal-Complexed π-Hydrocarbon Ligands

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　　Trialkylaluminum compounds (AlR_3, R = Me, Et) interact with the organotransition-metal cations $[(arene)Mn(CO)_3]^+$ (1) and $[Co(C_5H_5)]^+$ (2) to form "liquid clathrate" phases. Thermal decomposition of these phases results in isolation of a series of neutral cyclohexadienyl, 3a–d, or cyclopentadiene, 4, products which are simple addition products except in the case of 1d (arene = mesitylene), for which, depending upon the reaction conditions, isomeric forms of the novel dimer $(C_{18}H_{24})[Mn(CO)_3]_2$ (5a or 5b) have been isolated. It was found that preformed "liquid clathrates" containing the anions $[Al_2R_6Cl]^-$ (R = Me, Et), which possess a much higher degree of air stability than the corresponding free trialkylaluminum compounds, reacted with 1 and 2 to give the same range of products. The structures of 5a and 5b have been determined crystallographically. 5a: triclinic; $P\bar{1}$; a = 8.529 (3) Å, b = 9.189 (2) Å, c = 8.488 (3) Å; α = 104.21 (3)°, β = 118.10 (3)°, γ = 89.43 (3)°, V = 564.4 Å^3; Z = 1; ρ = 1.524 g cm^{-3}; R = 0.041. 5b: monoclinic; $P2_1/c$; a = 12.2916 (19) Å, b = 15.8372 (21) Å, c = 12.2308 (13) Å; β = 101.757 (11)°; V = 2331.0 Å^3; Z = 4; ρ = 1.477 g cm^{-3}; R = 0.057. The structure of the addition product 3d (R = Me) was also crystallographically determined, and exo addition of the methyl was thereby confirmed. 3d: monoclinic; $P2_1/n$; a = 11.956 (1) Å, b = 11.441 (1) Å, c = 10.104 (1) Å; β = 104.28 (1)°; V = 1339.4 Å^3; Z = 4; ρ = 1.360 g cm^{-3}; R = 0.042.

Introduction

　　Activation of π-hydrocarbon compounds toward nucleophilic addition via transition-metal complexation is one of the most widely studied phenomena in the field of organotransition-metal chemistry.[2] In this context addition of carbanionic moieties to monocationic organotransition-metal substrates has been a particularly widely studied reaction as the neutral addition products are often

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quite stable and facile to isolate. Addition of carbanionic moieties to cations [(arene)Mn(CO)$_3$]$^+$ (**1**)[3] and [Co-(C$_5$H$_5$)$_2$]$^+$ (**2**)[4] has therefore been studied by several groups with organolithium, Grignard, or organocuprate reagents having been utilized as carbanion sources to effect formation of neutral addition products.

In this report we outline the first use of neat trialkylaluminum reagents and alkylaluminates of general formula [Al$_2$R$_6$Cl]$^-$ (R = Me, Et) in the context of addition of carbanions to organotransition-metal moieties, in this case to the cations **1a–d** and **2** (thereby forming the corre-

1a: benzene   **2**
  b: toluene
  c: *p*-xylene
  d: mesitylene
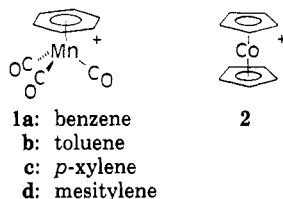
sponding neutral cyclohexadienyls **3a–h** and cyclopentadienes **4**). The anionic reagents were chosen as they offer several unique advantages over any of the more traditional reagents, all based upon the fact that they may be used most conveniently in the form of "liquid clathrates".[5] The anionic reagents therefore possess high hydrocarbon solubility, are relatively air stable, and are of nonstoichiometric but fixed composition.
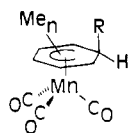
3a: *n* = 0; R = Me
  b: *n* = 1 (3-Me, 60%, 2-Me, 30%, 4-Me, 10%); R = Me
  c: *n* = 2 (2,5-Me$_2$); R = Me
  d: *n* = 3 (2,4,6-Me$_3$); R = Me
  e: *n* = 0; R = Et
  f: *n* = 1 (3-Me, 60%, 2-Me, 30%, 4-Me, 10%); R = Et
  g: *n* = 2 (2,5-Me$_2$); R = Et
  h: *n* = 3 (2,4,6-Me$_3$); R = Et
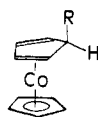
4: R = Me, Et

Experimental Section

A. General Procedures. All manipulations involving trialkylaluminum reagents were conducted in a Vacuum Atmospheres inert-atmosphere glovebox under an atmosphere of dinitrogen. Neat trialkylaluminum compounds were obtained from Texas Alkyls and used as supplied. The anionic reagents were prepared by mixing NMe$_4$Cl and 2 equivs of AlR$_3$ in freshly

distilled benzene (R = Me) or toluene (R = Et). The compositions of the liquid clathrates so formed were shown by ^{1}H NMR to be [NMe$_4$][Al$_2$Me$_6$Cl]·6benzene and [NMe$_4$][Al$_2$Et$_6$Cl]·13.8toluene, agreeing closely with the literature values.[5a] Although the liquid clathrates are stable in air for days, they are extremely moisture-sensitive so they were stored and handled in the glove box. ^{1}H and ^{13}C NMR spectra were obtained on Varian EM-360 and Nicolet 360NB spectrometers, respectively, and infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrophotometer.

[(Arene)Mn(CO)$_3$]$^+$ (arene = benzene, toluene, *p*-xylene, and mesitylene) cations were prepared in the form of their hexafluorophosphate salts from Mn(CO)$_5$Br and AlCl$_3$ in a manner similar to that described previously;[6] however, no solvent other than the arene itself was used. **1a:** ^{1}H NMR (acetone-*d$_6$*) δ 6.95 (s); ^{13}C NMR (acetone-*d$_6$*) δ 101.76 (d); IR (Nujol) ν$_{CO}$ 2090 s, 2030 b. **1b:** ^{1}H NMR (acetone-*d$_6$*) δ 6.97–6.63 (m, 5 H), 2.81 (s, 3 H); ^{13}C NMR (acetone-*d$_6$*) δ 120.81 (s), 102.94 (d), 100.19 (d), 97.43 (d), 20.09 (q); IR (Nujol) ν$_{CO}$ 2090 s, 2030 b. **1c:** ^{1}H NMR (acetone-*d$_6$*) δ 6.70 (s, 4 H), 2.51 (s, 6 H); ^{13}C NMR (acetone-*d$_6$*) δ 115.82 (s), 100.91 (d), 18.94 (q); IR (Nujol) ν$_{CO}$ 2090 s, 2030 b. **1d:** ^{1}H NMR (acetone-*d$_6$*) δ 6.39 (s, 3 H), 2.60 (s, 9 H); ^{13}C NMR (acetone-*d$_6$*) δ 121.60 (s), 96.57 (d), 19.87 (q); IR (Nujol) ν$_{CO}$ 2090 s, 2030 b.

[Co(C$_5$H$_5$)$_2$]$^+$ was obtained in the form of its hexafluorophosphate salt from Aldrich Chemical Co. and used as supplied.

B. Reaction of 1a–d and 2 with Trialkylaluminum Reagents. In order to determine optimum reaction conditions for obtaining **3a–h** and **4a,b**, several procedures were employed as outlined below.

Procedure i. **1a** (1.00 g, 2.76 mmol) was taken into the glovebox and placed in a 125-mL Erlenmeyer flask to which was added 50 mL of distilled toluene and 1.59 mL (16.6 mmol) of trimethylaluminum. Within 10 min at 20 °C the salt dissolved completely and exhibited the liquid–liquid layering effect characteristic of "liquid clathrate"[5] formation. The composition of the denser, salt-rich "clathrate" phase was shown by ^{1}H NMR to be [(benzene)Mn(CO)$_3$][PF$_6$(AlMe$_3$)$_6$]·19.0toluene.

Under the same conditions 1.00 g of **1b–d** and **4** were contacted with the appropriate volume of trimethylaluminum to give "liquid clathrates" of the following stoichiometries: **1b**, [(toluene)Mn-(CO)$_3$][PF$_6$(AlMe$_3$)$_6$]·14.7toluene; **1c**, [(*p*-xylene)Mn(CO)$_3$][PF$_6$-(AlMe$_3$)$_6$]·15toluene; **1d**, [(mesitylene)Mn(CO)$_3$][PF$_6$(AlMe$_3$)$_6$]·16toluene; **2**, [Co(C$_5$H$_5$)$_2$][PF$_6$(AlMe$_3$)$_6$]·15.4toluene.

Attempts to crystallize adducts from the "liquid clathrate" phases and hence determine if any of the trimethylaluminum molecules were bonded to carbonyl groups in addition to the hexafluorophosphate moiety failed even at –70 °C. At this temperature the phases were observed to be stable for at least 3 months. Under ambient conditions, however, slow decomposition of the "liquid clathrate" phases occurred to give colored toluene solutions. The aforementioned "liquid clathrate" phases were left to stand in the reacton vessel at room temperature for 3 weeks under ambient conditions. After this time breakdown of the binary liquids had occurred completely to yield toluene soluble yellow (**3a–d**) or red (**4a**) compounds. The air-stable neutral products were isolated via quenching the reaction mixture with ice water, separating and drying the toluene phase with molecular sieves, and removing the toluene by rotoevaporation and extraction with distilled hexanes. Following elution on silica gel with distilled hexanes compounds **3a–d** and **4a** were isolated from **1a–d** and **2**, respectively.

Procedure i was also followed for the other alkylaluminum reagents utilized in this study: AlEt$_3$, [AlMe$_3$Cl]$^-$, and [AlEt$_3$Cl]$^-$. The triethylaluminum reagents produced, of course, the corresponding ethylation products **3e–h** and **4b**. All the alkylation products were spectroscopically characterized (details in Table I), and the new compounds that were isolated as pure compounds gave satisfactory C, H analysis results (**3c** (mp 30 °C). Calcd for C$_{12}$H$_{13}$MnO$_3$: C, 55.40; H, 5.04. Found: C, 55.87; H, 5.21. **3e** (liquid). Calcd for C$_{11}$H$_{11}$MnO$_3$: C, 53.68; H, 4.50. Found: C, 53.96; H, 4.57. **3g** (liquid). Calcd for C$_{13}$H$_{15}$MnO$_3$: C, 56.95; H, 5.51. Found: C, 57.18; H, 5.55). Compounds **3b** and **3f** were isolated as mixtures of the three possible isomeric products. The ratio of products was found to be 6:3:1 (meta:ortho:para) via ^{1}H and ^{13}C NMR integraton of the resonances associated with the exo substituent.

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**Table I. Yield[a] and Spectrosopic Data for 3a–h and 4a,b**

compd	R	yield (%)	ν_{CO} (cm^{-1}), (CDCl$_3$)	^{13}C NMR (δ)	solv	peak assignmt
3a	Me	62	2010 s, 1925 b	95.60 (d, C1), 79.25 (d, C2), 58.75 (d, C3), 29.86 (d, C4), 27.91 (q, C5)	b	
3e	Et	70	2010 s, 1925 b	95.90 (d, C1), 79.54 (d, C2), 57.49 (d, C3), 36.53 (d, C4), 35.21 (t, C5), 8.56 (q, C6)	b	
3b[d]	Me	73	2005 s, 1925 b	110.67 (s, C1), 94.25 (d, C2), 80.13 (d, C3), 60.29 (d, C4), 59.05 (d, C5), 31.28 (d, C6), 28.29 (q, C7), 22.70 (q, C8)	c	
3f[d]	Et	67	2005 s, 1925 b	110.99 (s, C1), 94.55 (d, C2), 80.40 (d, C3), 58.89 (d, C4), 57.76 (d, C5), 37.97 (d, C6), 22.43 (q, C7), 35.33 (t, C8), 8.59 (q, C9)	c	
3c	Me	54	2000 s, 1920 b	109.0 (s, C1), 93.32 (d, C2), 77.64 (d, C3),[e] 57.09 (d, C5), 37.18 (d, C6), 24.89 (q, C7), 22.04 (q, C8), 21.56 (q, C9)	b	
3g	Et	57	2000 s, 1920 b	109.23 (s, C1), 93.74 (d, C2), 77.89 (d, C3), 75.86 (s, C4), 54.89 (d, C5), 43.84 (d, C6), 22.42 (q, C7), 21.92 (q, C8), 32.48 (t, C9), 9.45 (q, C10)	b	
3d	Me	19	2010 s, 1925 b	~91 (s, C1), 95.17 (d, C2), 70.19 (s, C3), 41.86 (d, C4), 21.6 (q, C5),[g] 20.10 (q, C6), 21.6 (q, C7)[g]	c	
3h	Et	42[f]	2010 s, 1925 b	90.86 (s, C1), 95.63 (d, C2), 68.81 (s, C3), 48.26 (d, C4), 23.27 (q, C5), 20.20 (q, C6), 31.09 (t, C7), 11.66 (q, C8)	c	
4a	Me	<5				
4b	Et	24		79.15 (d, C$_5$H$_5$), 74.73 (d, C1), 54.47 (d, C2), 44.17 (d, C3), 34.47 (t, C4), 10.20 (q, C5)	b	

[a] Based upon cation; procedure ii. [b] Benzene-d_6. [c] CDCl$_3$. [d] ^{13}C data for meta isomer only. [e] C4 resonance obscured by other resonance. [f] Minor reduction products 5a and 5b also isolated. [g] C5 and C7 same chemical shift.

Significantly, the trialkylaluminate reagents were observed to give similar yield and product distribution ratios to the neat trialkylaluminum reagents, although for 1d with neat AlEt$_3$ an unexpected additional minor reduction product, 5a, crystallized in the reaction vessel mixture prior to workup. 5a was only isolated in very small quantities, thereby preventing all but crystallographic characterization (see Section C).

Procedure ii. The same quantities and methodology as procedure i were followed except the reactions were conducted at 70 °C for only 24 h. No significant differences in product distribution were noted, but yields were significantly higher than those obtained via procedure i and are listed in Table I.

For 1d with AlEt$_3$ another unexpected minor (<5%) reduction product, 5b, was eluted as the second distilled hexanes-soluble fraction. Yellow crystals of 5b were obtained via cooling a toluene solution of 5b at −15 °C for 24 h. The structure of 5b was confirmed crystallographically (see section C).

5a   5b
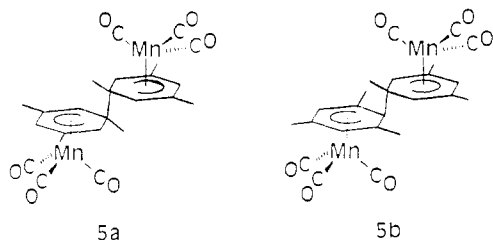
Procedure iii. The same as procedure i but the reactions were conducted for 48 h at 70 °C. No significant difference in either product yield or distribution compared to those obtained via procedure ii were noted.

Procedure iv. The same as procedure i except 50 mL of distilled, dried dichloromethane was utilized as the reaction solvent, and the reaction was stopped after only 24 h at room temperature. No liquid–liquid layering effect was noted, although the same color changes as those seen for procedure i were observed. Yields were higher than those obtained via procedure i but not as high as those obtained via procedure ii.

Procedure v. The same as procedure i except 50 mL of distilled, dried hexanes was utilized as the reaction solvent. After initial contact of the salt with the trialkylaluminum reagent, an oily, hexanes-insoluble solid was formed, and, over the 3-week reaction period, a gradual discoloration of the hexanes phase to give the expected colors was noted. Following workup product yield and distributions similar to those seen for procedure i were observed.

C. X-ray Crystallography. Single crystals of 3d, 5a, and 5b were sealed in glass capillaries. Data collection and structure solution parameters are presented in Table II. Absorption corrections were not effected for 3d and 5b, but absorption

Table II. Data Collection and Structure Refinement Summary for Compounds 3d, 5a, and 5b

	3d	5a	5b
formula	MnC$_{13}$H$_{15}$O$_3$	Mn$_2$C$_{24}$H$_{24}$O$_6$	·Mn$_2$C$_{24}$H$_{24}$O$_6$
fw	274.2	518.3	518.3
diffractometer	Picker	Picker	Nonius CAD-4
radiatn	Mo Kα	Mo Kα	Mo Kα
cryst system	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	11.956 (1)	8.529 (3)	12.2916 (19)
b, Å	11.441 (1)	9.189 (2)	15.8372 (21)
c, Å	10.104 (1)	8.488 (3)	12.2308 (13)
α, deg		104.21 (3)	
β, deg	104.28 (1)	118.10 (3)	101.757 (11)
γ, deg		89.43 (3)	
V, Å^3	1339.4	564.4	2331.0
Z	4	1	4
d_{calcd}, g cm^{-3}	1.360	1.524	1.477
μ, cm^{-1}	9.4	11.2	10.8
cryst dimens, mm	0.27 × 0.30 × 0.43	0.15 × 0.45 × 0.55	0.20 × 0.20 × 0.20
scan type	θ–2θ	θ–2θ	θ–2θ
2θ range, deg	0–55	0–60	0–45
reflctns measd	3097	5004	2979
reflctns obsd	1434[a]	3349[a]	1947[b]
parameters refined	198	187	307
ratio data parameter	7.24	17.91	6.34
R	0.042	0.041	0.057
R_w	0.044	0.058	0.086

[a] $I > 3\sigma(I)$. [b] $I > 2.5\sigma(I)$.

correction was effected for 5a (corrections ranged from 1.20 to 1.56). The manganese atoms were located following Patterson map inspection, and structure solution and refinement proceeded routinely for 3d and 5b. For 5a, however, refinement was not routine and a full discussion of how we arrived at a disordered model is in order. The initial refinement converged at $R = 0.056$. Considering the quality of the data, this value was unexpectedly high, and other anomalous aspects of the structure were immediately apparent. Two of the atoms (corresponding roughly to C(1B) and C(5A) in Figure 2) had extraordinarily large anisotropic displacement parameters, and some of their nearest-neighbor contacts were (at approximately 2.4 Å) too long for bonds and too short for van der Waals contacts. Study of the electron density at these sites revealed that the distributions were in fact bimodal, with each site comprising two apparently equal peaks separated by about 0.7 Å. When these atoms were each replaced by a pair of independent half-atoms, convergence occurred at a more typical $R = 0.041$. (Atomic parameters are given in Table VI.) Various

hypotheses may be entertained. (a) The structure is disordered. The average unit cell contains a superposition of the molecule represented in Figure 2 and its centrosymmetrically related enantiomer. Most of the atoms in one enantiomer overlap an atom of the other fairly completely, with no obvious indication of bimodality. (b) The space group is really $P1$. Only one enantiomer is present in the crystal, but postulating a center of symmetry (space group $P\bar{1}$) results in the appearance of disorder. (c) The structure is disordered, comprising a superposition of two (or more) distinct chemical species.

We regard (c) as so unlikely as to merit no further consideration. (b) is in principle possible, but given a molecule so nearly centrosymmetrical a meaningful refinement could not be effected. We regard (a) as by far the most plausible hypothesis but point out that *either* (a) or (b) is consistent with our conclusion that the specimen material is **3d**.

It is emphasized that the bond lengths and angles (however plausible) are subject to incommensurable systematic error. In a structure of this sort *all* electron-density peaks must be regarded as bimodal, with a separation between contributing peaks which can range from zero to the limit of resolution of the experiment (nominally about 0.4 Å). A separation of, for example, 0.2 Å could scarcely be inferred from the displacement parameters but would have serious implications for any evaluation of bond lengths. The displacement parameters of the methyl carbon atoms C(7) and C(9) suggest a substantial separation; and a more sophisticated model might be justified for these atoms. (The carbonyl group C(12)–O(3) has large displacement parameters also, but high thermal motion can reasonably be expected for such groups.)

Locatable hydrogen atoms were refined isotropically for **5a**, with fixed temperature factors for **3d**, and fixed to the appropriate carbon atom for **5b**. The computer programs used for **3d** and **5a** have been described in ref 8, and atomic scattering factors were taken from ref 9. The structure of **5b** was solved by the NRC VAX crystal structure system[10] locally adapted for a Wicat Systems S-1260 computer.

Results and Discussion

Trialkylaluminum compounds interacted with the hexafluorophosphate salts of **1a–d** and **2** to form adducts that resulted in "liquid clathrate" formation. These phases slowly reacted to yield a series of neutral alkylation or, in the case of **1d**, alkylation and reduction products. We found that both neat trialkylaluminum reagents and their anionic analogues effected alkylation of cations **1a–d** in moderate yields and cation **2** in low yields and that no significant difference in either yield or product distribution was noticed between the two classes of reagent. The expected neutral addition products **3a–h** and **4a,b**, from **1a–d** and **2**, respectively, were isolated. It is perhaps unsurprising that the neat trialkylaluminum compounds give the same results as those obtained as the preformed alkylaluminates as in the former case alkylaluminates are presumably generated in situ. The optimum conditions are somewhat more forcing than those required for more conventional reagents such as lithium, magnesium, and copper alkyls, which often react spontaneously at lower than room temperature;[11] nevertheless, the additions gave the expected exo products as exemplified by **3d** (R = Me), which was crystallographically characterized.

Isolation of reduction products in addition to the expected alkylation products from **1d** has important mechanistic implications. The compounds isolated were isomers

Scheme I

of the novel dimeric compound $[(C_9H_{12})Mn(CO)_3]_2$ (**5a** and **5b**). The X-ray structures of **5a** and **5b** represent the first crystallographically characterized bis(cyclohexadienyl) complexes[12] and reveal that **5a** is joined unexpectedly[13] through methylated ring carbon atoms whereas **5b** is joined through one methylated and one non-methylated ring carbon atom. Isolation of **5a** and **5b** is an indication that the mechanism in the reactions reported herein could be based upon electron-transfer (ET) rather than nucleophilic processes. The latter are generally assumed to prevail when more conventional carbanion sources are utilized.[14] **5a** and **5b** are presumably formed via coupling of the neutral 19-electron complex $[(C_9H_{12})Mn(CO)_3]$ (**6**),[15] which could also be a precursor to the alkylated addition products (see Scheme I). Such a mechanism would be consistent with reactions of AlR_3[16] and MeLi[17] with organic substrates, which are now considered by some workers to be based upon ET rather than nucleophilic processes. It is also relevant that reaction of carbanionic[18] and borohydride[19] reagents with $[(arene)_2Fe]^{2+}$ dications has previously been reported to lead to one-electron reduction of the dication to the corresponding 19-electron $[(arene)_2Fe]^+$ monocations and that related studies we have concurrently conducted upon interaction of alkylaluminates with $(C_5H_5)_2TiCl_2$ show that one-electron reduction to $[(C_5H_5)_2TiCl]_2$ occurs quantitatively and spontaneously.[20] Dimerization of moieties such as **6** has precedence not only in metal arene chemistry[21] but also in a more general sense
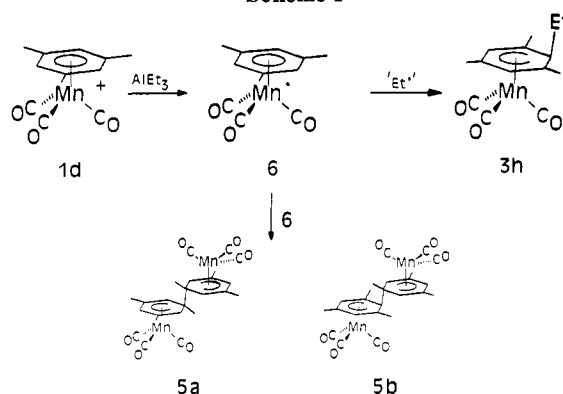
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(11) Typically reactions are conducted in a polar solvent such as tetrahydrofuran at −78 °C. See ref 3 for specific details.

(12) Similar complexes have been reported recently, but they are not directly analogous having been derived via two-electron reduction of biphenyl-bridged bimetallics: (a) Lacoste, M.; Varret, F.; Toupet, L.; Astruc, D. *J. Am. Chem. Soc.* **1987**, *109*, 6504 [(μ-η^6:η^5-biphenyl){Fe(C$_5$H$_5$)}$_2$—X-ray]. (b) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699 [(μ-η^6:η^5-biphenyl)(Cr(CO)$_3$)$_2$]—spectroscopy).

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(18) (a) Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437. (b) Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. *Ibid.* **1984**, *106*, 3381. Electron-transfer mechanisms have also been demonstrated when LiAlH$_4$ reacts with [C$_5$Me$_5$Fe^{II}(dppe)(CO)]$^+$ at −80 °C: Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1984**, *3*, 817.

(19) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

(20) Cameron, T. S.; Dubois, R. H.; Linden, A.; Zaworotko, M. J.; unpublished results.

(21) The neutral 19-electron complexes [Fe(C$_5$H$_5$)(arene)] dimerize via unsubstituted ring carbon atoms (spectroscopic evidence): (a) Nesmeyanov, A. N.; Vol'Kenau, N. A.; Petrakova, V. A. *J. Organomet. Chem.* **1977**, *136*, 363. (b) Moinet, C.; Roman, E.; Astruc, D. *J. Organomet. Chem.* **1977**, *128*, C45.

Table III. Final Fractional Coordinates for 3d

atom	x	y	z	B(iso), Å²
Mn	0.34029 (5)	0.23324 (5)	0.15836 (6)	3.36 (3)
C(1)	0.3236 (4)	0.1527 (4)	-0.1049 (4)	4.2 (2)
C(2)	0.3564 (4)	0.2742 (4)	-0.0518 (4)	4.4 (2)
C(3)	0.2724 (4)	0.3415 (4)	-0.0132 (4)	4.4 (3)
C(4)	0.1809 (4)	0.2918 (4)	0.0314 (4)	4.1 (2)
C(5)	0.1810 (4)	0.1689 (4)	0.0361 (4)	4.3 (2)
C(6)	0.2630 (4)	0.1009 (4)	-0.0048 (4)	4.0 (2)
C(7)	0.2522 (5)	0.1487 (5)	-0.2530 (5)	6.6 (4)
C(8)	0.4601 (5)	0.3302 (5)	-0.0841 (5)	7.3 (4)
C(9)	0.0891 (5)	0.3633 (5)	0.0708 (5)	6.3 (3)
C(10)	0.2675 (5)	-0.0291 (4)	0.0149 (6)	6.5 (3)
C(11)	0.4115 (4)	0.3583 (4)	0.2479 (5)	4.5 (2)
C(12)	0.2954 (4)	0.1896 (4)	0.3065 (4)	4.9 (3)
C(13)	0.4668 (4)	0.1437 (4)	0.1886 (4)	4.5 (3)
O(11)	0.4580 (3)	0.4388 (3)	0.3028 (3)	6.6 (2)
O(12)	0.2641 (3)	0.1640 (3)	0.4020 (4)	7.8 (3)
O(13)	0.5470 (3)	0.0859 (3)	0.2065 (3)	6.9 (2)
H(1)	0.400 (3)	0.104 (3)	-0.096 (3)	4.0 (0)
H(3)	0.279 (3)	0.420 (3)	-0.008 (3)	4.0 (0)
H(5)	0.127 (3)	0.133 (3)	0.073 (3)	4.0 (0)
H(7A)	0.290 (4)	0.174 (4)	-0.318 (5)	8.0 (0)
H(7B)	0.231 (4)	0.068 (4)	-0.277 (4)	8.0 (0)
H(7C)	0.176 (4)	0.194 (4)	-0.259 (5)	8.0 (0)
H(8A)	0.488 (4)	0.397 (4)	-0.034 (4)	8.0 (0)
H(8B)	0.529 (4)	0.281 (4)	-0.073 (5)	8.0 (0)
H(8C)	0.449 (4)	0.341 (4)	-0.182 (4)	8.0 (0)
H(9A)	0.115 (4)	0.431 (4)	0.099 (4)	8.0 (0)
H(9B)	0.059 (4)	0.318 (4)	0.133 (5)	8.0 (0)
H(9C)	0.025 (4)	0.369 (4)	-0.013 (5)	8.0 (0)
H(10A)	0.219 (4)	-0.062 (4)	-0.060 (4)	8.0 (0)
H(10B)	0.341 (4)	-0.067 (4)	0.021 (5)	8.0 (0)
H(10C)	0.232 (4)	-0.049 (4)	0.092 (4)	8.0 (0)
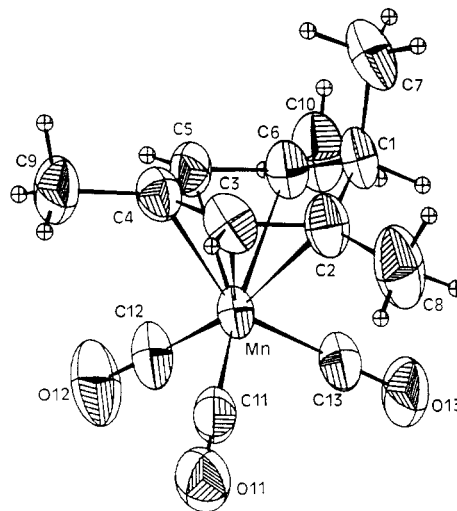
Figure 1. Perspective view of **3d**.

Figure 2. Perspective view of **5a**. C(5A)', C(5B), C(1A), and C(1B)' belong to the other enantiomer so do not appear in this plot.

Table IV. Interatomic Distances (Å) for 3d

Mn–C(2)	2.229 (4)	C(2)–C(3)	1.395 (6)
Mn–C(3)	2.122 (4)	C(2)–C(8)	1.502 (7)
Mn–C(4)	2.126 (4)	C(3)–C(4)	1.402 (7)
Mn–C(5)	2.129 (4)	C(4)–C(5)	1.407 (6)
Mn–C(6)	2.262 (4)	C(4)–C(9)	1.498 (6)
Mn–C(11)	1.791 (5)	C(5)–C(6)	1.392 (6)
Mn–C(12)	1.782 (4)	C(6)–C(10)	1.499 (6)
Mn–C(13)	1.790 (4)	C(11)–O(11)	1.147 (5)
C(1)–C(2)	1.507 (6)	C(12)–O(12)	1.156 (5)
C(1)–C(6)	1.503 (6)	C(13)–O(13)	1.142 (5)
C(1)–C(7)	1.529 (7)		

in that other hydrocarbon ligands complexed to 19-electron metals have been observed to couple.[22] Isolation of **5a** and **5b** does not, of course, preclude the existence of a more traditional nucleophilic mechanism in the formation of **3a–d** and **4**, but it does suggest that a more thorough investigation of the mechanism of "nucleophilic" carbanionic addition to transition-metal-complexed hydrocarbons is in order.

Spectroscopy. The spectra of the "liquid clathrate" phases are consistent with those observed for prototypical "liquid clathrates".[5] Even though transition-metal cyclohexadienyl and cyclopentadiene complexes have been known since the 1950s, ^{13}C NMR data on such moieties is quite sparse. The data presented in Table I are consistent with earlier work on Cr, Mn, and Fe cyclohexadienyls,[12b] the ring carbon atoms showing the expected upfield chemical shift trend toward the sp³-ring carbon atom. The ^{1}H NMR spectra exhibit similar trends, and the infrared spectra demonstrate, as expected, that the ν_{CO} stretches for **3a–d** occur at lower wavenumbers than the precursor salts **1a–d**.

Table V. Selected Bond Angles (deg) for 3d

C(2)–C(1)–C(6)	104.5 (3)	C(4)–C(5)–C(6)	123.0 (4)
C(2)–C(1)–C(7)	114.2 (4)	C(1)–C(6)–C(5)	118.1 (4)
C(6)–C(1)–C(7)	113.7 (4)	C(1)–C(6)–C(10)	118.2 (4)
C(1)–C(2)–C(3)	117.8 (4)	C(5)–C(6)–C(10)	121.4 (4)
C(1)–C(2)–C(8)	118.2 (4)	Mn–C(11)–O(11)	178.5 (4)
C(3)–C(2)–C(8)	121.0 (4)	Mn–C(12)–O(12)	178.1 (4)
C(2)–C(3)–C(4)	122.6 (4)	Mn–C(13)–O(13)	179.1 (4)
C(3)–C(4)–C(5)	114.9 (4)	C(11)–Mn–C(12)	90.2 (2)
C(3)–C(4)–C(9)	123.0 (4)	C(11)–Mn–C(13)	95.4 (2)
C(5)–C(4)–C(9)	122.1 (4)	C(12)–Mn–C(13)	96.5 (2)

X-ray Structures. a. 3d. An ORTEP view of **3d** is presented in Figure 1. Final positional parameters are given in Table III, and intramolecular bond distances and selected bond angles are presented in Tables IV and V, respectively. The structure reveals that the methyl group has added in an exo fashion to the coordinated mesitylene ring. The Mn(CO)₃ tripod is oriented such that one carbonyl ligand is eclipsed by the sp³-ring carbon atom as it is in the prototypical cyclohexadienyl (C₆H₇)Mn(CO)₃ (**7**).[23] The Mn–C(carbonyl) (average 1.79 Å) and Mn–C(ring)

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(22) (a) Pearson, A. J.; Chen, Y.-S.; Daroux, M. L.; Tanaka, A. A.; Zettler, M. *J. Chem. Soc., Chem. Commun.* **1987**, 155. (b) Iienda, C. S.; Schore, N. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 255. (c) Ernst, R. D.; Ma, H.; Sergeson, G.; Zahn, T.; Ziegler, M. L. *Organometallics* **1987**, *6*, 848.
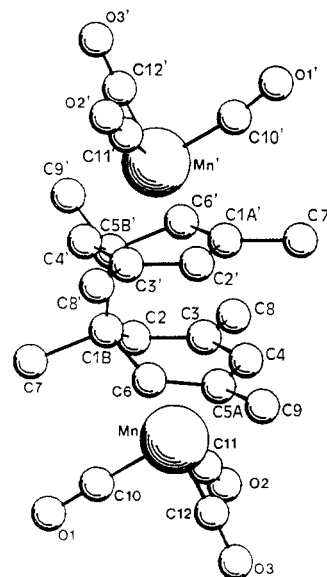
(23) Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950.

Table VI. Final Fractional Coordinates for 5a[a]

atom	x	y	z	B(iso), Å²
C(1A)	0.7443 (5)	0.4405 (4)	0.8542 (5)	2.4 (1)
C(1B)	0.8073 (4)	0.4892 (4)	0.8648 (5)	2.1 (1)
C(2)	0.7741 (2)	0.3300 (2)	0.7306 (3)	2.5 (1)
C(3)	0.8983 (2)	0.2282 (2)	0.7932 (3)	2.5 (1)
C(4)	0.9936 (2)	0.2413 (2)	0.9854 (3)	2.6 (1)
C(5A)	0.9600 (5)	0.3469 (4)	1.1089 (5)	2.3 (1)
C(5B)	1.0336 (5)	0.4022 (4)	1.1218 (5)	2.1 (1)
C(6)	0.8491 (2)	0.4543 (2)	1.0434 (3)	2.4 (1)
C(7)	0.6155 (4)	0.5549 (4)	0.7930 (4)	5.0 (1)
C(8)	0.9197 (4)	0.1015 (3)	0.6548 (4)	3.9 (1)
C(9)	1.0708 (5)	0.3711 (4)	1.3176 (3)	5.8 (2)
C(10)	0.4759 3)	0.2457 (3)	0.7894 (3)	3.4 (1)
C(11)	0.6412 (3)	0.0210 (3)	0.7534 (3)	3.1 (1)
C(12)	0.7015 (4)	0.1658 (4)	1.0778 (4)	4.8 (2)
O(1)	0.3276 (2)	0.2603 (3)	0.7233 (3)	5.3 (1)
O(2)	0.5978 (3)	−0.1024 (2)	0.6676 (3)	4.4 (1)
O(3)	0.6918 (4)	0.1299 (5)	1.1946 (3)	9.5 (3)
Mn	0.70843 (4)	0.21551 (3)	0.89050 (4)	2.5 (0)
H(2)	0.691 (3)	0.322 (3)	0.592 (3)	2.7 (5)
H(4)	1.057 (3)	0.160 (3)	1.021 (3)	2.8 (5)
H(6)	0.805 (3)	0.521 (3)	1.123 (3)	2.4 (4)
H(8A)	0.802 (4)	0.070 (3)	0.526 (4)	4.3 (6)
H(8B)	0.962 (5)	0.142 (4)	0.590 (5)	7.0 (9)
H(8C)	0.955 (4)	0.023 (3)	0.710 (4)	4.1 (6)

[a] Hydrogen atoms were not locatable for C(7) and C(9).

Table VII. Final Fractional Coordinates for 5b

atom	x	y	z	B(iso), Å²
Mn(1)	0.71395 (14)	0.11820 (11)	0.08518 (14)	2.68 (8)
C(11)	0.7958 (12)	0.1838 (10)	0.1846 (12)	4.7 (7)
O(11)	0.8489 (10)	0.2289 (8)	0.2500 (9)	7.8 (7)
C(12)	0.7295 (11)	0.0315 (9)	0.1793 (11)	3.9 (6)
O(12)	0.7397 (9)	−0.0240 (7)	0.2429 (8)	6.1 (6)
C(13)	0.5988 (12)	0.1581 (8)	0.1376 (11)	4.1 (6)
O(13)	0.5259 (9)	0.1844 (8)	0.1737 (9)	7.6 (7)
C(31)	0.7470 (8)	0.0050 (7)	−0.0832 (8)	2.1 (5)
C(32)	0.8303 (9)	0.0652 (8)	−0.0157 (9)	2.7 (5)
C(33)	0.8175 (9)	0.1522 (8)	−0.0308 (10)	2.8 (5)
C(34)	0.7084 (9)	0.1857 (8)	−0.0693 (9)	2.6 (5)
C(35)	0.6153 (9)	0.1287 (7)	−0.0836 (9)	2.7 (5)
C(36)	0.6380 (9)	0.0418 (7)	−0.0637 (9)	2.6 (5)
C(37)	0.7631 (11)	−0.0844 (7)	−0.0350 (9)	2.8 (6)
C(38)	0.9146 (10)	0.2116 (9)	−0.0013 (11)	3.8 (6)
C(39)	0.5003 (10)	0.1627 (8)	−0.1105 (12)	4.1 (7)
Mn(2)	0.78028 (14)	−0.07136 (10)	−0.40680 (13)	2.52 (8)
C(21)	0.7474 (11)	0.0333 (10)	−0.4641 (12)	4.1 (7)
O(21)	0.7239 (10)	0.0980 (7)	−0.4983 (10)	7.1 (6)
C(22)	0.6905 (11)	−0.1272 (8)	−0.5196 (11)	4.1 (7)
O(22)	0.6363 (10)	−0.1617 (8)	−0.5926 (9)	7.7 (7)
C(23)	0.8939 (11)	−0.0876 (8)	−0.4753 (11)	3.8 (6)
O(23)	0.9656 (10)	−0.1000 (7)	−0.5190 (9)	6.3 (6)
C(41)	0.7521 (9)	0.0090 (6)	−0.2121 (9)	2.1 (4)
C(42)	0.8611 (8)	−0.0149 (6)	−0.2427 (8)	2.1 (5)
C(43)	0.8868 (9)	−0.0999 (7)	−0.2522 (9)	2.5 (5)
C(44)	0.8029 (10)	−0.1613 (7)	−0.2767 (10)	2.9 (5)
C(45)	0.6903 (10)	0.1337 (7)	0.2962 (10)	3.0 (6)
C(46)	0.6673 (9)	−0.0474 (7)	−0.2882 (9)	2.7 (5)
C(47)	0.9509 (10)	0.0500 (8)	−0.2335 (10)	3.3 (6)
C(48)	0.8346 (14)	−0.2560 (8)	−0.2801 (13)	4.8 (8)
C(49)	0.5506 (10)	−0.0158 (10)	−0.3231 (12)	4.4 (7)

bond distances (ranging from 2.122 (4) to 2.262 (4) Å) are likewise close to the values observed in 7 (Mn–CO = 1.79 Å average; Mn–C(ring) = 2.141–2.219 Å) and the only [(arene)Mn(CO)₃]⁺ cation thus far crystallographically characterized, [(dodecahydrotriphenylene)Mn(CO)₃]⁺ (8),[24] (Mn–CO = 1.79 Å average; Mn–C(ring) = 2.21 Å average). The ring carbon atoms C(2)–C(6) are planar to 0.01 Å, with C(1) lying 0.59 Å out of the plane. No unusual intermolecular approaches are present.

(24) Gommans, L. H. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1985**, *284*, 345.

Table VIII. Bond Distances (Å) for 5a

molecule 1		molecule 2 (as for molecule 1 or)	
C(1B)–C(2)	1.551 (4)	C(5B)–C(4)	1.563 (4)
C(1B)–C(5B)′	1.636 (5)	C(5B)–C(1B)′	1.636 (5)
C(1B)–C(6)	1.502 (4)	C(5B)–C(6)	1.517 (4)
C(1B)–C(7)	1.623 (4)	C(5B)–C(9)	1.637 (5)
C(2)–C(3)	1.405 (3)		
C(3)–C(4)	1.412 (3)		
C(3)–C(8)	1.514 (3)		
C(4)–C(5A)	1.379 (4)	C(1A)–C(2)	1.386 (5)
C(5A)–C(6)	1.390 (4)	C(1A)–C(6)	1.394 (4)
C(5A)–C(9)	1.521 (4)	C(1A)–C(7)	1.514 (4)
Mn–C(2)	2.166 (2)		
Mn–C(3)	2.152 (2)		
Mn–C(4)	2.166 (2)		
Mn–C(5A)	2.167 (4)	Mn–C(1A)	2.208 (4)
Mn–C(6)	2.264 (2)		
Mn–C(10)	1.803 (2)		
Mn–C(11)	1.802 (2)		
Mn–C(12)	1.785 (3)		
C(10)–O(1)	1.139 (3)		
C(11)–O(2)	1.141 (3)		
C(12)–O(3)	1.156 (4)		
C(1A)···C(1B)	0.661 (5)[a]		
C(5A)···C(5B)	0.761 (5)[a]		

[a] Bimodal peak separation.

Table IX. Bond Distances (Å) for 5b

Mn(1)–C(11)	1.753 (15)	Mn(2)–C(21)	1.813 (17)
Mn(1)–C(12)	1.777 (15)	Mn(2)–C(22)	1.812 (14)
Mn(1)–C(13)	1.784 (14)	Mn(2)–C(23)	1.788 (14)
Mn(1)–C(32)	2.234 (11)	Mn(2)–C(42)	2.237 (10)
Mn(1)–C(33)	2.158 (12)	Mn(2)–C(43)	2.117 (11)
Mn(1)–C(34)	2.160 (11)	Mn(2)–C(44)	2.111 (11)
Mn(1)–C(35)	2.177 (11)	Mn(2)–C(45)	2.153 (12)
Mn(1)–C(36)	2.227 (11)	Mn(2)–C(46)	2.235 (11)
C(11)–O(11)	1.168 (18)	C(21)–O(21)	1.122 (19)
C(12)–O(12)	1.163 (18)	C(22)–O(22)	1.139 (17)
C(13)–O(13)	1.155 (17)	C(23)–O(23)	1.137 (17)
C(31)–C(32)	1.516 (15)	C(41)–C(42)	1.511 (14)
C(31)–C(36)	1.523 (15)	C(41)–C(46)	1.535 (14)
C(31)–C(37)	1.531 (15)	C(42)–C(43)	1.392 (15)
C(31)–C(41)	1.592 (14)	C(42)–C(47)	1.496 (16)
C(32)–C(33)	1.394 (16)	C(43)–C(44)	1.405 (16)
C(33)–C(34)	1.430 (16)	C(44)–C(45)	1.423 (17)
C(33)–C(38)	1.504 (16)	C(44)–C(48)	1.553 (16)
C(34)–C(35)	1.440 (16)	C(45)–C(46)	1.404 (17)
C(35)–C(36)	1.415 (16)	C(46)–C(49)	1.497 (16)
C(35)–C(39)	1.485 (16)		

Table X. Selected Bond Angles (deg) for 5a

|			
C(5B)′–C(1B)–C(2)	111.6 (3)	C(1B)′–C(5B)–C(4)	113.3 (3)
C(5B)′–C(1B)–C(6)	114.4 (3)	C(1B)′–C(5B)–C(6)	115.9 (3)
C(5B)′–C(1B)–C(7)	114.1 (3)	C(1B)′–C(5B)–C(9)	115.3 (3)
C(2)–C(1B)–C(6)	102.8 (2)	C(4)–C(5B)–C(6)	100.9 (2)
C(2)–C(1B)–C(7)	106.5 (2)	C(4)–C(5B)–C(9)	104.8 (3)
C(6)–C(1B)–C(7)	106.6 (3)	C(6)–C(5B)–C(9)	105.1 (3)
C(1B)–C(2)–C(3)	117.9 (2)	C(5B)–C(4)–C(3)	117.7 (2)
C(2)–C(3)–C(4)	118.6 (2)		
C(2)–C(3)–C(8)	120.1 (2)		
C(4)–C(3)–C(8)	121.2 (2)		
C(3)–C(4)–C(5A)	121.0 (2)	C(3)–C(2)–C(1A)	120.9 (2)
C(4)–C(5A)–C(6)	118.2 (3)	C(2)–C(1A)–C(6)	118.2 (3)
C(4)–C(5A)–C(9)	121.8 (3)	C(2)–C(1A)–C(7)	122.5 (3)
C(6)–C(5A)–C(9)	118.6 (3)	C(6)–C(1A)–C(7)	119.0 (3)
C(5A)–C(6)–C(1B)	122.9 (2)	C(1A)–C(6)–C(5B)	121.6 (2)
C(10)–Mn–C(11)	89.0 (1)		
C(10)–Mn–C(12)	91.9 (1)		
C(11)–Mn–C(12)	90.6 (1)		
Mn–C(10)–O(1)	178.0 (2)		
Mn–C(11)–O(2)	179.3 (2)		
Mn–C(11)–O(2)	179.3 (2)		

b. 5a and 5b. ORTEP views of **5a** and **5b** are displayed in Figures 2 and 3, respectively. Final fractional coordinates (Tables VI and VII), intramolecular bond distances
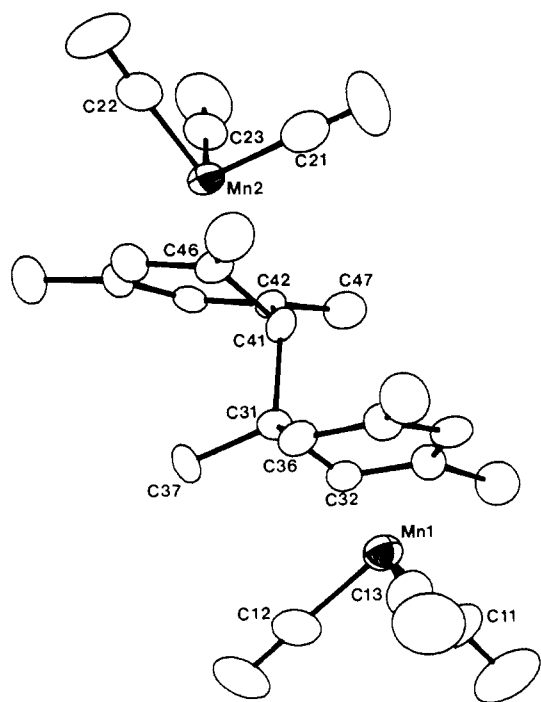
Figure 3. Perspective view of **5b**.

Table XI. Selected Bond Angles (deg) for 5b

C(11)–Mn(1)–C(12)	92.6 (6)	C(21)–Mn(2)–C(22)	95.7 (6)
C(11)–Mn(1)–C(13)	85.7 (6)	C(21)–Mn(2)–C(23)	94.8 (6)
C(12)–Mn(1)–C(13)	91.7 (6)	C(22)–Mn(2)–C(23)	89.2 (6)
Mn(1)–C(11)–O(11)	178.5 (13)	Mn(2)–C(21)–O(21)	177.7 (12)
Mn(1)–C(12)–O(12)	178.4 (12)	Mn(2)–C(22)–O(22)	177.9 (13)
Mn(1)–C(13)–O(13)	178.5 (12)	Mn(2)–C(23)–O(23)	178.3 (12)
C(32)–C(31)–C(36)	101.1 (9)	C(31)–C(41)–C(42)	116.8 (8)
C(32)–C(31)–C(37)	110.6 (8)	C(31)–C(41)–C(46)	114.7 (8)
C(32)–C(31)–C(41)	110.9 (8)	C(42)–C(41)–C(46)	103.4 (8)
C(36)–C(31)–C(37)	110.0 (9)	C(41)–C(42)–C(43)	119.4 (9)
C(36)–C(31)–C(41)	110.7 (8)	C(41)–C(42)–C(47)	119.1 (9)
C(37)–C(31)–C(41)	112.9 (9)	C(43)–C(42)–C(47)	119.7 (10)
C(31)–C(32)–C(33)	120.2 (10)	C(42)–C(43)–C(44)	121.2 (10)
C(32)–C(33)–C(34)	118.9 (10)	C(43)–C(44)–C(45)	118.0 (10)
C(32)–C(33)–C(38)	121.6 (10)	C(43)–C(44)–C(48)	119.8 (11)
C(34)–C(33)–C(38)	119.4 (10)	C(45)–C(44)–C(48)	122.2 (11)
C(33)–C(34)–C(35)	118.4 (10)	C(44)–C(45)–C(46)	119.3 (10)
C(34)–C(35)–C(36)	117.7 (9)	C(41)–C(46)–C(45)	119.2 (10)
C(34)–C(35)–C(39)	119.8 (10)	C(41)–C(46)–C(49)	118.1 (10)
C(36)–C(35)–C(39)	122.4 (10)	C(45)–C(46)–C(49)	120.1 (10)
C(31)–C(36)–C(35)	119.6 (10)		

(Tables VIII and IX), and selected bond angles (Tables X and XI) are also given. **5a** and **5b** represent the first examples of crystallographically characterized bis(cyclohexadienyl) complexes so a detailed discussion of the structures is in order. Overall, the bonding to the manganese atoms and the bond distances and angles within the cyclohexadienyl moiety are similar to those observed for **3d** and **7**. The Mn(CO)$_3$ tripods are oriented so that the sp^3 ring carbon atoms are eclipsed by carbonyl ligands. Therefore, in the case of **5b**, one tripod (Mn(1)) is eclipsed by methylated ring carbon atoms and the other tripod (Mn(2)) is eclipsed by nonmethylated ring carbon atoms. An ideal situation therefore exists for studying the electronic effects that trans methyl groups could have upon M–CO bond length. Such factors are considered relevant in the context of determining structure-reactivity relationships in (arene)Cr(CO)$_3$ complexes.[25] One observes that, within experimental error, no effects on Mn–CO bond

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distance exist, although the average distance to Mn(1) of 1.77 Å is shorter than the 1.80 Å to Mn(2). In **5a** the Mn–CO distances also average 1.80 Å and the Mn–C(ring) bond lengths of 2.152 (2)–2.264 (2) Å correlate with the ranges observed in **3d**, **5**, and **7**. Surprisingly no strong evidence of steric strain is seen in **5a** and **5b**. The five sp^2-carbon atoms of each cyclohexadienyl ring that are bonded to manganese are planar to within 0.02 Å, and the remaining sp^3-carbon atom lies ca. 0.6Å out of the plane as it does in **3d** and **7**. The C–C bonds joining the two rings are somewhat long, however, at 1.636 (5) and 1.592 (14) Å for **5a** and **5b**, respectively, perhaps indicating a degree of weakness in the bond as the corresponding C–C distance in **3d** is only 1.529 (7) Å. It is interesting to note that the conformation about these C–C bonds differs between **5a** and **5b**. Both **5a** and **5b** adopt staggered conformations (as shown by torsion angles), but in **5a** the cyclohexadienyl rings are disposed in a gauche conformation whereas in **5b** they are disposed anti. The conformation preferences
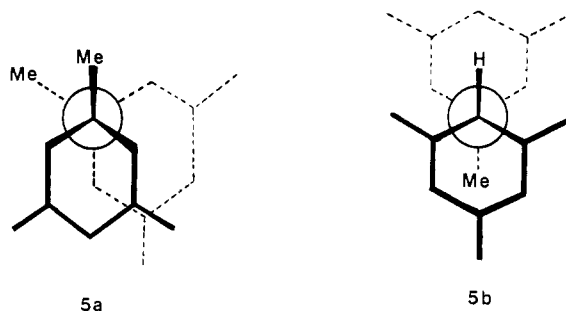
could be a result of the steric bulk of one of the cyclohexadienyl rings in **5b** or simply a packing effect.

That **5b** was isolated from a reaction at 70 °C whereas **5a** was isolated from a room-temperature reaction could indicate that **5b** is the thermodynamically favored product and that **5a** and **5b** are interconvertible. Attempts to isolate **5a**, **5b**, or **6** by direct chemical reduction of **1d** (using Na/Hg and Zn/Hg) have so far proven fruitless; however, they are still underway.

Conclusions

Neat trialkylaluminum compounds and trialkylaluminates effect alkylation of [(arene)Mn(CO)$_3$]$^+$ and [Co(C$_5$H$_5$)$_2$]$^+$ cations to give the expected neutral addition products **3a–h** and **4** in moderate yields, however, under more forcing conditions than those required by more conventional carbanion sources. The alkylaluminates show the same reactivity as neat trialkylaluminum compounds in the systems we studied and therefore offer potential for more widespread use of alkylaluminum reagents as they are practically more facile to handle and store than the corresponding neat trialkylaluminum compounds. Isolation of the reduction products **5a** and **5b** from reactions involving [(mesitylene)Mn(CO)$_3$]$^+$ are an indication that the reaction mechanism could involve electron transfer rather than the generally accepted nucleophilic processes. We are attempting to isolate **5a** and **5b** via reduction of **1d** and an ESR investigation of this system is underway.[26]

(26) In collaboration with C. Mailer (University of New Brunswick).

The First Group 6 (η^2-Olefin)(η^4-diene)M(CO)₃ Complexes: Photochemical Synthesis and Structure of *mer*-Tricarbonyl(η^2-olefin)(η^4-norbornadiene)tungsten Compounds

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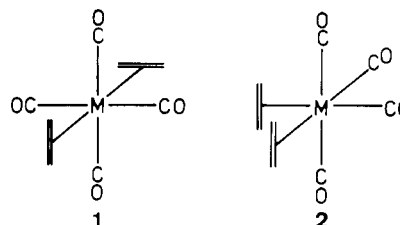*Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany*

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The photoreactions of (η^4-norbornadiene)W(CO)₄ (3) with (Z)-cyclooctene and ethene yield *mer*-(η^2-(Z)-cyclooctene)(η^4-norbornadiene)W(CO)₃ (4) and *mer*-(η^2-ethene)(η^4-norbornadiene)W(CO)₃ (5), respectively. Single-crystal X-ray diffraction analyses of 3 and 5 establish distorted octahedral coordination geometries, in the case of 5 with a *mer*-W(CO)₃ structure and a trans-orthogonal orientation of the ethene and one of the norbornadiene C=C units. The W—C distances of the latter are shorter, by 0.1 Å, than those of the other C=C unit, trans to a CO group. Crystals of 3 are monoclinic, space group $P2_1/c$, with $a = 9.744$ (2) Å, $b = 9.929$ (1) Å, $c = 11.394$ (1) Å, $\beta = 91.16$ (1)°, and $Z = 4$. The structure was solved and refined to $R = 0.031$ and $R_w = 0.035$ by using 4790 independent reflections. Crystals of 5 are monoclinic, space group $P2_1/n$, with $a = 8.225$ (1) Å, $b = 12.571$ (2) Å, $c = 11.327$ (1) Å, $\beta = 92.51$ (1)°, and $Z = 4$. The structure was solved and refined to $R = 0.035$ and $R_w = 0.041$ by using 3395 independent reflections. 4 and 5 were characterized by elemental analysis and UV–vis, IR, and ^{1}H and ^{13}C NMR spectroscopy. The *trans*-(η^2-C=C)₂M substructure of 4 and 5 provides for optimum metal (d_π)→olefin (π*) back-donation, thus accounting for the extraordinary stability of the complexes. Moreover, it is associated with unusually large ^{13}C NMR coordination shifts of the olefinic carbon atoms, which may serve as a general criterion for recognizing the relative positions of olefinic units and CO groups in octahedral complexes. The dynamic behavior reveals that olefin rotation occurs with $E_a = 58$ kJ mol⁻¹ (4) and $E_a = 54.8$ kJ mol⁻¹ (5).

Introduction

Group 6 metal carbonyls undergo sequential photosubstitution of two CO groups for monoolefin ligands, yielding (η^2-olefin)M(CO)₅ and, ultimately, stable *trans*-(η^2-olefin)₂M(CO)₄ (1),[1-7] with orthogonal arrangement of the two monoolefin units. Labile[5,6] *cis*-(η^2-olefin)₂M(CO)₄ isomers (2) are suspected to be involved as intermediate products.[7]

Further CO photosubstitution, with introduction of a third olefin ligand, has not yet been accomplished. How-

ever, such an undertaking might have a good chance of success when starting with a (η^4-diene)M(CO)₄ complex, bearing in mind the stabilizing diene chelate effect.

Results and Discussion

Irradiation of (η^4-norbornadiene)W(CO)₄ (3)[8] in the presence of excess olefin ((Z)-cyclooctene, ethene) results in the formation of the *mer*-(η^2-olefin)(η^4-norbornadiene)W(CO)₃ complexes (4, olefin = (Z)-cyclooctene; 5, olefin = ethene; eq 1), which are the first representatives

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