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Syntheses and Reactions of Manganese Cycloheptadienyl–Carbene Adducts

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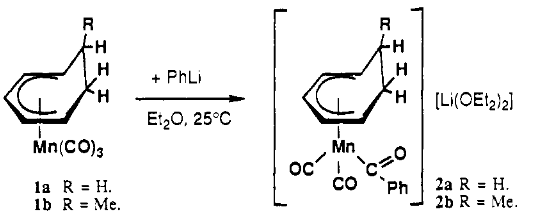
Abstract: Treatment of [$Mn(CO)_3(\eta^5\text{-}C_7H_9)$] (**1**) with phenyllithium in diethyl ether gave the acyl complex [$Li(Et_2O)_2$][$Mn(CO)_2(C(O)Ph)(\eta^5\text{-}C_7H_9)$] (**2**), which in turn reacted with $(CH_3)_3SiCl$ to form the bicyclo[3.2.1]oct-2-ene complex **3** via intramolecular carbene–cycloheptadienyl coupling. Protonation of **3** gave the bidentate η^2-olefin–η^6-arene cation **4**, which can be desilylated with excess acid to form the hydroxy derivative **5**. The regiochemistry of the carbene–cycloheptadienyl coupling reaction has been probed using the methyl-substituted species [$Mn(CO)_3(\eta^5\text{-}C_7H_8Me)$] (**1b**). The protonation reaction was shown to occur exclusively at the olefin of the σ-allyl moiety in **3** using the methyl-substituted derivative **3b**. Complexes **4** and **5** added nucleophiles (H^-, $[CH(CO_2Me)_2]^-$, and MeMgCl) to the arene ligand, rather than at the predicted olefin site, to form the cyclohexadienyl species **6** and **7**, respectively. Treatment of **3** with PPh_3 in CH_2Cl_2 gave a novel species, [$(\eta^3\text{-}C_8H_9)(OTMS)(\eta^2\text{-}Ph)$]$Mn(CO)_2(PPh_3)$ (**8**), in which a distorted manganese–η^2-arene group is present. The rhenium analog of **2** was prepared and gave the stable carbene complex **9** upon treatment with $(CH_3)_3SiCl$.

With the exception of the cyclopentadienyl ligand, few transition metal polyene complexes containing either carbene or acyl ligands have been reported. This is due, in part, to a lack of suitable synthetic routes to these species. For example, a Fischer[1] acyl or carbene synthesis, via alkyl- or aryllithium addition to a carbonyl ligand of a polyene–carbonyl complex, often leads to attack at the polyene,[2] particularly when the complex is cationic.[3] On the other hand, an approach similar to that used for cyclopentadienyl complexes, involving metathesis of a cyclopentadienyl salt with a metal halide,[4] often fails for other polyenyl species due to the instability of noncyclically conjugated polyenyl anions and their propensity to undergo redox reactions.[5] In the few cases where polyene–acyl[6,7] or polyene–carbene[7,8] species have been prepared or invoked, the two ligands often couple to form new complexes.[6,8]

Our interest in this area is the development of a synthetic methodology that involves the coupling of two ligands within a transition metal coordination sphere. This *intra*molecular approach allows greater regio- and stereocontrol in the bond-forming process and complements known *inter*molecular methodologies[2,3] for the functionalization of polyene ligands. In particular, we have pursued the synthesis of species that contain a polyenyl as well as a carbene or acyl moiety. Herein we describe full details of our study on manganese complexes that arise via the intramolecular coupling of a carbene ligand with the C(1) and C(5) carbon atoms of a coordinated cycloheptadienyl ring. A portion of this work has been previously communicated.[9]

Results and Discussion

Carbene–Cycloheptadienyl Coupling. The dropwise addition of phenyllithium to dry diethyl ether solutions of [$Mn(CO)_3(\eta^5\text{-}C_7H_8R)$][3c] (**1a** R = H, **1b** R = 6-*exo*-Me) causes a color change from pale yellow to deep red. Upon removal of the solvent, excellent yields of the highly air and moisture sensitive orange crystalline salts [$Li(Et_2O)_2$][$Mn(CO)_2(C(O)Ph)(\eta^5\text{-}C_7H_8R)$] (**2a,b**) can be isolated (eq 1). These salts were characterized



(1)

using ^1H and ^{13}C NMR and IR spectroscopy (see Experimental Section and Table I), although their extreme sensitivity to oxygen and moisture prevented satisfactory elemental analyses from being obtained. Further support for the assigned structures of **2a,b** comes from the similarity of their spectral data with that reported for the six-membered ring analog, [$Li(Et_2O)$][$Mn(CO)_2(C(O)Ph)(\eta^5\text{-}C_6H_6R)$] (R = 6-*exo*-Me), which was crystallographically characterized as its $[N(PPh_3)_2]^+$ salt.[7a]

The acyl complexes **2a,b** undergo a novel reaction with (TMS)-Cl (TMS = $Si(CH_3)_3$) to give the new species **3a,b** (eq 2). Thus, addition of equimolar amounts of chlorotrimethylsilane to diethyl ether solutions of **2** at room temperature leads to orange solutions of the carbene–cycloheptadienyl adduct **3** and precipitation of

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(1) Fischer, E. O.; Maasbol, A. *Chem. Ber.* **1967**, *100*, 2445.

(2) See, for example: (a) Roell, B. C., Jr.; McDaniel, K. F. *J. Am. Chem. Soc.* **1990**, *112*, 9004. (b) Kuendig, E. P.; Bernardinelli, G.; Liu, R.; Ripa, A. *J. Am. Chem. Soc.* **1991**, *113*, 9676. (c) Kuendig, E. P.; Bernardinelli, G. *Organometallics* **1991**, *10*, 2921 and references therein. (d) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. (e) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497.

(3) See, for example: (a) Pearson, A. J. In *Chemistry of the Carbon-Metal Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, U.K., 1987; Vol. 4, Chapter 10. (b) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1683. (c) Haque, F.; Miller, J.; Pauson, P. L.; Tripathi, J. B. *J. Chem. Soc. A* **1971**, 743.

(4) For examples, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 165–173.

(5) (a) Bates, R. B.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1967**, 199–204. (b) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2036 and references therein.

(6) (a) Williams, G. M.; Fisher, R. A.; Heyn, R. H. *Organometallics* **1986**, *5*, 818. (b) Williams, G. M.; Rudisill, D. E. *Inorg. Chem.* **1989**, *28*, 797. (c) Williams, G. M.; Rudisill, D. E. *Tetrahedron Lett.* **1986**, *27*, 3465. (d) Williams, G. M.; Rudisill, D. E.; *J. Am. Chem. Soc.* **1985**, *107*, 3357.

(7) (a) Sheridan, J. B.; Padda, R. S.; Chaffee, K.; Huang, Y.; Wang, C.; Lalancette, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1539. (b) Padda, R. S.; Sheridan, J. B.; Chaffee, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1226.

(8) (a) Chen, J.; Lei, G.; Jin, Z.; Hu, L.; Wei, G. *Organometallics* **1988**, *7*, 1652 and references therein. (b) Chen, J.; Yin, J.; Lei, G.; Wang, Y.; Lin, G. *J. Chem. Soc., Dalton Trans.* **1989**, 635. (c) Chen, J.; Yin, J.; Fan, Z.; Xu, W. *J. Chem. Soc., Dalton Trans.* **1988**, 2803 and references therein. (d) Chen, J.; Lei, G.; Xu, W.; Pan, Z.; Zhang, S.; Zhang, Z.; Jin, X.; Shao, M.; Tang, Y. *Organometallics* **1987**, *6*, 2461. (e) O'Connor, J. M.; Pu, L.; Woolard, S.; Chadha, R. K. *J. Am. Chem. Soc.* **1990**, *112*, 6731 and references therein.

(9) Wang, C.; Lang, M. G.; Sheridan, J. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 3236.

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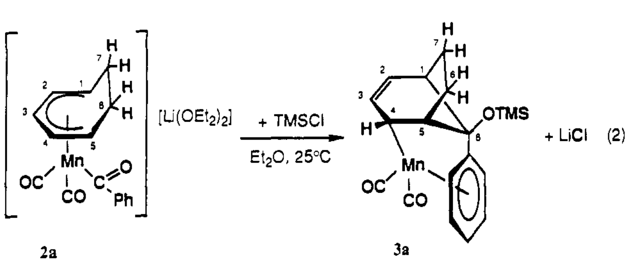


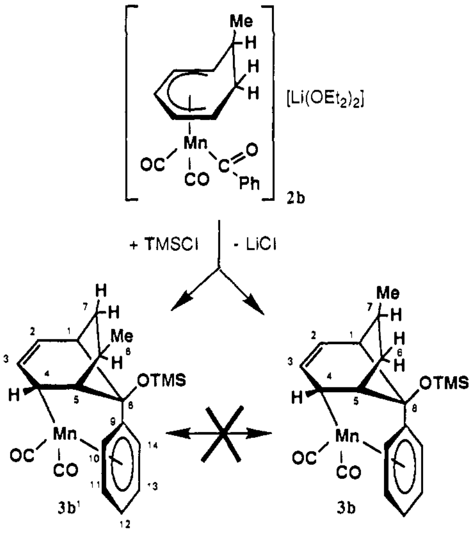
LiCl. The bicyclic ring in 3 is formed from the coupling of a transient phenyl(trimethylsiloxy)carbene group and the terminal dienyl carbons (C(1) and C(5)) of the cycloheptadienyl ring. As shown, the metal is σ-bonded to the original C_7 ring at C(4) but is also coordinated to the arene substituent of the former acyl/carbene carbon C(8). The new complex contains a σ,π-bidentate bicyclo[3.2.1]oct-2-enyl[10] ligand.

Complex **3a** was isolated in 84% yield (based on **1a**) as a moderately stable orange solid and was fully characterized by elemental analysis, ^1H, ^{13}C, ^1H–^1H (2D COSY), ^1H–^{13}C (2D COSY) NMR, and IR spectroscopy (Table I). The proton NMR spectrum is most informative and clearly shows the presence of a TMS group (δ 0.06) and 14 additional protons associated with the phenyl (5H) and bicyclo[3.2.1]octenyl (9H) rings. The absence of η^5-dienyl signals (typically 3 signals in a 1H:2H:2H ratio) and the presence of two signals at δ 5.18 and 5.81 assigned to the olefinic protons H(2) and H(3) provide evidence for σ-allyl rather than η^5-dienyl or η^3-allyl coordination of the C_7 ring. Similarly, η^6-complexation of the arene substituent at C(8) was confirmed by 5 resonances between δ 4.90 and 6.20, typical of π-bonded arenes,[8c] as well as by the absence of any signals in the aromatic region. The carbon-13 NMR data is consistent with the assigned structure and shows two distinct carbonyl carbon signals at δ 227.4 and 229.1, as well as six phenyl carbon signals between δ 83 and 122. This suggests a static structure for the σ-allyl ligand of **3a** (i.e. the metal does *not* migrate between C(4) and C(2) via an η^3-allyl intermediate). No evidence for a carbene carbon signal at low field was found. Repeated attempts to obtain crystals of this material for an X-ray diffraction study failed; however the bicyclo[3.2.1]octenyl moiety has been structurally characterized in derivative **8** described below.

The reaction between the methyl-substituted cycloheptadienyl–acyl species **2b** and (TMS)Cl also resulted in carbene–dienyl coupling. In this case, however, the presence of a methyl group allows for the possibility of two isomers of the adduct, **3b**, **b′** (Scheme I). The ^1H NMR spectrum of the product shows two isomers do indeed form, with characteristic doublets at δ 0.96 and 1.06, in an approximate 5:1 ratio, assigned to the methyl groups of **3b** and **3b′**, respectively. The isomers were identified as those shown from the 2D ^1H–^1H COSY NMR spectrum of the mixture but could not be separated because partial decomposition on a chromatographic column permitted only flash chromatography.

The major species, **3b**, was fully characterized as that with the methyl substituent at C(7) (Table I). Isomers **3b**,**b′** may interchange via an η^3-allyl intermediate similar to that described for **3a**, but no evidence for such a process was observed. For example, the ^{13}C NMR spectrum of **3b** shows two distinct carbonyl resonances of equal intensity at δ 226 and 228,[11] and heating the mixture of **3b**,**b′** to 45 °C did not cause any changes in the ^1H NMR data. Any reversible change in the relative intensities of the signals due to the two isomers would have indicated some exchange. Heating the sample to higher temperatures resulted in decomposition of the complex.

Scheme I. Ratio **3b**:**3b′** ≈ 5:1



The formation of 3 may be viewed as an intramolecular (5 + 1) cycloaddition between a carbene ligand and a dienyl moiety. Related coupling reactions between carbene ligands and coordinated dienes have been observed by Chen et al. for tricarbonyl(η^4-diene)iron(0) complexes,[8a–d] including one example in which the phenyl substituent of a carbene ligand is η^6-coordinated to an iron dicarbonyl unit.[8c] However no dienyl–carbene couplings have been observed prior to this work. A proposed mechanism for this process and the formation of 3 is shown in Scheme II.

The first step involves electrophilic addition of (TMS)Cl to the acyl oxygen of **2**, forming a carbene intermediate (I). Anionic

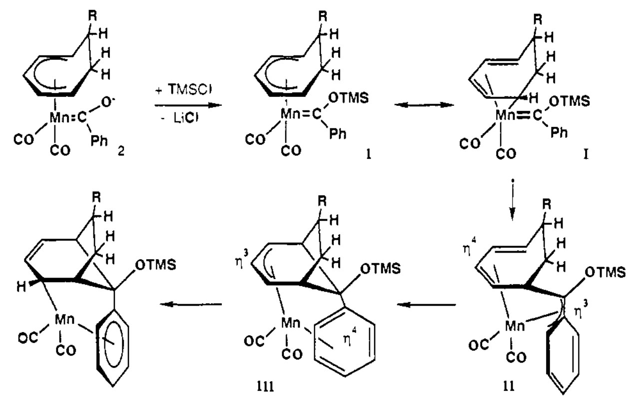
Table I. Proton and ^{13}C NMR Data for Complexes 2 and 3[a]

complex	$\delta(^1H)^b$	$\delta(^{13}C)^b$
2a	1.07 (10H, s(brd), Et_2O), 1.61 (2H, s(brd), H_6, H_7), 2.13 (2H, s(brd), $H_{6'}$, $H_{7'}$), 3.22 (8H, s(brd), Et_2O), 3.60 (2H, s(brd), H_1, H_5), 4.66 (2H, s(brd), H_2, H_4), 5.55 (1H, s(brd), H_3), 6.95–7.30 (5H, m, Ph)[c]	16.1 (Et_2O), 33.0 (C_6, C_7), 65.6 (Et_2O), 79.9 (C_1, C_5), 93.6 (C_3), 102.5 (C_2, C_4), 123, 154 (Ph), 226 (CO)[c,d]
3a	0.06 (9H, s, $(CH_3)_3Si$), 1.66 (2H, m, $H_{6'}$, $H_{7'}$), 1.79 (1H, dd, H_4), 1.90 (1H, m, H_6), 2.27 (1H, m, H_7), 2.65 (1H, m, H_1), 3.22 (1H, m, H_5), 4.97 (1H, t, H_{12}), 5.10 (1H, d, H_{14}), 5.18 (1H, dd, H_2), 5.69 (1H, d, H_{10}), 5.81 (1H, dd, H_3), 5.90 (1H, t, H_{11}), 6.14 (1H, t, H_{13})[e]	1.6 ($(CH_3)_3Si$), 32.2 (C_6), 33.2 (C_4), 35.0 (C7), 46.5 (C_1), 69.7 (C_5), 83.6 (C_{12}), 86.2 (C_{10}), 86.6 (C_8), 97.1 (C_{11}), 99.9 (C_{13}), 105.2 (C_{14}), 116.5 (C_2), 122.5 (C_9), 141.9 (C_3), 227.4, 229.1 (CO)[e]
3b	0.05 (9H, s, $(CH_3)_3Si$), 0.96 (3H, d, $J = 7$ Hz, Me), 1.20 (1H, dd, $J = 12.5$, 8 Hz, $H_{6'}$), 1.97 (1H, t, $J = 4$ Hz, H_4), 2.05 (1H, dt, $J = 12.5$, 8 Hz, H_6), 2.43 (1H, t, $J = 4.5$ Hz, H_1), 2.89 (1H, m(brd), H_7), 3.17 (1H, m, H_5), 4.73 (1H, t, $J = 6$ Hz, H_{12}), 4.95 (1H, d, H_{14}), 5.04 (1H, dd, $J = 6$, 8.5 Hz, H_2), 5.47 (1H, d, $J = 6$ Hz, H_{10}), 5.60 (1H, t, $J = 6$ Hz, H_{11}), 5.85 (1H, t, H_{13}), 5.97 (1H, dd, $J = 8.5$, 5.5 Hz, H_3)[f] 1.06 (3H, d, $J = 7$ Hz, Me)[g]	2.0 ($(CH_3)_3Si$), 15.2 (Me), 34.2 (C_4), 41.0 (C_6, C_7), 50.8 (C_1), 70.1 (C_5), 82.0 (C_{12}), 84.6 (C_{10}), 87.1 (C_8), 95.5 (C_{11}), 98.5 (C_{13}), 104.4 (C_{14}), 112.5 (C_2), 122.5 (C_9), 143.8 (C_3), 226.0, 228.2 (CO)[f]

[a] Assignments refer to eq 2 and Scheme I. [b] ^1H-decoupled spectra. [c] In C_6D_6. [d] Remaining Ph signals obscured by solvent. [e] In $[^2H_6]$-acetone. [f] In $CDCl_3$. [g] Methyl signal for minor isomer **3b′**.

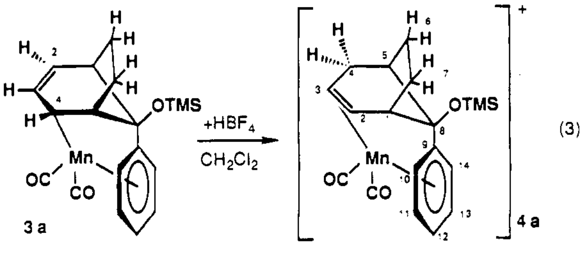
acylmetalates like **2** typically react with electrophiles at this site, and in other work, we have isolated related cyclohexadienyl–carbene complexes via the addition of (TMS)Cl to the cyclohexadienyl complex $[Li(Et_2O)][Mn(CO)_2(C(O)Ph)(\eta^5\text{-}C_6H_6R)]$ (R = 6-*exo*-Me).[7a] In addition, the rhenium analog of I has been isolated and is described later. The manganese–carbene intermediate shown (I) was not detected, even at low temperature (−78 °C), as it rapidly rearranges to **3**. We propose this occurs via sequential carbene–alkyl and olefin–alkyl migratory insertions as shown. Attempts to stop the reaction at intermediates II or III by synthesizing **2** with vinyl or diene substituents at the acyl ligand failed. However, Chen and co-workers have isolated an analog of intermediate II in which the metal coordinates to an allyl moiety following a single insertion of a carbene into a coordinated diene.[8a,d] The preference for structure **3b** over **3b′** in the substituted species may be due to an unfavorable 1,3 interaction between the methyl substituent and H(4) in **3b′**. Such an interaction is not present in the major species **3b**. This selection of **3b** over **3b′** most likely occurs at the final stage of the reaction, during the η^3 to η^1 slip of the allyl moiety in III.

Scheme II. Proposed Mechanism for Dienyl-Carbene Coupling (R = H or Me)



The carbene–dienyl coupling reaction forming **3** is unique to the benzoyl derivatives **2a,b**. Attempts to generate analogues of **3** from acyls containing methyl or butyl substituents failed to produce any tractable products. Likewise, attempted alkylation of **2** with MeI, Me_3O^+, or Et_3O^+ also resulted in decomposition of **2**, with **1** being the only detectable organometallic species. Addition of Ph_3SnCl or Me_3SnCl to **2** gave dicarbonyl complexes ($SnPh_3$ species, $\nu_{max}(CO)$ 1950 and 1898 cm^{-1} (hex); $SnMe_3$ derivative, $\nu_{max}(CO)$ 1949 and 1895 cm^{-1} (hex)) that are presumably isostructural with **3**. However, these could not be purified nor further characterized.

Protonation of the σ-Allyl Ligand in 3. The addition of $HBF_4{\cdot}Et_2O$ to **3a** in CH_2Cl_2 at 0 °C gave the new cation **4a** as a pale yellow precipitate in excellent yield (eq 3). Complex **4a** was fully characterized by elemental analysis, ^1H and ^{13}C NMR, and IR spectroscopy (Table II) as the bidentate bicyclo[3.2.1]-oct-2-ene–dicarbonyl η^2,η^6 species shown. Characteristic features of the ^1H NMR spectrum are five signals between δ 5.5 and 7.0 assigned to the η-arene ligand and two resonances at δ 3.93 (H_3) and 4.61 (H_2) due to the coordinated olefinic protons. Complex **4a** is similar to the known (η-benzene)dicarbonyl(η-ethylene)-manganese(I) cations,[12] although it differs in that the olefin and arene are part of the same bidentate ligand.

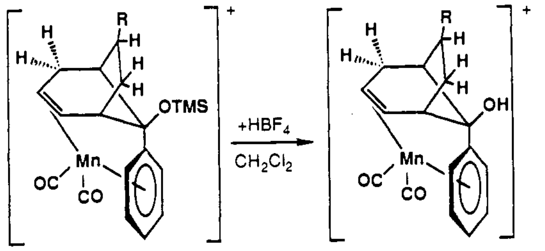


3a 4a (3)

The formation of **4** involves protonation of the σ-allyl group of **3** at either C(2) or C(4). A determination of which carbon is attacked is possible using **3b,b′** (Scheme III). Thus, protonation at C(2) of **3b** would give **4b**, with a methyl substituent at C(6). Alternatively, addition to C(4) of **3b** would lead to **4b′**, in which the methyl group is at C(7). Likewise, protonation of **3b′** at C(2) and C(4) would yield **4b′** and **4b**, respectively. The stereochemical rigidity of the bicyclic ligand in **3** eliminates the possibility of any crossover in this experiment.

Protonation of the mixture of **3b,b′** (≈5:1) gave an approximate 5:1 mixture of the two cations **4b,4b′**, which were spectroscopically characterized (Table II). This unequivocally confirms the site of electrophilic attack as the olefinic carbon C(2) and is consistent with other studies in which electrophiles typically add to the noncoordinated terminus of σ-allyl complexes.[13]

Complexes **4a,b** are sensitive to excess acid. Thus, when 1 equiv of $HBF_4{\cdot}Et_2O$ is added to **4** at room temperature, the trimethylsilyl group is replaced by H^+, yielding the hydroxy species **5a,b** (Table II, eq 4). These species were also isolated as pale yellow solids and characterized by comparison of their spectroscopic data with those of **4a,b**. The spectral data are virtually identical for the hydroxy and O(TMS) derivatives; however, **5a,b** show strong broad absorptions in the IR around 3500 cm^{-1}, due to the OH group, and singlet ^1H NMR signals assigned to the OH proton at δ 3.57 and 3.77, respectively. As expected, no TMS signal is present in either of the proton NMR spectra of **5**.

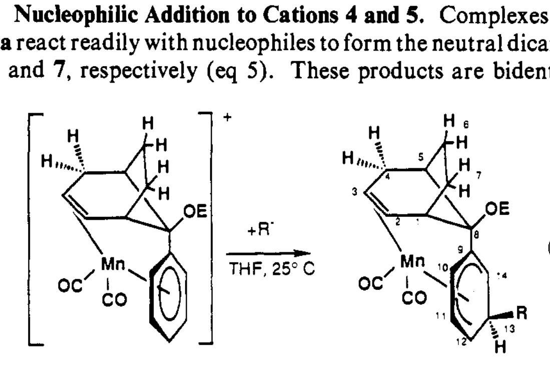


4a R = H.
4b R = Me.

5a R = H
5b R = Me

(4)

Nucleophilic Addition to Cations 4 and 5. Complexes **4a** and **5a** react readily with nucleophiles to form the neutral dicarbonyls **6** and **7**, respectively (eq 5). These products are bidentate η^2-olefin–η^5-cyclohexadienyl complexes, in which the regiochemistry of addition to the coordinated arene is meta to the bicyclic



4, E = TMS
5, E = H

6a, R = H, E = TMS.
6b, R = $CH(CO_2CH_3)_2$, E = TMS.
6c, R = CH_3, E = TMS.
7a, R = H, E = H.
7b, R = $CH(CO_2CH_3)_2$, E = H.

(5)

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[10] Complexes of this ligand have previously been made from strained ring iron–carbene complexes: (a) Bly, R. S.; Silverman, G. S.; Bly, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 7730. (b) Bly, R. S.; Silverman, G. S. *Organometallics* **1984**, *3*, 1765.

[11] Two additional resonances are observed at δ 223 and 227, assigned to the minor isomer **3b′**.

[12] Halpin, W. A.; Williams, J. C., Jr.; Hanna, T.; Sweigart, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 376.

[13] Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189.

Scheme III. Protonation of **3b,b′** showing H^+ addition to C(2)

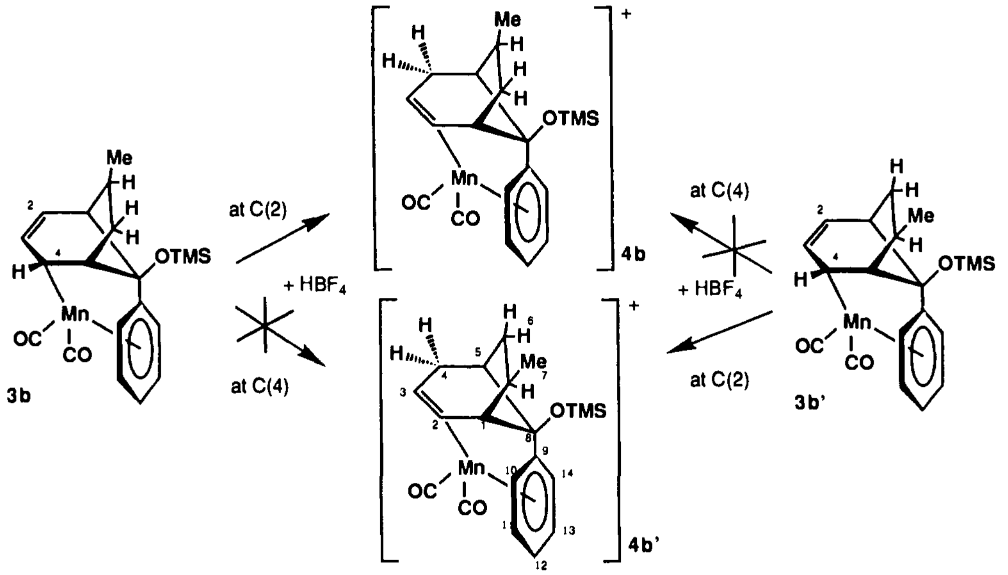


Table II. Proton and ^{13}C NMR Data for Cations **4** and **5**[a]

complex	$\delta(^1H)$[b]	$\delta(^{13}C)$[b,c]
4a	0.07 (9H, s, $(CH_3)_3Si$), 1.77 (1H, t, $J_{H_{6'}H_{7'}}$, $J_{H_{6'}H_6}$ = 10.5 Hz, $H_{6'}$), 2.06 (1H, m, $H_{7'}$), 2.26 (1H, m, H_7), 2.34 (1H, m, H_6), 2.65 (2H, m, $H_{4'}$, H_5), 3.28 (1H, dd, $J_{H_4H_5}$ = 8 Hz, $J_{H_4H_{4'}}$ = 19 Hz, H_4), 3.42 (1H, m, H_1), 3.93 (1H, m, H_3), 4.61 (1H, dd, $J_{H_2H_3}$, $J_{H_2H_1}$ = 6 Hz, H_2), 5.56 (1H, m, H_{12}), 5.96 (1H, d, $J_{H_{10}H_{11}}$ = 6 Hz, H_{10}), 6.70 (1H, d, H_{14}), 6.96 (1H, m, H_{11}), 7.04 (1H, m, H_{13})	2.0 ($(CH_3)_3Si$), 33.8 (C_7), 35.2 (C_6), 40.0 (C_4), 42.0 (C_5), 54.9 (C_1), 76.0 (C_3), 84.6 (C_{12}), 85.8 (C_8), 86.4 (C_2), 97.6 (C_{14}), 104.2 (C_{11}), 105.6 (C_{10}), 107.3 (C_{13}), 120.0 (C_9), 223, 227 (CO)
4b	0.06 (9H, s, $(CH_3)_3Si$), 1.12 (3H, d, Me), 1.49 (1H, m, $H_{7'}$), 2.45 (2H, m(brd), H_5, H_7), 2.95 (3H, m(brd), H_4, $H_{4'}$, H_6), 3.38 (1H, t, H_1), 3.92 (1H, m, H_3), 4.64 (1H, t(brd), H_2), 5.58 (1H, t, H_{12}), 5.96 (1H, d, H_{10}), 6.68 (1H, d, H_{14}), 6.98 (1H, m, H_{11}), 7.02 (1H, m, H_{13}), 1.18 (3H, d, J = 7 Hz, Me)[d]	1.9 ($(CH_3)_3Si$), 15.7 (Me), 30.3 (C_7), 36.7 (C_6), 41.1 (C_4), 46.1 (C_5), 55.3 (C_1), 75.8 (C_3), 84.6 (C_{12}), 86.3 (C_8), 87.2 (C_2), 96.9 (C_{14}), 104.3 (C_{11}), 105.5 (C_{10}), 107.3 (C_{13}), 120.3 (C_9), 223, 226.5 (CO)
5a	1.76 (1H, t, $J_{H_{6'}H_{7'}}$, $J_{H_{6'}H_6}$ = 10.5 Hz, $H_{6'}$), 2.07 (1H, m, $H_{7'}$), 2.26 (1H, m, H_7), 2.35 (1H, m, H_6), 2.53 (1H, t, J = 4 Hz, H_5), 2.63 (1H, dd, $J_{H_4H_{4'}}$ = 18, $J_{H_{4'}H_3}$ = 4 Hz, $H_{4'}$), 3.25 (1H, dd, $J_{H_4H_5}$ = 8 Hz, $J_{H_4H_{4'}}$ = 18 Hz, H_4), 3.40 (1H, m, H_1), 3.57 (1H, s, OH), 3.93 (1H, m, H_3), 4.62 (1H, t, J = 6 Hz, H_2), 5.54 (1H, t, J = 6 Hz, H_{12}), 5.87 (1H, d, J = 6 Hz, H_{10}), 6.68 (1H, d, H_{14}), 6.93 (1H, m, H_{11}), 7.02 (1H, m, H_{13})	33.5 (C_7), 34.9 (C_6), 39.8 (C_4), 41.7 (C_5), 52.5 (C_1), 75.9 (C_3), 83.7 (C_8), 84.4 (C_{12}), 86.6 (C_2), 97.2 (C_{14}), 104.3 (C_{11}), 105.2 (C_{10}), 107.4 (C_{13}), 119.7 (C_9), 223, 226 (CO)
5b	1.11 (3H, d, J = 7 Hz, Me), 1.50 (1H, dd, $J_{H_6H_{7'}}$ = 8 Hz, $J_{H_7H_{7'}}$ = 13.5 Hz, $H_{7'}$), 2.35 (1H, m(brd), H_5), 2.43 (1H, m, H_7), 2.94 (3H, m(brd), H_4, $H_{4'}$, H_6), 3.38 (1H, t, J = 6 Hz, H_1), 3.77 (1H, s, OH), 3.90 (1H, m, H_3), 4.64 (1H, t, J = 6 Hz, H_2), 5.54 (1H, t, J = 6 Hz, H_{12}), 5.87 (1H, d, J = 6 Hz, H_{10}), 6.65 (1H, d, H_{14}), 6.94 (1H, m, H_{11}), 7.02 (1H, m, H_{13}), 1.19 (3H, d, J = 7 Hz, Me)[e]	15.8 (Me), 30.0 (C_7), 36.6 (C_6), 41.6 (C_4), 45.7 (C_5), 52.7 (C_1), 75.6 (C_3), 84.1 (C_8), 84.4 (C_{12}), 87.4 (C_2), 96.6 (C_{14}), 104.4 (C_{11}), 105.3 (C_{10}), 107.4 (C_{13}), 120.1 (C_9), 223, 227 (CO)

[a] Assignments refer to eq 3 and Scheme III. [b] In $[^2H_3]$-nitromethane unless otherwise stated. [c] ^1H-decoupled spectra. [d] Methyl signal for minor isomer **4b′**. [e] Methyl signal for minor isomer **5b′**.

substituent and exo with respect to the metal. The O(TMS) derivatives **6a–c** were prepared by addition of hydride, dimethylmalonate enolate, and methylmagnesium chloride to **4a**, whereas the hydroxy species **7a,b** were isolated from the reaction of hybride and dimethylmalonate enolate with **5a**. Reaction of MeMgCl with **5a** did not lead to tractable organometallic products.

All the new neutral complexes were isolated as pale yellow solids in 56–82% yield and spectroscopically characterized (Table III). The ^1H NMR data for these species are similar and show two clearly defined signals around δ 4.7 (dd) and 5.9 (d) assigned to the inner dienyl protons H(11) and H(10), respectively. The fact that only two signals are seen in this region confirms not only that nucleophilic addition is at the coordinated arene but that it is meta to the bicyclic substituent at C(9). Addition to the olefin at C(2) or C(3) of **4** and **5** would form products containing 5-coordinated aryl protons whose signals would appear in this region of the ^1H NMR spectrum. The samples of **6** and **7** also contain very small amounts of an another isomer, as evidenced by small signals in the low-field region of the ^1H NMR spectra. For example, the spectrum of **6a** shows two additional resonances between δ 4.8 and 5.0 ($\approx$5%), that may be assigned to the inner dienyl protons of a para-disubstituted cyclohexadienyl ring. These signals are also present for **7a** but are much smaller (<2%). The regiochemistry of nucleophilic addition to coordinated arenes has been well documented,[3b,14] and addition may be ortho, or more often meta, to a substituent like OMe or Me. It is clear from our results that the bicyclic group containing either OH or O(TMS) at C(8) is a strong meta-directing ligand in nucleophilic additions to the arene ring in **4** and **5**, much more so than OMe or Me in the related $[Mn(CO)_3(\eta\text{-arene})]^+$ series.[3b,14] The exo stereochemistry of the added group at C(13) was confirmed from the chemical shift of the endo proton H(13) in **6b,c** and **7b**. This

Table III. Proton and ^{13}C NMR Data for Cyclohexadienyl Complexes 6 and 7[a]

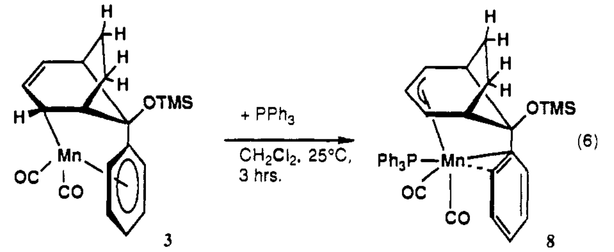
complex	$\delta(^1H)^b$	$\delta(^{13}C)^{b,c}$
6a (R = H)	0.04 (9H, s, $(CH_3)_3Si$), 1.09 (1H, t, $H_{6'}$), 1.32 (1H, m(brd), H_5), 1.41 (1H, d, $J_{H_{13}H_{13'}}$ = 12.5 Hz, $H_{13'}$), 1.55 (1H, m, $H_{7'}$), 1.65 (1H, dd, $J_{H_{4'}H_3}$ = 5 Hz, $J_{H_{4'}H_4}$ = 17 Hz, $H_{4'}$), 1.95 (2H, m, H_6, H_7), 2.19 (2H, m, H_4, H_{12}), 2.27 (1H, m, H_{13}), 2.34 (1H, d, $J_{H_{14}H_{13}}$ = 6 Hz, H_{14}), 2.86 (1H, t, H_1), 2.90 (1H, dd, H_3), 3.26 (1H, dd, $J_{H_2H_3}$ = 5.5 Hz, $J_{H_2H_1}$ = 2 Hz, H_2), 4.70 (1H, dd, $J_{H_{11}H_{10}}$, $J_{H_{11}H_{12}}$ = 6 Hz, H_{11}), 5.96 (1H, d, H_{10})	2.0 ($(CH_3)_3Si$), 24.1 (C_{13}), 31.9 (C_7), 33.5 (C_6), 37.5 (C_4), 38.8 (C_{12}), 40.1 (C_5), 50.0 (C_1), 62.1 (C_3), 65.2 (C_{14}), 73.2 (C_2), 84.2 (C_{10}), 86.9 (C_8), 96.6 (C_{11}), 110.4 (C_9), 228, 240 (CO)
6b {R = $CH(CO_2Me)_2$}	0.08 (9H, s, $(CH_3)_3Si$), 1.03 (1H, t, $H_{6'}$), 1.40 (1H, m(brd), H_5), 1.48 (1H, m, $H_{7'}$), 1.55 (1H, dd, $J_{H_{4'}H_3}$ = 4.5 Hz, $J_{H_{4'}H_4}$ = 17 Hz, $H_{4'}$), 1.88 (2H, m, H_6, H_7), 2.13 (1H, dd, H_4), 2.57 (1H, t, J = 5.5 Hz, H_{12}), 2.76 (2H, m, H_{15}, H_1), 2.85 (1H, dd, $J_{H_3H_2}$ = 7 Hz, $J_{H_3H_{4'}}$ = 4.5 Hz, H_3), 3.18 (1H, m, H_2), 3.21 (3H, s, Me), 3.23 (3H, s, Me), 3.30 (1H, d, $J_{H_{14}H_{13}}$ = 6 Hz, H_{14}), 3.66 (1H, m, H_{13}), 4.75 (1H, dd, $J_{H_{11}H_{10}}$, $J_{H_{11}H_{12}}$ = 6 Hz, H_{11}), 5.86 (1H, d, H_{10})	2.1 ($(CH_3)_3Si$), 32.1 (C_7), 33.6 (C_6), 34.4 (C_{13}), 37.4 (C_4), 40.1 (C_{12}), 41.1 (C_5), 50.3 (C_1), 51.7, 51.8 ($CH(CO_2Me)_2$), 60.8 ($CH(CO_2Me)_2$), 63.3 (C_3), 70.0 (C_{14}), 73.5 (C_2), 85.1 (C_{10}), 87.1 (C_8), 95.6 (C_{11}), 109.9 (C_9), 166.6, 167.1 ($CH(CO_2Me)_2$), 228.1, 238.7 (CO)
6c (R = Me)	0.08 (9H, s, $(CH_3)_3Si$), 0.16 (3H, d, J = 7 Hz, Me), 1.12 (1H, t, $H_{6'}$), 1.35 (1H, m(brd), H_5), 1.58 (1H, m, $H_{7'}$), 1.71 (H, dd, $J_{H_{4'}H_3}$ = 5 Hz, $J_{H_{4'}H_4}$ = 17 Hz, $H_{4'}$), 1.96 (2H, m, H_6, H_7), 2.25 (1H, m, H_4), 2.29 (1H, m, H_{13}), 2.56 (1H, t, $J_{H_{12}H_{13}}$, $J_{H_{12}H_{11}}$ = 7 Hz, H_{12}), 2.61 (1H, d, $J_{H_{14}H_{13}}$ = 6 Hz, H_{14}), 2.88 (2H, m, H_1, H_3), 3.29 (1H, dd, $J_{H_2H_3}$ = 5.5 Hz, $J_{H_2H_1}$ = 2 Hz, H_2), 4.66 (1H, dd, $J_{H_{11}H_{10}}$, $J_{H_{11}H_{12}}$ = 6 Hz, H_{11}), 5.86 (1H, d, H_{10})	2.2 ($(CH_3)_3Si$), 26.1 (Me), 29.7 (C_{13}), 32.1 (C_7), 33.7 (C_6), 37.7 (C_4), 40.4 (C_5), 48.3 (C_{12}), 50.4 (C_1), 61.9 (C_3), 72.4 (C_{14}), 74.7 (C_2), 83.9 (C_{10}), 87.0 (C_8), 94.5 (C_{11}), 108.1 (C_9), 229. 239 (CO)
7a (R = H)	0.84 (1H, s, OH), 1.04 (2H, m, H_5, $H_{6'}$), 1.41 (1H, d, $J_{H_{13}H_{13'}}$ = 13 Hz, $H_{13'}$), 1.52 (1H, m, $H_{7'}$), 1.62 (1H, dd, $J_{H_{4'}H_3}$ = 5 Hz, $J_{H_{4'}H_4}$ = 17 Hz, $H_{4'}$), 1.88 (2H, m, H_6, H_7), 2.30 (4H, m, H_4, H_{12}, H_{13}, H_{14}), 2.67 (1H, dd, $J_{H_1H_2}$ = 4.5 Hz, $J_{H_1H_7}$ = 9 Hz, H_1), 2.90 (1H, dd, $J_{H_2H_3}$ = 5.5 Hz, $J_{H_2H_1}$ = 4.5 Hz, H_3), 3.23 (1H, dd, H_2), 4.74 (1H, dd, $J_{H_{11}H_{10}}$, $J_{H_{11}H_{12}}$ = 6 Hz, H_{11}), 5.85 (1H, d, H_{10})	24.0 (C_{13}), 31.7 (C_7), 33.2 (C_6), 37.4 (C_4), 38.9 (C_{12}), 39.7 (C_5), 48.0 (C_1), 62.1 (C_3), 64.8 (C_{14}), 73.0 (C_2), 83.6 (C_{10}), 84.3 (C_8), 96.8 (C_{11}), 110.6 (C_9), 229, 240 (CO)
7b {R = $CH(CO_2Me)_2$}	1.03 (1H, t , $H_{6'}$), 1.21 (1H, m(brd), H_5), 1.51 (1H, m, $H_{7'}$), 1.57 (1H, dd, $J_{H_{4'}H_3}$ = 4.5 Hz, $J_{H_{4'}H_4}$ = 17 Hz, $H_{4'}$), 1.82 (1H, s, OH), 1.89 (2H, m, H_6, H_7), 2.18 (1H, dd, H_4), 2.58 (1H, d, J = 9 Hz, H_{15}), 2.65 (2H, m, H_{12}, H_1), 2.86 (1H, dd, $J_{H_3H_2}$ = 7.5 Hz, $J_{H_3H_{4'}}$ = 4.5 Hz, H_3), 3.07 (1H, d, $J_{H_{14}H_{13}}$ = 7 Hz, H_{14}), 3.19 (3H, s, Me), 3.24 (3H, s, Me), 3.27 (1H, m, H_2), 3.42 (1H, m, H_{13}), 4.70 (1H, dd, $J_{H_{11}H_{10}}$, $J_{H_{11}H_{12}}$ = 6 Hz, H_{11}), 5.72 (1H, d, H_{10})	31.8 (C_7), 33.3 (C_6), 34.1 (C_{13}), 37.3 (C_4), 39.8 (C_{12}), 42.3 (C_5), 48.2 (C_1), 51.7 ($CH(CO_2Me)_2$), 60.5 ($CH(CO_2Me)_2$), 63.2 (C_3), 67.2 (C_{14}), 74.3 (C_2), 84.1 (C_{10}), 84.3 (C_8), 95.5 (C_{11}), 110.0 (C_9), 167.0, 167.4 ($CH(CO_2Me)_2$), 228.1, 238.8 (CO)

[a] Assignments refer to eq 5. [b] In C_6D_6 unless otherwise stated. [c] ^1H-decoupled spectra.

appears at lower field (**6b**, δ 3.66; **7b**, δ 3.42; **6c**, δ 2.56) than the exo proton H(13′) in **6a** and **7a** (**6a**, δ 1.41).

Particularly noteworthy is that the site of nucleophilic addition is *not* the predicted[15] olefin group C(2) or C(3). For instance, $[(\eta\text{-}C_6Me_6)Mn(CO)_2(\eta\text{-}C_2H_4)][PF_6]$ reacts with nucleophiles (H^-, CN^-) at the olefin to give alkyl complexes.[12] Given that **4** and **5** are structurally and electronically similar to $[(\eta\text{-}C_6Me_6)Mn(CO)_2(\eta\text{-}C_2H_4)][PF_6]$, addition to the olefin in **4** and **5** would be expected. It is possible, however, that the kinetic products of addition to **4** and **5** are indeed ones in which the nucleophile adds to the olefin moiety but that these are unstable relative to the arene adducts due to the ring strain incurred by maintaining chelation of the bidentate ligand. Unfortunately, no intermediate species could be observed by IR spectroscopy, even when the reactions were performed at -78 °C.

Synthesis and X-ray Crystal Structure of an η^2-Arene Complex. Complexes similar to **3**, that contain a coordinated arene as well as an alkyl ligand, have been prepared by the Brookhart[16] group from the addition of alkyl halides to the anion $[Mn(CO)_2(\eta\text{-benzene})]^-$, as well as by Sweigart[12] and co-workers as described earlier. In each case, these species react with donor ligands like PPh_3 to form endo- substituted cyclohexadienyl complexes, via an alkyl migration to the endo face of the arene ligand. In contrast, PPh_3 reacts with **3** to partially decomplex the arene and form the highly distorted η^2-arene complex **8** (eq 6).



Complex **8** was isolated in 40% yield as analytically pure deep red microcrystals. Its structure was confirmed by ^1H, ^{13}C, and ^{31}P NMR, and IR spectroscopy (Table IV), as well as by an X-ray diffraction study (Figure 1).[17] The crystallographic study showed **8** to be a $Mn(CO)_2(PPh_3)$ fragment bonded in a bidentate fashion to the bicyclic ligand from **3**. In **8**, however, the metal is η^3-bound to the seven-membered ring and η^2-bonded to the phenyl substituent at C(8′). The geometry about the metal is essentially octahedral with the phosphine trans to the coordinated arene. The Mn–C(11) distance of 2.445(10) Å is clearly a bond, albeit weak, and the long Mn–C(12) distance of 2.567(10) Å suggests that both C(11) and C(12) are involved in a highly distorted η^2-arene–metal interaction. The next closest phenyl carbon atom to the metal, after C(11) and C(12), is C(16) at a distance of 3.250(11) Å. The distortion in the η^2-ligand is such

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(14) Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053.

(15) (a) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Nouv. J. Chim.* **1977**, *1*, 445. (b) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

(16) (a) Brookhart, M.; Pinhas, A. R.; Lukacs, A. *Organometallics* **1982**, *1*, 1730. (b) Rush, P. K.; Noh, S. K.; Brookhart, M. *Organometallics* **1986**, *5*, 1745.

(17) Details of the X-ray structural characterization of **8** are included in the supplementary material for ref 9.

Table IV. Proton and ^{13}C NMR Data for Complexes **8** and **9**[a]

complex	$\delta(^1H)$	$\delta(^{13}C)$
8	–0.20 (9H, s, $(CH_3)_3Si$), 2.12 (4H, s(brd), H_9, H_{10}, $H_{9'}$, $H_{10'}$), 2.78 (2H, s(brd), H_4, H_8), 3.94 (2H, dd, H_5, H_7), 4.41 (1H, m, H_6), 7.0–7.9 (20H, m, Ph)	1.2 ($(CH_3)_3Si$), 36.4 (C_9, C_{10}), 49.6 (C_4, C_8), 68.4 (C_5, C_7), 82.4 (C_3), 88.4 (C_6), 118.3 (C_{11}), 120.2 (C_{12}, C_{16}), 128.8 (PPh_3), 129.6 (C_{13}, C_{15}), 129.9 (PPh_3), 131.2 (C_{14}), 133.2 (PPh_3), 134.5 (PPh_3), 233.2 (d, J_{CP} = 40Hz, CO)[b]
9	0.09 (9H, s, $(CH_3)_3Si$), 1.89 (4H, m(brd), H_6, H_7, $H_{6'}$, $H_{7'}$), 4.04 (2H, d(brd), J = 9.4 Hz, H_1, H_5), 4.90 (2H, dd, H_2, H_4), 5.40 (1H, t, J = 5.9 Hz, H_3), 7.00 (3H, m, Ph), 7.28 (2H, t, Ph)	1.0 (q, J = 119 Hz, $(CH_3)_3Si$), 34.2 (dt, J = 6, 127 Hz, C_6, C_7), 76.4 (dd, J = 153, 8 Hz, C_1, C_5), 87.8 (dd, J = 168, 11 Hz, C_3), 105.5 (d, J = 161 Hz, C_2, C_4), 123.9 (dt, J = 157, 6 Hz, Ph), 127.6 (dt, J = 164, 4 Hz, Ph), 128.9 (dd, J = 159, 8 Hz, Ph), 161 (Ph), 203.4 (CO), 295.6 (Re=*C*)[c]

[a] Assignments refer to Figure 1 and eq 7; in C_6D_6. [b] ^1H-decoupled spectrum. [c] ^1H-coupled spectrum.

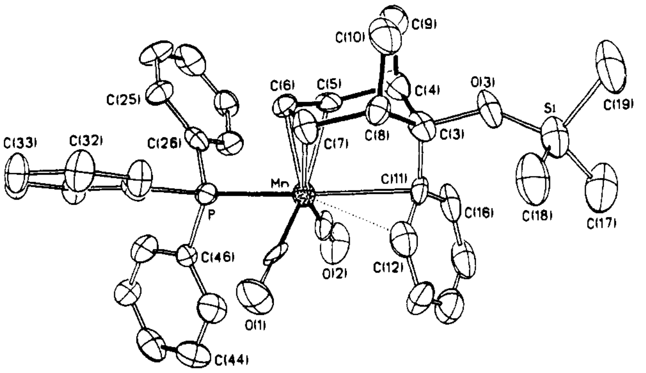
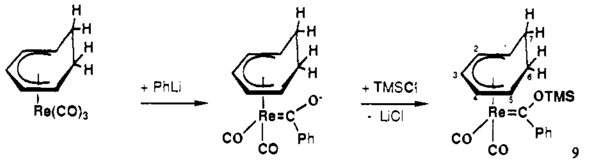


Figure 1. Molecular structure and labeling scheme for **8**. Mn-P, 2.266(3); Mn-C(5), 2.265(11); Mn-C(6), 2.081(11); Mn-C(7), 2.214(11); Mn-C(11), 2.445(10); Mn-C(12), 2.567(10) Å. C(1)-Mn-C(2), 105.5(5); C(1)-Mn-P, 85.5(4); C(2)-Mn-P, 83.8(4); P-Mn-C(11), 167.3(3); C(1)-Mn-C(11), 104.4(5); C(2)-Mn-C(11), 85.9(4); C(5)-C(6)-C(7), 118.2(9)°.

that it appears almost η^1-bonded to manganese; however, there is a twist of the phenyl ring about the C(3)–C(11) axis which allows C(12) to bond to the metal. An asymmetry in the η^3-allyl bonding and a tilt of the bicyclic ring occurs such that C(7) is 0.051 Å closer to Mn than C(5). In solution, **8** does not adopt the rigid structure shown in Figure 1 and NMR spectroscopy reveals an equivalence of the bicyclic ring carbon atoms C(4) and C(8), C(5) and C(7), and C(9) and C(10), as well as the protons attached to these carbon atoms. An equivalence of the phenyl ring carbons C(12) and C(16) and C(13) and C(15) is observed with no ^{31}P coupling between the phosphine phosphorus and C(11) or C(12). This suggests the η^2-ligand decomplexes allowing the phenyl ring to rotate about the C(11)–C(3) bond. Surprisingly, the solution NMR spectra of dissolved pure crystalline **8** show a small amount of **3** and free PPh_3, indicating an equilibrium between **3** and PPh_3 and **8**. A species somewhat similar to **8** has been prepared by Chen and co-workers,[8d] in which an iron atom is η^4-bound to a bicyclo[4.2.1]nona-2,4,7-triene ligand that has an η^2-coordinated aryl group at C(9). In this case, as for **8**, no evidence for the η^2-arene interaction was seen in the ^1H NMR spectrum. Surprisingly, this complex did not form an η^6-arene species as observed for **3** and other iron derivatives.[8c]

Addition of excess PPh_3 to **3** did not yield a bis(phosphine) derivative with complete arene dissociation, presumably due to steric factors. Similarly, the addition of smaller species (PEt_3, PMe_3, and CO) to **3** or **8** did not lead to $Mn(CO)_2L_2$ or $Mn(CO)_3L$ complexes with a decomplexed aryl group. However, gas chromatograph–mass spectroscopic data from these reaction solutions did suggest the presence of the free bicyclic species, but these could not be isolated nor further characterized.

Rhenium Complexes. The rhenium analog of **1**, $[Re(CO)_3(\eta^5\text{-}C_7H_9)]$,[18] reacts with phenyllithium to give an acylmetalate which can be reacted with (TMS)Cl to form carbene complex **9** (eq 7).



(7)

Complex **9** shows a resonance at δ 295.6 in its ^{13}C NMR spectrum assigned to the carbene carbon, as well as ^1H NMR spectral data consistent with an η^5-cycloheptadienyl ring (Table IV). The complex is very sensitive to air and heat and decomposes at room temperature over a period of 12–24 h. Attempts to induce carbene–cycloheptadienyl coupling, through (i) refluxing a toluene solution of the complex or (ii) the addition of PPh_3, resulted in no tractable organometallic products. The absence of such a coupling reaction is consistent with the fact that insertion reactions are rare for second and third row metals, due in part to the stronger M=C bond.

Conclusions

We have demonstrated that the addition of phenyllithium to $[M(CO)_3(\eta^5\text{-}C_7H_8R)]$ (M = Mn, Re; R = H, Me) leads to cycloheptadienyl-acyl complexes. The manganese species are precursors to transient cycloheptadienyl–carbene intermediates in which coupling of the two ligands leads to the formation of a bidentate bicyclo[3.2.1]octenyl species. We have shown that protonation of the bicyclic ligand occurs at the olefin of the σ-allyl group, giving cationic η^2-olefin–η^6-aryl bicyclo[3.2.1]oct-2-ene complexes, that disilylate with excess acid. Nucleophilic addition to these cations is at the exo face of the aryl group and meta with respect to the bicyclic substituent. The regioselectivity of this latter reaction is unusual since the predicted site for attack would be the ligated olefin. The reaction of the carbene-cycloheptadienyl adduct with triphenylphosphine led to a partial decomplexation of the aryl group and the formation of a novel η^2-arene complex which has been crystallographically characterized. Treatment of the rhenium–acyl species with (TMS)Cl gave a carbene complex for which no carbene–dienyl coupling was observed. These results demonstrate that a coupling of both carbene and cyclic polyenyl ligands may be a viable approach to the construction of bicyclic rings at transition metal centers and further extend the known series of carbene and cyclodienyl ligand transformations.

Experimental Section

The preparation, purification, and reactions of all complexes described were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. 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. THF or diethyl ether solutions of organolithium reagents and all other materials were used as supplied by the Aldrich Chemical Co. (Milwaukee, WI) or Alfa Products (MA). The complexes $[(\eta^5\text{-}C_7H_8R)M(CO)_3]$ (M = Mn, Re;

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(18) Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1975**, *14*, 664.

R = H, Me) were prepared using the literature procedures.[3c,18] Infrared spectra were recorded using a Nicolet 5ZDX FT instrument operated in the transmittance mode. NMR spectra were recorded on a Brucker WP 200 or Varian VXR-400S NMR spectrometer, using the COSY-45 pulse sequence for all two-dimensional work. Microanalyses were carried out by Schwarzkopf Microanalytical Laboratories (Woodside, NY). Gas chromatography–mass spectrometry (GCMS) was performed using a Hewlett Packard HP5890 gas chromatograph connected to a Finnegan Mat Incos 50 mass spectrometer (70 eV).

Preparation of $[Li(OEt_2)_2][\eta^5\text{-}C_7H_9)(OC)_2MnC(O)Ph]$ (2a). Phenyllithium (1.20 equiv) was added dropwise by syringe to a stirred solution of $[(\eta^5\text{-}C_7H_9)Mn(CO)_3]$ (**1a**) (1.0 g, 4.3 mmol) in diethyl ether (20 mL) at room temperature. The product **2a** precipitated as bright orange crystals from the resulting dark red solution upon partial removal (50–70%) of the solvent in vacuo. Removal of the remaining mother liquor via cannula, washing with *n*-hexane (3 × 20 mL), and drying in vacuo gave bright orange crystals of **2a** as a $[Li(OEt_2)_2]^+$ salt: yield 1.60 g, 95%; $\nu_{max}(CO)/cm^{-1}$ 1905 and 1816 (Et_2O). This salt is extremely air sensitive, and repeated attempts at obtaining satisfactory elemental analyses proved unsuccessful. The complex $[Li(OEt_2)_2][(\eta^5\text{-}C_7H_8Me)(OC)_2MnC(O)Ph]$ (**2b**) ($\nu_{max}(CO)/cm^{-1}$ 1903 and 1805 (Et_2O)) was prepared similarly from **1b** and used for the synthesis of **3b** without further characterization.

Preparation of 3a. Chlorotrimethylsilane (0.45 g, 4.10 mmol) was added to a stirred orange solution of $[Li(OEt_2)_2][(\eta^5\text{-}C_7H_9)(OC)_2MnC(O)Ph]$ (**2a**) (1.60 g, 4.10 mmol) in diethyl ether (100 mL) at room temperature. The reaction was monitored by IR spectroscopy and after 1 h the solvent removed in vacuo. Extraction of the residue with *n*-hexane (500 mL), removal of solvent, and recrystallization from *n*-hexane at −10 °C gave **3a** as an orange crystalline solid (1.48 g, 94%): $\nu_{max}(CO)/cm^{-1}$ 1963 and 1920 (hex). Anal. Calcd for $C_{19}H_{23}MnO_3Si$: C, 59.68; H, 6.06. Found: C, 59.67; H, 6.24. Complex **3b** was prepared similarly from **2b** and (TMS)Cl: yield 62%; $\nu_{max}(CO)/cm^{-1}$ 1963 and 1920(hex).

Preparation of 4a. Tetrafluoroboric acid (diethyl ether complex) (1.0 equiv) was added dropwise to a solution of **3a** (0.50 g, 1.30 mmol) in CH_2Cl_2 (20 mL) at 0 °C, forming an orange precipitate. Further stirring for 20 min, removal of solvent in vacuo, and recrystallization of the residue from acetone/diethyl ether or nitromethane/diethyl ether gave **4a** as a yellow-orange powder (0.58 g, 95%): $\nu_{max}(CO/cm^{-1}$ 2034 and 1995 (CH_2Cl_2). Anal. Calcd for $C_{19}H_{24}MnO_3SiBF_4$: C, 48.53; H, 5.14. Found: C, 49.07; H, 4.80. Complex **4b** was prepared similarly from **3b** and $HBF_4{\cdot}Et_2O$: yield 87%; $\nu_{max}(CO)/cm^{-1}$ 2035 and 1996 (CH_2Cl_2).

Preparation of 5a. Tetrafluoroboric acid (diethyl ether complex) (1.0 equiv) was added dropwise to a stirred suspension of **4a** (0.45 g, 0.96 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The reaction was monitored by IR spectroscopy, and following 10 min, the solvent was removed in vacuo. Recrystallization of the residue from nitromethane/diethyl, ether gave **5a** as a pale yellow powder (0.39 g, 99%): IR (CH_2Cl_2) $\nu_{max}(CO)/cm^{-1}$ 2029 and 1992: IR (KBr) $\nu_{max}(OH)/cm^{-1}$ 3496, $\nu_{max}(CO)/cm^{-1}$ 2035 and 1983. Anal. Calcd for $C_{16}H_{16}MnO_3BF_4$: C, 48.28; H, 4.05. Found: C, 46.91; H, 3.82. Complex **5b** was prepared similarly from **4b** and $HBF_4{\cdot}Et_2O$. **5b**: yield 92%; IR (CH_2Cl_2) $\nu_{max}(CO)/cm^{-1}$ 2029 and 1992; IR (KBr) $\nu_{max}(OH)/cm^{-1}$ 3495, $\nu_{max}(CO)/cm^{-1}$ 2035 and 1983. Anal. Calcd for $C_{17}H_{18}MnO_3BF_4$: C, 49.55; H, 4.40. Found: C, 49.00; H, 4.23.

Addition of Hydride to 4a. Tetrabutylammonium borohydride (1.0 equiv) was added to an orange solution of **4a** (0.20 g, 0.43 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The resulting yellow solution was stirred for a further 20 min, filtered through Celite, and the residue evaporated to dryness in vacuo. The residue was extracted with *n*-hexane (100 mL) and recrystallized at −10 °C to give the product **6a** as a pale yellow powder: yield 0.135 g, 82%; $\nu_{max}(CO)/cm^{-1}$ 1964 and 1910 (hex). Anal. Calcd for $C_{19}H_{25}MnO_3Si$: C, 59.38; H, 6.51. Found: C, 60.07; H, 6.39.

Addition of $[(CH_3CO_2)_2CH]^-$ to 4a. A solution of $Na[(CH_3CO_2)_2CH]$ was prepared by stirring dimethylmalonate (0.1 mL, 0.9 mmol) and NaH (1.2 equiv) in THF (20 mL) at room temperature for 30 min, followed by filtration through Celite. This solution was added dropwise to a suspension of **4a** (0.20 g, 0.43 mmol) in THF (20 mL) at 0 °C until all of **4a** had been consumed (≈1–2 equiv of malonate enolate, monitored by IR spectroscopy). The resulting clear yellow solution was warmed to room temperature and solvent removed in vacuo. Extraction of the residue with diethyl ether, removal of solvent in vacuo and further extraction with *n*-hexane, and final removal of solvent afforded **6b** as a yellow powder: yield 0.151 g, 69%; $\nu_{max}(CO)/cm^{-1}$ 1970, 1917, 1759, and 1743 (hex).

Addition of MeMgCl to 4a. Methylmagnesium chloride (1.2 equiv of a 3.0 M solution in THF) was added dropwise via syringe to a stirred solution of **4a** (0.20 g, 0.43 mmol) in THF (100 mL) at −78 °C. The mixture was slowly warmed to room temperature (2 h), filtered through Celite, and the solvent removed in vacuo. The residue was extracted with *n*-hexane (250 mL) and recrystallized at −10 °C following partial removal of solvent in vacuo. The product **6c** was isolated as a pale yellow powder: yield 0.096 g, 56%; $\nu_{max}(CO)/cm^{-1}$ 1965 and 1911 (hex). Anal. Calcd for $C_{20}H_{27}MnO_3Si$: C, 60.30; H, 6.78. Found: C, 60.35; H, 6.70.

Addition of Hydride to 5a. Tetrabutylammonium borohydride (1.0 equiv) was added to a stirred solution of **5a** (0.10 g, 0.25 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The resulting yellow solution was stirred for a further 20 min, filtered through Celite, and the residue evaporated to dryness in vacuo. The residue was extracted with *n*-hexane (50 mL). Removal of the solvents in vacuo afforded **7a** as a pale yellow oil: yield 0.059 g, 75%; $\nu_{max}(CO)/cm^{-1}$ 1965 and 1911 (hex).

Addition of $[(CH_3CO_2)_2CH]^-$ to 5a. A solution of $Na[(CH_3CO_2)_2CH]$ was prepared as described above and filtered through Celite prior to its addition to **5a**. This solution was added dropwise to a stirred suspension of **5a** in THF (20 mL) at 0 °C. Monitoring of the reaction and workup as for **6b** gave the malonate derivative **7b** as a pale yellow solid: yield 0.076 g, 80%; $\nu_{max}(CO)/cm^{-1}$ 1970, 1917, 1758, and 1743 (hex). Anal. Calcd for $C_{21}H_{23}MnO_7$: C, 57.02; H, 5.24. Found: C, 57.88; H, 5.29.

Reaction of 3a with Triphenylphosphine. A solution of **3a** (0.15 g, 0.4 mmol) and PPh_3 (0.24 g, 0.92 mmol) in CH_2Cl_2 (15 mL) was stirred under reflux for 1 h. The resulting rose-colored solution was filtered through Celite and the solvent removed in vacuo. Recrystallization of the residue from CH_2Cl_2/hexane gave **8** as a red-purple crystalline solid (0.111 g, 43%): $\nu_{max}(CO)/cm^{-1}$ 1935 and 1867 (CH_2Cl_2). Anal. Calcd for $C_{37}H_{38}MnO_3SiP$: C, 68.93; H, 5.94. Found: C, 68.52; H, 5.89.

Preparation of $[(\eta^5\text{-}C_7H_9)(OC)_2Re{=}C(OSiMe_3)Ph]$ (9). Phenyllithium (1.20 equiv) was added dropwise by syringe to a stirred solution of $[(\eta^5\text{-}C_7H_9)Re(CO)_3]$ (0.26 g, 0.72 mmol) in diethyl ether (20 mL) at room temperature. The solution becomes orange and turbid. Monitoring by IR spectroscopy showed the acyl intermediate $[(\eta^5\text{-}C_7H_9)(OC)_2ReC(O)Ph]^-$ as the only carbonyl-containing species present ($\nu_{max}(CO)/cm^{-1}$ 1918 and 1808 (Et_2O)). Addition of chlorotrimethylsilane (0.1 g, ≈1.2 equiv) and further stirring for 1 h gave a red solution. Filtration through Celite, removal of solvent in vacuo and extraction of the residue with *n*-hexane (50 mL), and evaporation to dryness gave **9** as a red oil (0.29 g, 78%): $\nu_{max}(CO)/cm^{-1}$ 1967 and 1907 (hex). This oil cannot be further purified and contains a small amount of the tricarbonyl species. Complex **9** is extremely air and temperature sensitive and decomposes under nitrogen at room temperature in 12–24 h.

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