results in the formation of the coordinately unsaturated **3**. The photolysis experiments indicate that **3** reacts readily with formate, which in turn is rapidly formed from the reaction of CO with hydroxide, to yield the formate complex **4**. The chromium formate complex readily loses CO_2 to form **5** at ambient temperature, while the tungsten formate may be readily isolated and decarboxylates slowly and may be isolated, in accord with the results recently reported by the Darensbourg group.[10] Protonation of **5** has been reported to yield H_2.[10]

Studies of other homogeneous WGSR systems have pointed toward associative mechanisms.[7,11] The similarities between the heterogeneous WGSR and the homogeneous WGSR catalyzed by the group 6 metal carbonyls are worthy of note.

Registry No. Formate, 71-47-6.

---

(11) Ford, P. C. *Acc. Chem. Res.* **1981,** *14,* 31.

Reaction of Lithium Dimethylcuprate with $C_6H_6Mn(CO)_3^+$. Observation of Methyl Group Migration from Manganese to the Arene Ring in $C_6H_6(CO)_2Mn-CH_3$[†]

M. Brookhart,* Allan R. Pinhas, and Alexander Lukacs

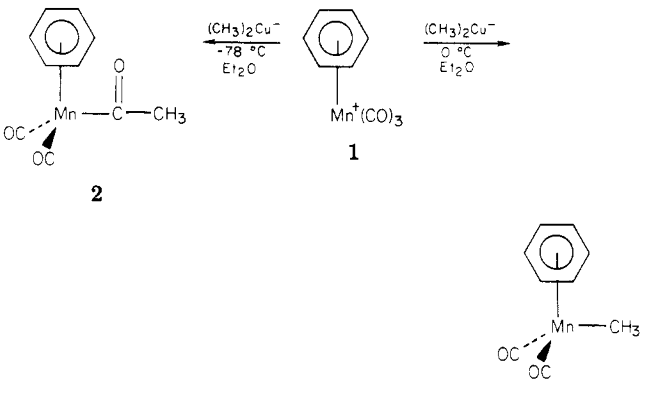
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received August 31, 1982

Summary: $C_6H_6(CO)_2Mn-CH_3$, prepared by the reaction of lithium dimethylcuprate with $C_6H_6Mn(CO)_3^+$, yields 6-*endo*-$C_6H_6(CH_3)Mn(CO)_2(PPh_3)$ via intramolecular methyl migration to the arene ring in the presence of triphenylphosphine.

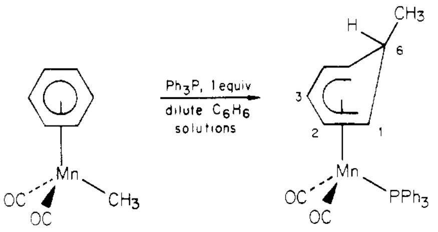
The reaction of (arene)manganese tricarbonyl cations with nucleophiles normally results in exo attack at the ring and formation of the corresponding 6-exo-substituted cyclohexadienylmanganese tricarbonyl complexes.[1-3] In the reaction of the unsubstituted cation $C_6H_6Mn(CO)_3^+$, **1**, with lithium aluminum hydride, a minor side product, $C_6H_6(CO)_2Mn-CH_3$, **3** (0.6%), can be observed, apparently formed from hydride reduction of coordinated CO.[1] Yields of the dicarbonyl methyl complexes rise as the ring is progressively alkylated. Thus, hydride reduction of the $C_6Me_6Mn(CO)_3^+$ system yields ca. 8% $C_6Me_6(CO)_2Mn-CH_3$.[1] A similar trend is noted for addition of methyllithium. Reaction of $C_6H_6Mn(CO)_3^+$ with CH_3Li yields solely (6-*exo*-methylcyclohexadienyl)manganese tricarbonyl;[1,2a] however, for $C_6Me_6Mn(CO)_3^+$ the acyl complex $C_6Me_6(CO)_2Mn-COCH_3$ is formed in ca. 33% yield as the only isolated product.[1]

We wish to report that, in contrast to methyllithium, reaction of lithium dimethylcuprate with the parent, unsubstituted cation, **1**, results exclusively in products which are apparently derived from attack at CO and not from exo methyl addition to the ring. Treatment of **1** at −78 °C in ether with 2.5 equiv of Me_2CuLi followed by rapid workup gives the acyl complex $C_6H_6(CO)_2Mn-COCH_3$, **2**, in 45% yield.[4] The same reaction carried out at 0 °C gives the methyl complex $C_6H_6(CO)_2Mn-CH_3$, **3**, in 42% yield.[5] The latter complex, **3**, presumably results from initial formation of the acyl species **2** followed by decarbonylation; however, the manner in which decarbonylation occurs is not known.[6]



2 **1** **3**

The dimethylcuprate reaction thus provides an easy and viable synthetic entry into the alkyl and acyl complexes **2** and **3**, which are analogues of the exhaustively studied alkyl and acyl derivatives $Fp-CH_3$ and $Fp-COCH_3$ (Fp = $Cp(CO)_2Fe$). Initial results indicate that interesting differences in the chemistry of these manganese and iron analogues can be observed. Treatment of $Fp-CH_3$ with phosphines invariably results in CO insertion and formation of acyls $Cp(CO)(L)Fe-COCH_3$ (L = phosphine).[7] In contrast, treatment of **3** (0.04 M) with 1 equiv of $(C_6H_5)_3P$ in refluxing benzene (80 °C) for 5 days ($t_{1/2}$ ca. 30 h) results in intramolecular migration of the methyl group to the arene and formation of (*endo*-methylcyclohexadienyl)manganese dicarbonyl triphenylphosphine, **4** (68% yield). The spectral properties are completely in accord with structure **4**, and the endo stereochemistry is confirmed by the observed $J_{6x,1} = J_{6x,5} = 0$ vicinal coupling constant.[8]



4

[†] Dedicated to the memory of Rowland Pettit. His enthusiasm for chemistry and elegant, incisive work established standards of dedication and excellence for all of us who knew him.

(1) Munro, G. A. M.; Pauson, P. L. *Isr. J. Chem.* **1976-1977,** *15,* 258.

(2) (a) Jones, D.; Wilkinson, G. *J. Chem. Soc.* **1964,** 2479. (b) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961,** 3807. (c) Green, M. L. H.; Davies, S. G.; Mingos, D. M. P. *Tetrahedron* **1978,** *34,* 3047. (d) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshituji, G.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979,** *101,* 3535. (e) Lamanna, W.; Brookhart, M. *Ibid.* **1981,** *103,* 989.

(3) Attack of amines and alcohols have been noted to occur at carbonyl; see for example: (a) Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972,** *11,* 1754. (b) Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973,** *7,* 621.

(4) Spectral properties of this species are similar to those of other acyl complexes previously reported:[1] ^1H NMR (C_6D_6) δ 2.60 (3 H, br s), 4.52 (6 H, s); IR (ν_{CO}, diethyl ether) 1965 (s), 1915 (s), 1630 (m) cm^{-1}.

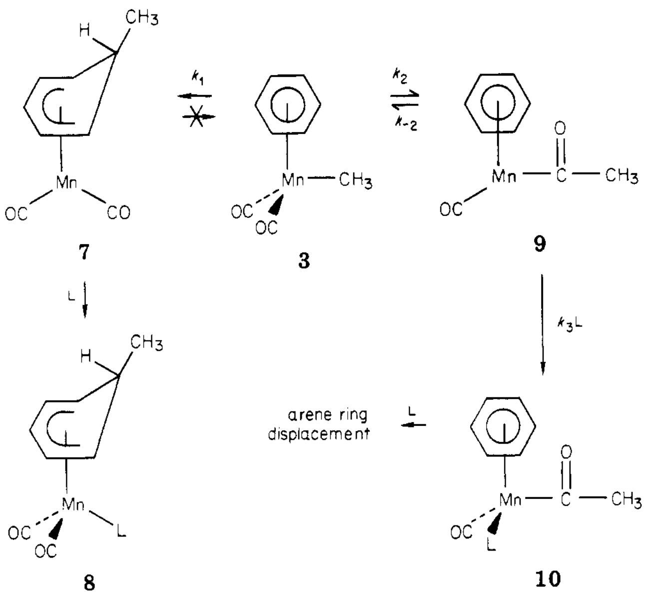
(5) Spectral properties: ^1H NMR (C_6D_6) δ 0.17 (3 H, s), 4.40 (6 H, s); IR (ν_{CO}, isopentane) 1975 (s), 1930 (s) cm^{-1}; high-resolution mass spectrum, calculated 203.9983, found 203.9988. Anal. Calcd for $C_9H_9MnO_2$: C, 52.96; H, 4.44; Mn, 26.92. Found: C, 52.99; H, 4.51; Mn, 26.84.

(6) In some reactions carried out at 0 °C contamination of **3** by **2** was observed. If a sample of pure **2** is stirred in ether at 25 °C, it does not yield **3**; thus, decarbonylation is not strictly a thermal process. If **2** is irradiated for 0.5 h, a 3:1 ratio of **2** to **3** is observed by ^1H NMR spectroscopy. However, prolonged irradiation results in total decomposition.

(7) See, for example: (a) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974,** *96,* 2814. (b) Brunner, H.; Schmidt, E. *Angew. Chem., Int. Ed. Engl.* **1969,** *8,* 616. (c) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* **1966,** *5,* 889.

0276-7333/82/2301-1730$01.25/0 © 1982 American Chemical Society

Scheme I



The acyl complex from CO insertion $C_6H_6(CO)(PPh_3)$-Mn–$COCH_3$, **5** (Ph = phenyl), can be observed by treating **3** in more concentrated solutions (0.12 M) with a fivefold excess of PPh_3 in benzene at 55 °C. The approximate half-life for this reaction is 5 h. When the reaction is monitored by ^1H NMR (C_6D_6) the acyl **5** is observed to form by appearance of new proton signals at δ 2.58 (3 H, $COCH_3$) and 4.48 (6 H, d, J_{PH} = 2 Hz, C_6H_6).[9] However, simultaneous with insertion the acyl species **5** decomposes, apparently by loss of the arene ring; thus, **5** cannot be formed quantitatively from **3**. Substantial decomposition is evident in this reaction and the secondary products have not been identified.[10] The details of this insertion reaction are more clearly evident when $(MeO)_3P$ is employed. Treatment of **3** (0.13 M) with $(MeO)_3P$ (2.5 M) in benzene at 55 °C results in initial formation of the acyl complex $C_6H_6(CO)(P(OMe)_3)Mn$–$COCH_3$, **6** ($t_{1/2}$ ca. 5 h).[11] However, competitive with formation of **6** is its clean conversion to *mer*-$(P(OMe)_3)_3(CO)_2Mn$-CH_3 which is isolated as the sole product (76% yield) after 24 h.[12]

The reactions observed here suggest the general mechanism shown in Scheme I.

The formation of the 16-electron endo methyl intermediate **7** is likely to be essentially irreversible,[13] and thus formation of **8** is a first-order process. On the other hand, if formation of the 16-electron acyl **9** is rapid and reversible, then formation of saturated acyl complex **10** is second order. Thus, at low concentrations of external L the second-order formation of **10** is slow and the first-order process predominates, yielding **8**. At high concentrations of external L the second-order reaction is rapid (relative to k_1) and can be driven to yield acyl complex **10**.

There are two general points of interest in regard to these results. First, the observation of a methyl group migration from a metal to a coordinated arene ring is without precedent. The closest analogy is the report by Green[14] of the migration of the molybdenum-bound ethyl group to the C_5H_5 ring in $Cp_2Mo(Cl)(C_2H_5)$ in which the migration product is trapped as a phosphine adduct. In a general way, this migration models an olefin insertion into a metal–carbon bond, a reaction which has seldom been directly observed with isolated alkyl–olefin complexes but which has been frequently inferred in stoichiometric transformations, olefin polymerization, and other catalytic processes.[15,16]

Secondly, the sharp contrast in the mode of reaction between dimethylcuprate and methyllithium with (arene)manganese tricarbonyl cations suggests that alkylcuprates may prove to be useful complementary reagents in reactions with other (polyene)- and polyenylmetal carbonyl complexes. We are currently exploring these reactions and the chemistry of the now easily accessible $(arene)(CO)_2Mn$–COR and $(arene)(CO)_2Mn$–R complexes.

Acknowledgment is made to the National Institutes of Health (Grant 1 RO1 GM2893801) for support of this research.

Registry No. **1**, 41656-02-4; **2**, 83681-37-2; **3**, 65643-62-1; **4**, 83681-38-3; **5**, 83681-39-4; **6**, 83681-40-7; *mer*-$(P(OMe)_3)_3$-$(CO)_2Mn$-CH_3, 25868-36-4; Me_2CuLi, 15681-48-8.

---

[8] Spectral properties of **4**: ^1H NMR (C_6D_6) δ 1.46 (d, CH_3, $J_{Me,6x}$ = 6 Hz), 1.98 (d, H_1, $J_{1,2}$ = 4 Hz), 2.30 (quint, H_{6x}, $J_{6x,P}$ = $J_{6x,Me}$ = 6 Hz), 4.20 (m, H_2, $J_{2,P}$ = $J_{2,3}$ = 6 Hz), $J_{1,2}$ = 4 Hz), 5.36 (t, H_3, $J_{3,2}$ = 6 Hz), 7–8 (m, PPh_3); (coupling constants established via decoupling experiments); IR (ν_{CO}, isopentane) 1942 (s), 1886 (s) cm^{-1}; ^{13}C NMR (C_6D_6) 21.03 (Me), 29.67 (C_6), 51.83 (C_1), 81.98 (C_3), 96.35 (C_2), 135 (Ph) ppm. high-resolution mass spectrum, calculated 466.0895, found 466.0891.

[9] These parameters are completely consistent with those expected for **5** based on the spectrum of **2** and also on Fp–$COCH_3$.[7]

[10] A triplet observed at δ –0.29 may be due to $(PPh_3)_2Mn(CO)_3CH_3$.

[11] Spectral properties of acyl **6**: ^1H NMR (C_6D_6) δ 2.83 (3 H, s), 3.4–3.6 (9 H, m), 4.63 (6 H, d, J = 3 Hz); IR (ν_{CO}, diethyl ether) 1909 (s), 1560 (m) cm^{-1} (pure samples of **6** cannot be isolated due to contamination with $(P(OCH_3)_3)_3(CO)_2Mn$–CH_3 to which **6** decomposes with a rate competitive with its formation).

[12] Spectral properties: ^1H NMR (C_6D_6) δ 0.08 (3 H, q, J = 9 Hz, CH_3), 3.56 (27 H, m, $P(OMe)_3$); IR (ν_{CO}, CH_2Cl_2) 1942 (s), 1860 (s) cm^{-1}; high resolution mass spectrum, calculated 498.0383, found 498.0388. Anal. Calcd for $C_{12}H_{30}MnO_{11}P_3$: C, 28.93; H, 6.07; Mn, 11.03. Found: C, 29.10; H, 6.09; Mn, 11.11.

[13] The methyl migration is probably not completely irreversible; however, the conversion of **7** to **3** via insertion of manganese into an unstrained, saturated carbon–carbon bond is likely to be slow. All that is required for the applicability of Scheme I is that this reverse reaction (**7** → **3**) be slower than trapping by PPh_3. We are currently investigating the possible **7** → **3** conversion by attempting to generate **7** in the absence of ligand traps.

[14] (a) Green, M. L. H.; Benfield, F. W. S. *J. Chem. Soc., Dalton Trans.* **1974**, 1324. (b) For a related aryl migration in Cp_2V–C_6H_5 see: Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1974**, 516.

[15] Clark, H. C.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1971**, *10*, 18.

[16] For a recent summary of references see: Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

Synthesis and Molecular Structure of [Dicyclopentadienyl(tetrahydrofuran)titanium](μ-η^2-carbonyl)cyclopentadienyldicarbonylmolybdenum[†]

Joseph S. Merola,*[‡] Robert A. Gentile,[‡]
Gerald B. Ansell,[§] Michelle A. Modrick,[§] and
Susan Zentz[§]

Corporate Research Science Laboratories and
Analytical and Information Division
Exxon Research and Engineering Company
Linden, New Jersey 07036

Received September 28, 1982

Summary: Reaction of $Cp_2Ti(CO)_2$ with $[CpMo(CO)_2]_2$ in THF yields the novel complex $Cp_2Ti(THF)OCMo(CO)_2Cp$, **1**, containing a μ-η^2 metal carbonyl bridge between the Ti and Mo. The structure of **1** has been determined from

---

[†] Dedicated to the memory of Rowland Pettit.

[‡] Corporate Research Science Laboratories.

[§] Analytical and Information Division.

© 1982 American Chemical Society