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Notes

Synthesis, Characterization, and Thermochemistry of (η^1-$C_{13}H_9$)$Mn(CO)_5$ and (η^5-$C_{13}H_9$)$Mn(CO)_3$

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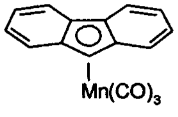
*Summary: Reaction of $LiC_{13}H_9$ with $Mn(CO)_5Br$ at −78 °C gave (η^1-$C_{13}H_9$)$Mn(CO)_5$, **2**. Thermal rearrangement of **2** yielded (η^5-$C_{13}H_9$)$Mn(CO)_3$, **1**, 9,9′-bifluorene, **3**, and $Mn_2(CO)_{10}$, **4**. The product distribution was controlled by the electron donor capacity of the reaction medium. The crystal structures of **1** and **2** have been determined.*

Introduction

Haptotropic rearrangements in metal complexes of fluorenide ($C_{13}H_9^-$) have attracted considerable interest.[1−6] The most thorough investigations have centered on manganese carbonyl complexes of fluorene and fluorenide, e.g., (η^5-$C_{13}H_9$)$Mn(CO)_3$, **1**. Two methods for the preparation of **1** have been developed: (1) via haptotropic inter-ring rearrangement;[2,3] (2) reaction of the fluorenide anion with manganese carbonyl halides.[7−9] The pathway for haptotropic rearrangements has been established,[10,11] but the pathway of the reaction of fluorenide with $Mn(CO)_5Br$ is poorly understood. The reaction could proceed by formation of (η^1-$C_{13}H_9$)$Mn(CO)_5$, **2**, with subsequent loss of two carbonyl ligands to give the final product, (η^5-$C_{13}H_9$)$Mn(CO)_3$, **1**. However, η^1-fluorenyl complexes have not been detected as intermediates in the synthesis of **1**, even though such complexes of fluorenyl and related ring systems are well known.[4,5,11] This prompted us to investigate the reaction between fluorenide and $Mn(CO)_5Br$ and to explore the intermediacy of (η^1-$C_{13}H_9$)$Mn(CO)_5$, **2**, in the synthesis of **1**.



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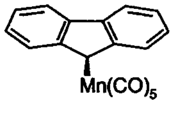

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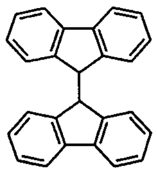
Results

King and Efraty isolated **1**, in 11% yield, by reacting sodium fluorenide with $Mn(CO)_5Br$ in refluxing THF.[7] We found that **1** can be prepared at room temperature by addition of a solution of $Mn(CO)_5Br$ in THF to $C_{13}H_9$-Li, generated in situ in THF. Orange complex **1** was produced in 30% yield, together with 9,9′-bifluorene (10%), fluorene (15%), and $Mn_2(CO)_{10}$ (20%). All spectroscopic data for **1** were in accord with that previously published.[2,3] Compound **1** was also identified by X-ray diffraction (Figure 1). At room temperature, there was no detectable intermediate in the reaction, but at −78 °C, yellow (η^1-$C_{13}H_9$)$Mn(CO)_5$, **2**, was isolated in 59% yield. Compound **2** was characterized by ^1H and ^{13}C NMR and IR spectroscopies, mass spectrometry, elemental analysis, and X-ray crystallography (Figure 2). It was moderately air and moisture sensitive, but could be stored under an inert atmosphere at −23 °C for several weeks.

Refluxing **2** in THF for 30 min resulted in a gradual color change from yellow to dark orange. The products were identified as (η^5-$C_{13}H_9$)$Mn(CO)_3$, **1**, obtained in 80% yield, 9,9′-bifluorene, **3**, and $Mn_2(CO)_{10}$, **4**, each in 20% yield. The conversion of **2** into **1**, **3**, and **4** was achieved in a variety of solvents and in the solid state (see Supporting Information). Under inert and dry atmospheres compounds **1**, **3**, and **4** were the only products, accounting for complete mass balance; **3** and



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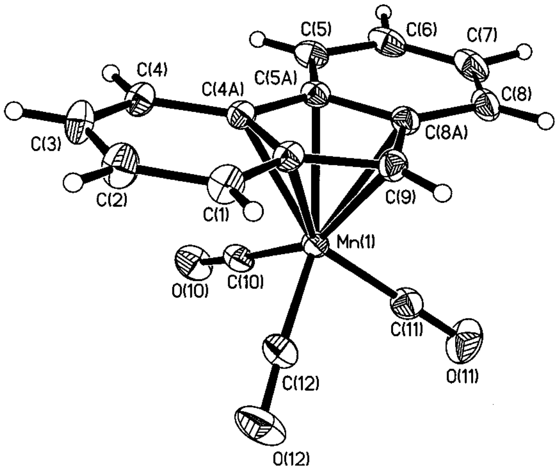

Figure 1. View of **1**, thermal ellipsoids at the 30% probability level.

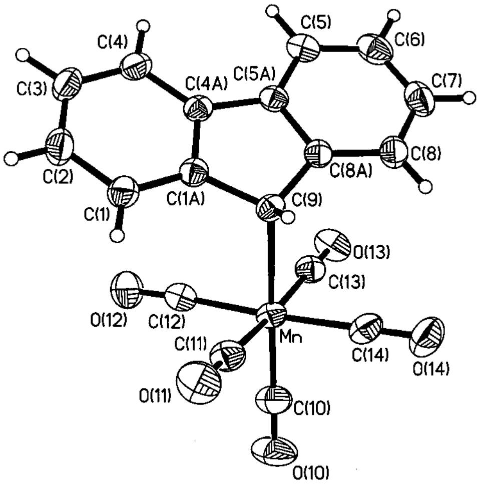

Figure 2. View of **2**, thermal ellipsoids at the 30% probability level.

4 were always produced in equimolar amounts. The reaction was much slower at 23 °C in THF, resulting in 60% yield of **1** after 5 days. A 60% yield was also obtained in the nonpolar solvent hexane after reflux for 30 min, and a 37% yield was obtained at 23 °C after 5 days. The yield of **1** was not influenced by water and was only slightly reduced under CO (1 atm), but only **3** and **4** were obtained under 10 atm of CO. The yield of **1** decreased to 51% under O_2 (1 atm), and fluorenone (8%) and fluorene (10%) were isolated as well as **3** (19%). Addition of benzylbromide to the reaction mixture decreased the yield of **1** only slightly, but produced $Mn(CO)_5Br$ instead of $Mn_2(CO)_{10}$. The conversion of **2** into **1**, **3**, and **4** proceeded at the same rate in the dark and was concentration independent in the range 0.02–0.00022 M. Thermolysis of **2**, generated in situ from $Mn(CO)_5Br$ and $C_{13}H_9Li$ in THF, gave a higher yield of **1** than prepurified **2**. Addition of $Mn_2(CO)_{10}$, fluorene, or bifluorene had no effect on product yields or distribution, but addition of MX (M = Li, Na, NEt_4; X = Cl, Br) greatly increased the yield of **1**. For example, at room temperature in THF, **2** gave **1** in 23% yield after 24 h, increasing to 61% upon addition of LiBr. $NaBPh_4$ did not increase the yield of **1**. The yields of **1** were slightly reduced when the sterically hindered THF derivatives 2,5-dimethyltetrahydrofuran and 2,2,5,5-tetramethyltetrahydrofuran[12] were used as solvents. There was no spectroscopic evidence for the formation of acyl complexes in donor solvents.[13] No reaction occurred between bifluorene, **3**, and $Mn_2(CO)_{10}$, **4**, nor between $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$, **1**, and CO (10 atm).

The indenyl analogue of **1**, $(\eta^5\text{-}C_9H_7)Mn(CO)_3$, **5**, was prepared from C_9H_7Li and $Mn(CO)_5Br$ in THF at −78 °C in 30% yield, together with 3,3′-biindene (14%), indene (13%), and $Mn_2(CO)_{10}$ (29%); no $(\eta^1\text{-}C_9H_7)Mn(CO)_5$, **6**, was observed.

Discussion

Our results are different from thermochemical and photochemical reactions of other $RMn(CO)_5$ (R = CH_3, C_2H_5, Ph, CH_2Ph, $CR'HCH{=}CH_2$), $(C_{13}H_9)Mn(CO)_3(PR''_3)_2$, $(C_{15}H_9)Mn(CO)_3(PR''_3)_2$, and $(C_{13}H_9)Re(CO)_5$ complexes. $(\eta^1\text{-}C_{13}H_9)Re(CO)_5$ gave exclusively $(\eta^5\text{-}C_{13}H_9)Re(CO)_3$ at 127 °C in methylcyclohexane,[14] but the reaction was much slower than that of **2**. Degradation of $(\eta^1\text{-}C_{13}H_9)Re(CO)_5$ was also concentration dependent and reversible under CO (1 atm). In contrast, thermolysis of **2** was independent of concentration and irreversible. The different chemical behavior of **2** and $(\eta^1\text{-}C_{13}H_9)Re(CO)_5$ is explained by much stronger Re−ligand bonds, preventing CO loss at ambient temperatures and homolytic cleavage of the fluorenyl−Re bond under the thermochemical conditions employed by Wrighton and co-workers. A difference in bond enthalpies was determined for the related $CH_3M(CO)_5$ complexes (CH_3−Re = 199 kJ mol^{-1}; CH_3−Mn = 115 kJ mol^{-1}; Re−CO = 185 kJ mol^{-1}; Mn−CO = 98 kJ mol^{-1}),[15] and a similar trend is expected for the fluorenyl complexes. Heating $(\eta^1\text{-}C_3H_4R')Mn(CO)_5$ (R′ = H, CH_3) gave the allylic complexes $(\eta^3\text{-}C_3H_4R')Mn(CO)_4$,[16] but there was no formation of **4** or the appropriate organic products. Heating $(\eta^1\text{-}C_{15}H_9)Mn(CO)_3(PEt_3)_2$ gave only intractable decomposition products,[11] and heating $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PEt_3)_2$ resulted exclusively in cleavage of the fluorenyl−Mn bond. Photochemical reactions of $RMn(CO)_5$ (R = CH_3, C_2H_5, Ph, and CH_2Ph) gave $Mn_2(CO)_{10}$, **4**, R−R, and R−H.[17,18]

Our results show conclusively that two, competing, irreversible and monomolecular pathways lead from **2** to **1** or **3**/**4**: (1) loss of CO, promoted by coordination of electron donors, followed by haptotropic rearrangement to give **1**, or (2) homolytic cleavage of the Mn−C(9) bond, followed by recombination of the resulting radicals to give **3** and **4**. The production of $Mn(CO)_5$ and $C_{13}H_9$ radicals was proven by trapping them with benzylbromide and O_2, respectively, giving $Mn(CO)_5Br$ and $C_{13}H_8O$. In the rearrangement of **2** → **1**, the first step must be loss of a carbonyl ligand to give **7** (Scheme 1). Compound **7** can convert to **8** by addition of an electron donor or to

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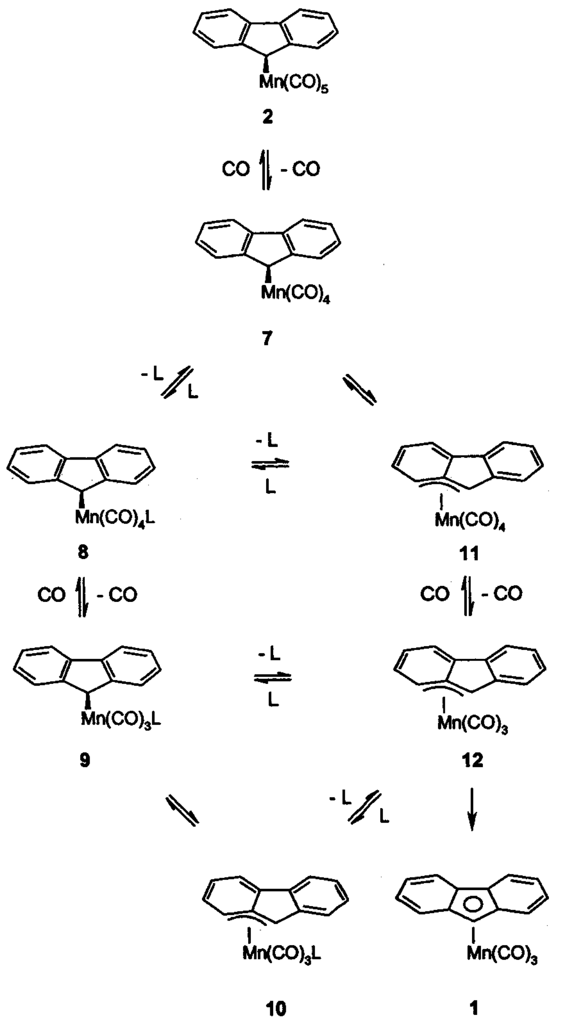
Scheme 1



11 by haptotropic rearrangement. Loss of CO from **8** or **11** would result in **9** or **12**, respectively, from which **10** and the final product **1** are obtained via haptotropic rearrangement. The evidence suggests that the pathways via **8**/**9** and **11**/**12** are in competition. The pathway via **11** and **12** occurs in the solid state and in noncoordinating solvents. The increased yield of **1** in coordinating solvents and in the presence of strong electron donors such as X^- (X = Br, Cl) is evidence for the rearrangement via **8** and **9**. Decreased yields of **1** upon replacement of THF by sterically demanding analogues further corroborates ligand coordination. The most likely irreversible step is the transformation of **12** to **1**.

Competition between CO loss and homolytic cleavage of the R−Mn bond has not been observed previously in reactions of $RMn(CO)_5$. The formation of **1**, **3**, and **4** at lower temperatures than for comparable systems must be due to low reactivities and high stabilities of the intermediates. It has been shown that rate constants for trapping the fluorenyl radical are significantly lower than for alkyl and aryl radicals.[19] The low reactivity of the fluorenyl radical facilitates the formation of **3**, which is competing with regeneration of **2**. Carbonyl loss from **2** can be accomplished under very mild conditions because the intermediates can be stabilized by coordination of electron donors and/or haptotropic rearrangement which cannot be attained for $RMn(CO)_5$ (R = alkyl, aryl) complexes. The pathways via intermediates **7**−**12** are also highly unlikely for $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PEt_3)_2$ and $(\eta^1\text{-}C_{15}H_9)Mn(CO)_3(PEt_3)_2$ due to the steric bulk of the phosphine groups and the increased strength of the Mn−CO bond. Competitive Mn−C(9) or Mn−CO cleavage in **2** implies similar activation barriers for both processes. This is supported by the similar dissociation enthalpies for alkyl−Mn (115 kJ mol^{-1}) and Mn−CO (98 kJ mol^{-1}) bonds.[15] The thermochemical behavior of $(\eta^1\text{-}C_{13}H_9)Mn(CO)_5$, **2**, is unprecedented. The analogous indenyl complex, $(\eta^1\text{-}C_9H_7)Mn(CO)_5$, **6**, is unknown. However, we prepared $(\eta^5\text{-}C_9H_7)Mn(CO)_3$, **5**, by reaction of $Mn(CO)_5Br$ with C_9H_7Li and isolated 3,3′-biindene and $Mn_2(CO)_{10}$ as major side products and conclude that the formation of **1** and **5** follow similar pathways. The relative stability of **2** in comparison to **6** is due to the unfavorable loss of local aromaticity in the six-membered rings in $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$. This effect is reduced for the indenyl ligand because of the lower degree of benzannelation.

In conclusion, we have synthesized $(\eta^1\text{-}C_{13}H_9)Mn(CO)_5$, **2**, and converted **2** to $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$, **1**, under a variety of reaction conditions. Generation of **1** is in competition with the formation of 9,9′-bifluorene, **3**, and $Mn_2(CO)_{10}$, **4**, and the product distribution is controlled by the donor capacity of the medium.

Experimental Section

General Considerations. All reactions were carried out under an atmosphere of argon utilizing standard Schlenk techniques. Solvents were dried and distilled according to standard procedures.[20] ^1H and ^{13}C NMR spectra were recorded on a Varian Unity 400 spectrometer at 399.99 and 100.6 MHz, respectively. Chemical shifts were referenced to residual solvent signals. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra were obtained on a Kratos MS-50 spectrometer. Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification. $Mn(CO)_5Br$ was prepared by a literature procedure.[21] Flash column chromatography was carried out using Merck silica gel (330−400 mesh). Elemental analyses were preformed by Galbraith Laboratories, Knoxville, TN.

$(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$, 1, was prepared using a modified literature procedure.[7] *N*-Butyllithium (0.8 cm^3, 1.6 M in hexanes, 1.28 mmol) was added dropwise to a solution of fluorene (0.158 g, 0.952 mmol) in THF (5 cm^3) at −78 °C. The reaction mixture was allowed to warm to room temperature, and $Mn(CO)_5Br$ (0.258 g, 0.939 mmol) in THF (10 cm^3) was added dropwise; the resultant mixture was stirred overnight. The solvents were removed under vacuum and the product purified by flash column chromatography using hexane to give **1** as an orange solid. Yield: 0.086 g, 0.284 mmol, 30%. Flash column chromatography using hexane as eluent also yielded 9,9′-bifluorene (0.018 g, 0.05 mmol), fluorene (0.025 g, 0.151 mmol), and $Mn_2(CO)_{10}$ (0.040 g, 0.103 mmol). Unreacted $Mn(CO)_5Br$ (0.032 g, 0.115 mmol) was obtained with CH_2Cl_2. IR and NMR spectral data of **1** matched that of the literature.[2,3] MS (EI, *m*/*z* (%), assignment): 304 (29) $\{C_{16}H_9MnO_3\}^+$ $\{(C_{13}H_9)Mn(CO)_3\}^+$; 276 (30) $\{C_{15}H_9MnO_2\}^+$ $\{(C_{13}H_9)Mn(CO)_2\}^+$; 248 (45) $\{C_{14}H_9MnO\}^+$ $\{(C_{13}H_9)Mn(CO)\}^+$; 220 (84) $\{C_{13}H_9Mn\}^+$; 165 (100) $\{C_{13}H_9\}^+$.

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(η^1-$C_{13}H_9$)Mn(CO)$_5$, 2. *N*-Butyllithium (1.70 cm^3, 1.6 M in hexanes, 2.72 mmol) was added dropwise to a solution of fluorene (0.346 g, 2.08 mmol) in THF (8 cm^3) at −78 °C and the reaction mixture stirred for 1 h at −78 °C. Mn(CO)$_5$Br (0.586 g, 2.13 mmol) in THF (16 cm^3) was cooled to −78 °C and added to the fluorenyllithium solution dropwise at −78 °C. The resulting reaction mixture was stirred for 2 h at −78 °C. Hexane (100 cm^3) was added, and the solvents were removed under vacuum. The product was purified by flash column chromatography using hexane to yield **2** as a yellow solid. Yield: 0.440 g, 1.22 mmol, 59%. Anal. Found: C, 59.48; H, 2.39. Anal. Calcd for $C_{18}H_9MnO_5$: C, 60.02; H, 2.53. Mp: 115 °C (dec). ^{1}H NMR (acetone-d_6 solution): δ 7.96 (d, 6.0 Hz, 2H); 7.70 (d, 6.8 Hz, 2H); 7.28 (m, 4H); 4.62 (s, 1H). ^{13}C NMR (benzene-d_6 solution): δ 210.5 (*C*O); 157.5; 136.4; 126.5; 124.5; 122.4; 120.9; 30.8 (*C*-9). IR (KBr disk): ν_{CO} 2106 (m-s); 2010 (s); 1988 (s) cm^{-1}. MS (EI, *m*/*z* (%), assignment): 360 (0.9) $\{C_{18}H_9MnO_5\}^+$ $\{(C_{13}H_9)Mn(CO)_5\}^+$; 332 (17) $\{C_{17}H_9MnO_4\}^+$ $\{(C_{13}H_9)Mn(CO)_4\}^+$; 330 (45) $\{C_{26}H_{18}\}^+$ $\{(C_{13}H_9)_2\}^+$; 304 (42) $\{C_{16}H_9MnO_3\}^+$ $\{(C_{13}H_9)Mn(CO)_3\}^+$; 276 (53) $\{C_{15}H_9MnO_2\}^+$ $\{(C_{13}H_9)Mn(CO)_2\}^+$; 248 (59) $\{C_{14}H_9MnO\}^+$ $\{(C_{13}H_9)Mn(CO)\}^+$; 220 (64) $\{C_{13}H_9Mn\}^+$; 165 (79) $\{(C_{13}H_9)\}^+$.

Thermal Rearrangement of (η^1-$C_{13}H_9$)Mn(CO)$_5$, 2. (η^1-$C_{13}H_9$)Mn(CO)$_5$ (0.036 g, 0.1 mmol) in solvent (5 cm^3) was reacted according to the conditions indicated in Table 1 (Supporting Information). The solvent was removed at ambient temperatures under vacuum, the remaining solid dissolved in $CDCl_3$ (2 cm^3), and the ratio of **1**:**3** established by ^{1}H NMR. Flash column chromatography with hexane as eluent was used to separate all products with the exception of Mn(CO)$_5$Br, which was obtained with CH_2Cl_2.

(η^5-C_9H_7)Mn(CO)$_3$, 5. The preparation was carried out analogously to that of **2**. *N*-Butyllithium (1.70 cm^3, 1.6 M in hexanes, 2.72 mmol), indene (0.25 cm^3, 0.248 g, 2.14 mmol), and Mn(CO)$_5$Br (0.543 g, 1.98 mmol) gave **5** as a yellow solid. Yield: 0.148 g, 0.583 mmol, 30%. IR and NMR spectral data of **5** matched that of the literature.[7] Flash column chromatography using hexane as eluent also yielded 3,3′-biindene (0.031 g, 0.135 mmol), indene (0.030 g, 0.259 mmol), and $Mn_2(CO)_{10}$ (0.114 g, 0.292 mmol). Unreacted Mn(CO)$_5$Br (0.041 g, 0.149 mmol) was obtained with CH_2Cl_2.

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Supporting Information Available: Tables of the reaction conditions for the rearrangement **2** → **1**, crystallographic data, atomic coordinates, interatomic distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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