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Novel Rearrangement of Fluorenylmanganese Tricarbonyl Involving Migration of Metal Coordination between Six- and Five-Membered Rings of the Hydrocarbon Ligand

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Received August 9, 1976 AIC60554K

Abstraction of a proton from $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_3]PF_6$ may be accomplished using weak bases such as triethylamine. The red crystalline product, $Mn(C_{13}H_9)(CO)_3$, retains the initial metal coordination to one six-membered ring on the fluorenyl ligand. This compound can be reprotonated to yield the starting complex or alkylated at the C(9) carbon of the fluorenyl ligand to give $[Mn(\textit{exo}\text{-}9\text{-}RC_{13}H_9)(CO)_3]^+$. The latter reaction is remarkably slow, indicating low nucleophilicity of the complex in such replacement reactions. On standing in solution or as a solid the complex rearranges irreversibly to give the known isomeric complex $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$.

Introduction

Recently[1,2] we reported on the deprotonation of $[Fe(C_5H_5)(\eta^6\text{-}C_{13}H_{10})]PF_6$. Bases such as potassium *tert*-butoxide remove one proton from the C(9) carbon of the fluorene ligand; the product formed is $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. Unexpectedly, coordination of the fluorenyl ligand to iron remains through one six-membered ring rather than through the five-membered ring as might have been expected. A single-crystal x-ray diffraction study, while confirming this general feature of the structure, also provided evidence concerning the ligand to metal bond. The fluorenyl ligand is somewhat distorted with five coordinated atoms (C(1), C(2), C(3), C(4), C(11)) in a plane and the sixth atom of this six-membered ring, C(10), bent slightly out of this plane away from the metal but still within bonding distance of the metal. The amount of distortion is not great, and considering these data in conjunction with the high chemical reactivity of the complex, we are inclined to describe the structure as being zwitterionic with positive charge on the metal, negative charge primarily on C(9) though delocalized somewhat into the remainder of the fluorenyl ligand. In a qualitative sense, the electronic distribution of a free fluorenide anion appears to be mirrored in the complex.

To the extent this model is correct the metal and cyclopentadienyl group have little overall effect on the fluorenyl ligand. However it seems reasonable to anticipate that a different metal–ligand combination coordinated to a fluorenyl ligand might cause substantial deviation from this simple model. In particular, good acceptor ligands such as CO on the metal would likely lead to delocalization of the negative charge at C(9) out of the fluorenyl ligand and into the metal carbonyl group. This delocalization should be accompanied by changes in geometry of this complex, with distortions of the fluorenyl ligand to allow it to behave as a cyclohexadienyl ligand. There should also be differences in chemical behavior from that observed for the iron compound.

The compound $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_3]PF_6$ appeared to be an excellent choice for this study. Although unknown prior to this work, its synthesis by the standard route[3] seemed likely to present little difficulty. The $Mn(CO)_3$ group is expected to have a substantially higher capability of electron withdrawal than the $Fe(C_5H_5)$ group. Moreover, the η^5 isomer of the deprotonated species $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ is already known, having been prepared by King and Efraty.[4] The possible existence of a second isomer of this compound would encourage further study of the reaction of metal migration between different coordination sites on the ligand.

It is with this background that we undertook a study of the deprotonation reaction of $[Mn(\eta^6\text{-}C_{13}H_{10})(CO)_3]PF_6$. Herein are reported the results of this study.

Experimental Section

All reactions were carried out under dry nitrogen. When noted, solvents were dried by appropriate measures; otherwise, all reagents were used as received. Analyses were performed by Galbraith Laboratories. High-resolution mass spectra were obtained on an AEI-MS9. ^1H NMR spectra were recorded on JEOL-MH100 or Bruker WH-270 instruments. ^{13}C NMR spectra were recorded on Varian XL-100, Bruker WH-270, or JEOL-FX60 instruments. All chemical shifts are expressed in ppm downfield from internal TMS. The NMR data are listed in Tables I and II. Infrared spectra were obtained on a Beckman IR-10 and are considered accurate to ±4 cm^{-1}. Melting points were determined in sealed capillaries and are uncorrected.

Preparation of $[Mn(C_{13}H_{10})(CO)_3]PF_6$. Following the procedure of Wilkinson et al.,[4] $Mn(CO)_5Br$ (5.07 g, 18.4 mmol) was refluxed in hexane with excess $C_{13}H_{10}$ (25 g) and $AlCl_3$ (4.5 g) for 5 h. A red oil was deposited. The reaction mixture was then hydrolyzed with cold water and benzene was added to redissolve the precipitated $C_{13}H_{10}$. The yellow aqueous layer was separated and the organic layer was extracted three times with water. The combined aqueous phase was treated with excess NH_4PF_6, resulting in immediate precipitation. The pale yellow microcrystals were collected by filtration, washed with water, benzene, and ether, and dried in vacuo to give 7.10 g (86%) of $[Mn(C_{13}H_{10})(CO)_3]PF_6$, mp >250 °C.

Anal. Calcd for $C_{16}H_{10}F_6MnO_3P$: C, 42.69; H, 2.24. Found: C, 42.63; H, 2.36. Infrared: ν(CO) 2062, 2006 cm^{-1} (CH_2Cl_2 solution).

Preparation of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$. A mixture of $[Mn(C_{13}H_{10})(CO)_3]PF_6$ (0.709 g, 1.57 mmol) and 1,8-bis(dimethylamino)naphthalene (0.339 g, 1.58 mmol) was stirred in 30 ml of CH_2Cl_2 at room temperature. After 3 h, the volume was reduced to ~5 mL, and 30 mL of hexane was added. The resulting white precipitate, $[C_{10}H_6N_2H_5]PF_6$ (0.541 g, 1.51 mmol), was separated by filtration using Schlenk techniques. The volume of red filtrate was reduced to ~15 mL by evaporation, and the resulting solution was chilled overnight at −78 °C. The red crystals formed were separated and dried in vacuo; the total yield of the product, $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$, was 0.398 g (83%), mp 50–55 °C. The red decantate was acidified with CF_3CO_2H resulting in immediate precipitation. Metathesis with aqueous NH_4PF_6 resulted in the recovery of 0.057 g (0.13 mmol, 8%) of $[Mn(C_{13}H_{10})(CO)_3]PF_6$, identified by IR and ^1H NMR spectra.

Anal. Calcd for $C_{16}H_9MnO_3$: C, 63.18; H, 2.98. Found: C, 63.86; H, 3.59. A mass spectrum parent peak was found at 303.9939 (calcd for $^{12}C_{16}{}^1H_9{}^{55}Mn^{16}O_3$ 303.9933.) Infrared: ν(CO) 2028, 1979, 1958 cm^{-1} (hexane solution).

This compound could also be prepared in lower yield using other bases. The weakest base used was triethylamine; others included potassium *tert*-butoxide and sodium methoxide.

Preparation of $[Mn(\textit{exo}\text{-}9\text{-}CH_3C_{13}H_9)(CO)_3]PF_6$. A sample of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ (0.164 g, 0.54 mmol) was dissolved in 25 mL of dry hexane and treated with freshly distilled CH_3OSO_2F (0.1 mL, ~1 mmol). A yellow solid slowly formed, and after 3 days at room temperature, the color of the supernatant changed from red to yellow-orange. The mixture was treated with aqueous NH_4PF_6 and filtered to yield 0.201 g of $[Mn(\textit{exo}\text{-}9CH_3C_{13}H_9)(CO)_3]PF_6$, mp >250 °C. A small amount of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ (0.025 g, 15%) was recovered from the hexane layer.

Anal. Calcd for $C_{17}H_{12}F_6MnO_3P$: C, 43.98; H, 2.61. Found: C, 44.14; H, 2.74. Infrared: ν(CO) 2066, 2004 cm^{-1} (CH_2Cl_2 solution).

Isomerization of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$. A sample of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ (0.230 g, 0.76 mmol) was refluxed in dry hexane. After

Table I. ^1H NMR Data for Fluorene-Manganese Complexes[a]

Compd	Uncomplexed six-membered ring protons	Complexed six-membered ring protons	Five-membered ring protons	Other
$[Mn(C_{13}H_{10})(CO)_3]PF_6$[b]	8.24, d, 7.5 7.83, d, 7.9 7.72, t, 7.4 7.64, t, 7.7	7.59, d, 6.8 7.53, d, 6.8 7.01, t, 6.6 6.79, t, 6.5	4.53, AB ($J = 25.7$, $\Delta\nu = 23.3$)	
$[Mn(exo\text{-}9\text{-}CH_3C_{13}H_9)(CO)_3]PF_6$[b]	8.21, d, 7.2 7.84, d, 7.7 7.73, t, 7.4 7.63, t, 7.8	7.58, d, 6.3 7.57, d, 6.1 7.02, t, 6.5 6.81, t, 6.4	4.59, q, 7.5	1.75, d, 7.5 (intens 3)
$Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$[c]	7.76, d, 7.7 7.70, d, 7.9 7.43, t, 7.5 7.16, t, 7.5	6.05, d, 5.9 5.32, d, 7.4 4.32, dd, 7.5, 5.7 4.13, t, 5.8	5.98, s	
$Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$[d]	8.1, m (intens 2) 7.5, m (intens 2) 7.2, m (intens 4)		5.62, s	

[a] Data given: chemical shift (δ), multiplicity, J (Hz). [b] 270 MHz, $(CD_3)_2CO$ solution. [c] 270 MHz, C_6D_6 solution. [d] 100 MHz, $CDCl_3$ solution.

Table II. ^{31}C NMR Data for Fluorene-Manganese Complexes

	Uncomplexed six-membered ring carbons		Complexed six-membered ring carbons		Five-membered ring carbons	
Compd	C-H carbons	Quaternary carbons	C-H carbons	Quaternary carbons	C-H carbon	CO carbons
$[Mn(C_{13}H_{10})(CO)_3]PF_6$[a]	133.3, 129.3, 127.0, 124.3	145.9, 134.8	101.2, 100.8, 97.4, 92.9	121.7, 120.7	37.9	216.5
$Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$[a]	127.7, 122.1, 121.2, 120.1	147.6, 130.8	97.9, 95.2, 87.2, 74.1	125.8, 88.9	93.6	222.6
$Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$[b]	127.7, 124.9 (2) 124.5			106.1, 95.2	59.9	225.2

[a] 25.2 MHz, $(CD_3)_2CO$ solution. [b] 15.04 MHz, $CDCl_3$ solution.

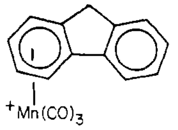
1.2 h, the color of the solution had changed from red to yellow-orange. The reaction mixture was filtered to remove a trace of solid, and the filtrate was reduced by evaporation and chilled to −78 °C. Yellow-orange crystals of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ (0.185 g, 80%) were separated by filtration, mp 115–117 °C (lit.[4] mp 118–119 °C). Infrared: $\nu(CO)$ 2018, 1948 cm^{-1} (hexane solution).

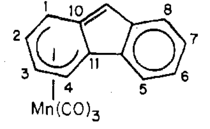
Discussion

The previously unreported fluorenemanganese tricarbonyl cation is conveniently prepared by the reaction of $Mn(CO)_5Br$ with excess fluorene in refluxing hexane in the presence of $AlCl_3$[4] and is isolated in good yield as the pale yellow hexafluorophosphate salt. A ^1H NMR spectrum (Table I) confirms the structural formulation as an η^6-arene complex. The protons on the complexed six-membered ring are shifted upfield from those on the uncomplexed ring by 0.3–0.8 ppm. This is a smaller upfield shift than observed previously in the analogous iron compound[2] but is in good agreement with the spectra of other arenetricarbonylmanganese cations.[5] The signal for the protons of the methylene group (at C(9)) appears as a single peak at 60 and 100 MHz, but at 270 MHz the resonance is resolved into the expected AB pattern. The infrared spectrum exhibits carbonyl stretches at 2062 and 2006 cm^{-1}, typical for a $[Mn(arene)(CO)_3]^+$ complex,[1] as well as absorptions near 830 and 560 cm^{-1}, characteristic of the hexafluorophosphate anion. The ionic complex, $[Mn(C_{13}H_{10})(CO)_3]PF_6$, is sparingly soluble in dichloromethane, soluble in acetone, and insoluble in water and nonpolar organic solvents.

A suspension of $[Mn(C_{13}H_{10})(CO)_3]PF_6$ in benzene reacts with potassium *tert*-butoxide to afford a deep red solution. Weaker bases such as triethylamine are also sufficiently strong to accomplish this deprotonation. Upon deprotonation $\nu(CO)$ is lowered by ~30 cm^{-1}. Observation of the disappearance of insoluble starting material, along with monitoring of the infrared spectrum, provides an easy measuring of the extent of the reaction. Isolation of $Mn(C_{13}H_9)(CO)_3$ in these reactions can be accomplished. More conveniently, isolation of this product from the reaction of a dichloromethane suspension of $[Mn(C_{13}H_{10})(CO)_3]PF_6$ with 1 equiv of 1,8-bis(dimethylamino)naphthalene is suggested. Partial evaporation of the solvent and addition of hexane results in the precipitation of the protonated amine hexafluorophosphate salt. Concentration of the filtrate, followed by cooling, results in the deposition of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$[18] as red crystals. This rapid method avoids problems arising due to the slow isomerization of this product to the more stable $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$.

The ^1H NMR and ^{13}C NMR spectra of this compound are similar to spectra obtained for $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. Again, resonances associated with nuclei on the two six-membered rings of the fluorenyl ligand are different, indicating that metal coordination to one six-membered ring has been retained. Two limiting structures which are in accord with this are





Attempts at vacuum sublimation of this compound led to the discovery of an interesting phenomenon. The sublimate is yellow-orange, rather than red, and IR and ^1H NMR spectra definitely identify it as the previously reported[4] $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$, an isomer of the initial product, contaminated with small amounts of fluorene. Clearly, this results from a six-membered to a five-membered ring transfer reaction

$$Mn(\eta^6\text{-}C_{13}H_9)(CO)_3 \rightarrow Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$$

Further experiments showed that $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ can be converted in high yield to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ by refluxing in hexane for about 1 h. Infrared monitoring provides information on this process since the product shows only two $\nu(CO)$ absorptions at 2018 and 1948 cm^{-1}, in contrast to three absorptions for the starting material at 2028, 1979, and 1958 cm^{-1}. Isomerization in solution at room temperature or as a solid is slower, generally requiring several days or more. Stored below about 0 °C, the compound is stable.

The failure to observe sharp melting points from this compound probably derives from this isomerization process. The mass spectra of both isomers of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ are the same, an indication of probable isomerization in the mass spectrometer inlet.

There are other aspects of chemical behavior which, though less spectacular than this isomerization reaction, are equally significant in distinguishing the manganese compound from $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. One obvious difference is their basicities. The manganese compound can be generated with bases as weak as triethylamine, while the iron compound is formed only with much stronger bases such as potassium *tert*-butoxide. This indicates a difference in basicity for the two compounds of approximately 10 orders of magnitude. The basicity of the iron complex was not much different from that of the fluorenide anion suggesting that both species have similar charge distributions. The lower basicity of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ indicates that there is a much lower negative charge residing at C(9). This can be explained by assuming extensive charge delocalization in the complex from C(9) to the metal carbonyl moiety. In turn this implies that a structure more like a localized cyclohexadienyl compound; in contrast to the iron compound $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$ is represented to be closer to the zwitterionic form.[2] An interesting comparison may be made with the complex $[Co(C_5H_5)(C_5H_4CH(C_6H_5)_2)]^+$. The proton on the substituent group is 10^{11} times more acidic than the proton on the model compound, triphenylmethane.[6] It is suggested that this enhancement is a consequence of stabilization in a fulvene resonance structure, $Co(C_5H_5)(C_5H_4{=}C(C_6H_5)_2)$, of the deprotonated product. Similar data pertain to the aniline(cyclopentadienyl)iron cation, which is less basic than aniline by 6 orders of magnitude.[7] Donation to the electron-deficient arene ring from the lone pair of the amino group, effectively allowing representation as the cyclohexadienylimmoniumiron cation, $Fe(C_5H_5)(C_6H_5{=}N^+H_2)$, is suggested.

The infrared data do not appear to fully confirm or deny this postulate. The absorptions for $\nu(CO)$ shift about 30 cm^{-1} on deprotonation of $[Mn(C_{13}H_{10})(CO)_3]PF_6$. In contrast shifts of 60–80 cm^{-1} occur on conversion of cationic arenemanganese tricarbonyl complexes to uncharged cyclohexadienylmanganese tricarbonyl.[3] However the two systems are not strictly comparable. In $Mn(C_{13}H_9)(CO)_3$ the charge distribution must be such that negative charge is also substantially delocalized within the fluorenyl ligand, consequently less reorientation of charge density to the metal and carbonyl groups is necessary.

Another interesting comparison can be made between our system and that arising on loss of the N–H proton in the arene complex $[Mn(C_6H_5NHR)(CO)_3]^+$ ($R = C_6H_5$).[5] This complex has $\nu(CO)$ values of 2065 and 2002 cm^{-1}. Deprotonation of this compound gives a cyclohexadienylimine complex $Mn^+(C_6H_5N^-R)(CO)_3$, with $\nu(CO)$ 2038, 1974, 1959 cm^{-1}. The small shifts in $\nu(CO)$, about 30 cm^{-1}, are about the same as seen for the fluorenylmanganese compound. This shift is accounted for by the partial delocalization of negative charge on nitrogen. Restricted rotation of the CN bond, evidence for charge delocalization, appears to confirm this assumption. If only partial delocalization of negative charge occurs, some negative charge must remain on nitrogen. This seems reasonable, considering this atom's electronegativity.

In accord with its reduced negative charge at C(9), $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ reacts more slowly with electrophilic reagents than does $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. At room temperature, the reaction of $Mn(C_{13}H_9)(CO)_3$ with excess CH_3OSO_2F in hexane requires 3 days to go to completion, while the same reaction with $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$ was completed in less than 1 min. The product obtained in the reaction was $[Mn(9\text{-}CH_3C_{13}H_9)(CO)_3]^+$. The ^1H NMR spectrum of the PF_6^- salt was only one doublet in the methyl group, even when recorded at 270 MHz. This demonstrates stereospecific addition of the methyl group; exo stereochemistry is assumed for $[Mn(9\text{-}CH_3C_{13}H_9)(CO)_3]^+$ by analogy with the corresponding iron compound.[2]

Protonation of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ with HCl or DCl occurs much more rapidly and, interestingly, the reaction is not stereospecific under the conditions used. This could be a consequence of random exo or endo addition occurring, and of course this implies random deprotonation as well.

Also in accord with the cyclohexadienyl representation is the higher solubility of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ in saturated hydrocarbons, compared to that of $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. This can be accounted for by a lower degree of charge separation in the manganese complex.

Examination of the ^1H NMR spectrum (Table I) of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ and comparison with the spectra of similar compounds lend support to the model involving substantial charge delocalization from C(9). In the spectra of cyclohexadienyltricarbonylmanganese complexes,[8–10] the central proton of the dienyl unit appears at lowest field, the inner protons appear at an intermediate position, and the outer protons appear at highest field. In the spectrum of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$, the coupling pattern requires that the center dienyl proton be assigned to the resonance at δ 4.32 and the outer dienyl proton to the resonance at δ 6.05. Alternatively, one could assign the center dienyl proton to the signal at δ 4.13 and the outer dienyl proton to the signal at δ 5.32. Regardless which assignment is correct, the center proton of the dienyl unit is observed at higher field than the outer proton, contrary to the situation for other transition metal–cyclohexadienyl complexes. It is interesting to note that in the previously mentioned cyclohexadienylimine complex, $Mn(C_6H_5NPh)(CO)_3$,[5] the center dienyl proton appears in the NMR spectrum at δ 5.65 while the outer protons appear at δ 4.38 and 4.73. In this case, the center proton is still observed at lower field than the outer proton, but the difference is less than the ~3-ppm difference observed in the other cyclohexadienylmanganese compounds. For $Mn(C_5H_5NPh)(CO)_3$, the decrease in the chemical shift difference between the center and outer dienyl protons is attributed to the deshielding of the outer dienyl protons by the imino group, as well as to contributions of a zwitterionic resonance structure.

The ^{13}C NMR spectrum of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ was conveniently measured by adding excess Et_3N to an acetone-d_6 solution of $[Mn(C_{13}H_{10})(CO)_3]PF_6$. The probe temperature was kept at −10 °C to retard the isomerization to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$. Data for this compound are given in Table II.

The distinction between C–H carbon and quaternary carbon assignments can be made by examination of a single-frequency off-resonance proton-decoupled spectrum.[11] The C–H carbons of the complexed and uncomplexed rings are distinguished through selective proton decoupling. Furthermore, the C(9) resonance is positively assigned. In acetone-d_6 solution in the presence of excess triethylamine, the C(9) position of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ is slowly deuterated, leading to the replacement of the singlet resonance at δ 93.6 in the broad-band proton-decoupled spectrum with a characteristic deuterium-coupled 1:1:1 triplet.

There is a significant departure from the trends observed in the ^{13}C NMR spectra of the analogous iron compounds.[2] In the iron compounds, the quaternary carbons in the uncomplexed six-membered ring are shifted upfield 20 ppm upon deprotonation, while the positions of the corresponding carbon resonances in the manganese compounds are little affected in going from $[Mn(C_{13}H_{10})(CO)_3]^+$ to $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$. This seems to indicate less accumulation of negative charge on the five-membered ring of the manganese compound. Only one of the quaternary carbons in the six-membered ring of the complex is significantly shifted upfield upon deprotonation of the cation. In the analogous iron system, both quaternary carbons in the complexed ring show significant upfield shifts on going from $[Fe(C_5H_5)(C_{13}H_{10})]^+$ to $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. This fact seems to indicate that $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ has more cyclohexadienyl character than does $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. The unshifted carbon atom, resonating at δ 125.8, probably corresponds to the sixth carbon of the complexed six-membered ring which is less closely bound to the manganese atom than the five carbons which form the dienyl unit. Unfortunately, the absence of ^{13}C NMR data on analogous metal–cyclohexadienyl systems makes comparisons impossible.

A final point to note is the position of the C(9) resonance. At δ 93.6, the C(9) resonance of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ is only 6.8 ppm downfield from the C(9) resonance of $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. If the cyclohexadienyl resonance structure is the only contributor to the bonding in $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$, this C(9) resonance would be expected[11] in the range δ 120–130. The observation of the C(9) resonance considerably upfield from this region probably indicates some negative charge is being localized on the C(9) position of the fluorenyl ligand through the participation of zwitterionic resonance structure in the bonding of the complex.

The combined evidence of the solubility, chemical reactivity, and the ^{13}C NMR data seems to indicate that the cyclohexadienyl resonance structure for $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ is a larger contributor to the overall bonding scheme of the complex than is the zwitterionic resonance structure. This is contrary to the observations for $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. It should be pointed out, however, that in the manganese complex, the zwitterionic structure does make some contribution to the bonding, as is evidenced by the ^1H NMR spectrum and the position of the C(9) resonance in the ^{13}C NMR spectrum. Clearly, it would be interesting to examine the crystal structure of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$, in order to ascertain structural differences implied by these data.

The occurrence of a six-membered to five-membered ring transfer in the isomerization of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ warrants further comment. This ring-transfer reaction is irreversible. This is demonstrated by the fact that $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ is inert to CF_3CO_2H. Since $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ reacts rapidly with CF_3CO_2H to give $[Mn(C_{13}H_{10})(CO)_3]^+$, if $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ were in equilibrium with its η^6 isomer, protonation should occur, resulting in the production of the $[Mn(C_{13}H_{10})(CO)_3]^+$ cation. This irreversibility in the fluorenyltricarbonylmanganese system contrasts with the behavior observed in the diindenyliron system,[12] in which the ring-transfer reaction is reversible. There, the protonation reaction (and subsequent five-membered to six-membered ring transfer) was believed to be initiated by protonation at the metal atom. The reason no ring transfer was observed upon attempted protonation of $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ may be that the manganese atom is too weakly basic for the initial protonation to occur. This conclusion is supported by studies of the basicity of transition metal complexes,[13,14] which have shown that $Mn(C_5H_5)(CO)_3$ is inert to strong acids, in contrast to $Fe(C_5H_5)_2$[13,15] which protonates on the iron atom. The organophosphine-substituted complexes $Mn(C_5H_5)(CO)_2L$ and $Mn(C_5H_5)(CO)L_2$ are protonated in CH_2Cl_2/CF_3CO_2H solutions,[14] due to the increased electron density caused by the enhanced donor characteristics of the phosphine ligands. It would be interesting to study the reaction of phosphine-substituted derivatives $Mn(\eta^5\text{-}C_{13}H_9)(CO)_{3-x}(phos)_x$. These should protonate at the metal atom, making a five-membered to six-membered ring transfer to yield the η^6-fluorene cation an attractive possibility.

The observed irreversibility in the ring-transfer reaction of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ to give $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ demonstrates that the η^5 complex is the thermodynamically more stable of the two isomers. This fact leads back to the question raised in the discussion of $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$. Does the failure to observe a ring transfer in the iron compound reflect a thermodynamic preference for the η^6 bonding mode, or is there only a kinetic barrier preventing the ring transfer to form the (unknown) $Fe(C_5H_5)(\eta^5\text{-}C_{13}H_9)$ complex? The answer to this question is not straightforward. The observation of six-membered to five-membered ring transfers under relatively mild conditions in the $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$, $[Fe(C_9H_7)(C_9H_8)]^+$, and $Cr(C_{13}H_9)(CO)_3^-$ [6] cases leads to the prediction of no greater kinetic barrier to ring migration in the $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$ case. Also, the unavailability of η^5-fluorenyliron complexes from standard routes[2,17] may indicate low stability for $Fe(C_5H_5)(\eta^5\text{-}C_{13}H_9)$. However, it must be pointed out that the kinetic barrier to migration in $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ is significant—the complex can be isolated and stored unchanged at low temperatures. A relatively minor enhancement of this kinetic barrier in the iron system could preclude the observation of a ring transfer, because $Fe(C_5H_5)(\eta^6\text{-}C_{13}H_9)$ thermally degrades at temperatures as low as 80 °C.

Acknowledgment. Fellowship support for J.W.J. from the University of Wisconsin Graduate School and from the National Science Foundation is acknowledged. The Syntex diffractometer and various NMR facilities, all Departmental equipment, were obtained with partial support from the NSF under its major instrument grants program.

Registry No. $[Mn(C_{13}H_{10})(CO)_3]PF_6$, 61484-34-2; $[Mn(\textit{exo}\text{-}9\text{-}CH_3C_{13}H_9)(CO)_3]PF_6$, 61477-49-4; $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$, 61477-47-2; $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$, 31760-87-9; $Mn(CO)_5Br$, 14516-54-2; CH_3OSO_2F, 421-20-5; ^{13}C, 14762-74-4.

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(18) The designation η^6 will be used here to designate coordination to one six-membered ring of the fluorenyl ligand. The actual structure as a η^6 compound is a simplification; see text to follow.

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Raman Spectra of the Cobalt Carbonyl Acetylene Complexes $Co_2(CO)_6C_2R_2$

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Received March 22, 1976 AIC602184

Raman spectra are reported and discussed for $Co_2(CO)_8C_2R_2$ species (R = H, CF_3, CH_3, $COOCH_3$, C_6H_5) and for $Fe_2(CO)_6S_2$. In the 2000-cm^{-1} region a definite assignment of $\nu_5(B_1)$ is achieved and a dependence of the separation between $\nu_2(A_1)$ and $\nu_6(B_2)$ in the electronegativity of R is revealed and explored in a simple normal-coordinate treatment. For the low-frequency spectral region the data for $Fe_2(CO)_6S_2$ facilitate the interpretation of the data for the cobalt species. This interpretation differs at several points from that of previous workers.

The relative ease of preparation of complexes of general formulation $Co_2(CO)_6RC{=}CR'$ has led to several studies aimed, at least in part, at comparing the vibrational characteristics of the coordinated and free alkyne.[1-4] By systematic variation of the ligand and by isotopic substitution it has proved possible to identify, with a fair degree of certainty, most of the internal vibrations of simple alkynes and to discuss the origin of the frequency changes observed.

In addition to studies on the alkynes there has also been interest in the vibrational spectra in the ν(CO) region although, again, almost all of the relevant reports have been concerned solely with infrared studies. As is well known, the coupling of the individual CO vibrators gives rise to well separated peaks, thus, in the present case for instance, offering the hope that the extent of coupling between the two $Co(CO)_3$ groups can be determined. Much of the work in this area on these compounds is that of Bor and his co-workers.[5-7] Their work has clearly shown that the interaction between CO groups of different $Co(CO)_3$ units may be comparable with the interactions between CO groups of the same unit.[7] In view of this wealth of information it might be supposed that Raman data would be superfluous. This is not the case for several reasons. First, there is a frequent uncertainty in the infrared spectrum over the assignment of $\nu_2(A_1)$ and $\nu_6(B_2)$. Raman depolarization data could enable a clear distinction. Second, a rather weak peak has been assigned to the $\nu_5(B_1)$ fundamental mode. A confirmation of this assignment from Raman studies is desirable. In practice, we have been able to achieve the latter demonstration. However, only in the complex of $C_2(CH_3)_2$ were the $\nu_2(A_1)$ and $\nu_6(B_2)$ modes sufficiently well resolved to make an unambiguous assignment possible on the basis of our Raman spectra.

Solid $Co_2(CO)_6C_2RR'$ species are reasonably stable in air but in solution or in the liquid state all decompose quite rapidly. Further, most are readily photodecomposed. In our Raman studies we have found that such decomposition could frequently only be avoided when the deep red krypton laser line (6764 Å) was used for excitation. Even at a low incident power, the 6471-Å line sometimes caused appreciable decomposition. In all cases, therefore, we have deemed it advisable to repurify all samples used in our Raman studies before reuse. In the present work we have studied species with R = R' = COOH, $COOCH_3$, C_6H_5, and $Fe_2(CO)_6S_2$. Only for the latter compound are we aware of previous Raman data;[8] for the ν(CO) region this work was on solid samples and at a lower resolution than the solution data reported in this paper.

Results and Discussion

We were successful in obtaining good-quality Raman spectra of the species with R = R' = H, CF_3, CH_3, and $COOCH_3$ and of $Fe_2(CO)_6S_2$, all in CCl_4 solution, in the ν(CO) region. A spectrum was similarly obtained for R = R' = C_6H_5 but this was of a rather lower quality. These spectra all show a common pattern. There is a high-frequency band and a lower frequency set of three bands, the separation between the three components being rather variable so that while those bands are clearly resolved for R = R = CF_3 (Figure 1) for $Fe_2(CO)_6S_2$ (Figure 2), one band is little more than a shoulder and in the case of R = R' = H (Figure 3) there are only two resolved bands.

Comparison with the infrared frequency data and our polarization measurements make it quite clear that even when three bands are observed they should not be necessarily assigned in the same way in all compounds. In the case of R = R' = CH_3, for instance, it is clear from such considerations that $\nu_2(A_1)$ and $\nu_6(B_2)$ are resolved. The normal pattern is that ν_6 appears at a higher frequency than ν_2. However, as the electronegativity of R (=R') increases, this separation decreases and for the most electronegative substituents the frequency order is actually reversed. Confirmatory evidence for this comes from two additional sources: first, from the relative infrared intensities of the two bands ($I(\nu_6) > I(\nu_2)$); second, from the observation of a correlation between the separation ($\nu_6 - \nu_2$) and the Taft parameter σ^{*}[9] (Figure 4). The extrapolation to the cases R = R' = CF_3 or $COOCH_3$ clearly requires that $\nu_6 - \nu_2$ be negative. The Raman spectral data are collected in Table I where they are compared with infrared data for the corresponding compounds. In making this comparison it must be remembered that the infrared data were obtained using hexane as a solvent so that small differences in solvent effects are to be expected. Unfortunately, paraffinic hydrocarbons do not prove to be generally suitable as solvents for these compounds in a Raman study. Our assignments, also given in Table I, generally concur with those of Bor.[7] In particular, our measurements of depolarization ratios clearly confirm the A_1 symmetry species of the highest