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Synthesis and Structures of the Novel Manganese(−I) Fullerene-[60] Complexes M[Mn(CO)$_4$(η^2-C$_{60}$)] (M = Na, PPN)

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Summary: The thermal and photochemical reactions of M[Mn(CO)$_5$] (M = Na, PPN) with C$_{60}$ and the photochemical reaction of Mn$_2$(CO)$_{10}$ with M[C$_{60}$] give the same green complex of Mn(−I), M[Mn(CO)$_4$(η^2-C$_{60}$)]. The C$_{60}$ coordinates conventionally via a six−six ring junction but appears to be a better π-acceptor than CO, since the average of the carbonyl stretching frequencies of PPN[Mn(CO)$_4$(η^2-C$_{60}$)] is ~77 cm^{-1} higher than the average of those of PPN[Mn(CO)$_5$].

Metal−C$_{60}$ compounds generally fall into one of three main categories, endohedral compounds in which the metal atom is encapsulated by the fullerene sphere,[1] alkali-metal fulleride compounds containing discrete anionic species C$_{60}$$^{n-}$ (n = 1−6),[2a,b] and η^2-transition metal complexes in which the fullerene behaves essentially as an electron-deficient alkene ligand.[3] While a few somewhat incompletely characterized transition metal fulleride compounds are known,[2c−n] none as yet has been observed to exhibit the high-temperature superconductivities of many alkali-metal fullerides. Nonetheless, one might anticipate that transition-metal fullerides, with the possibility of variations in d electron configurations, metal oxidation states, and nuclearities, present enticing opportunities for further research.

It is well established that C$_{60}$ contains a low-lying, triply degenerate LUMO, thus making possible facile reduction to the above-mentioned fullerides.[2a,b] We have previously noted that transition-metal carbonylate anions have sufficiently low ionization potentials that they should be able to reduce C$_{60}$ to the radical anion C$_{60}$$^{n-}$ and have demonstrated that the reaction of Na[Co(CO)$_4$] with C$_{60}$ in refluxing THF results in the formation of intermediate cobalt carbonyl compounds which eventually convert to the insoluble, bimetallic fulleride compound NaCoC$_{60}$·3THF and thence, on heating, to NaCoC$_{60}$.[4] Although neither the intermediates nor NaCoC$_{60}$·3THF could be characterized structurally, the latter exhibited antiferromagnetic properties which confirm the possibility of magnetic coupling in such materials. A small number of other reports of reduction of C$_{60}$ by electron-rich organometallics have appeared,[5] and we have extended our attention to other carbonylate complexes, many of which take part in electron transfer with C$_{60}$. We now report that reactions of salts of [Mn(CO)$_5$]$^-$ with C$_{60}$ result in the formation of salts of [Mn(CO)$_4$(η^2-C$_{60}$)]$^-$, the first well-characterized fullerene complex of a metal in a negative oxidation state. The same compounds are also formed via reactions of Mn$_2$(CO)$_{10}$ with salts of C$_{60}$$^-$.

The thermal reaction of Na[Mn(CO)$_5$] with C$_{60}$ (2:1 molar ratio) in refluxing THF differs significantly from that of the analogous cobalt reaction. Over the course of 18 h, a deep green color developed and the infrared absorptions characteristic of Na[Mn(CO)$_5$] (ν_{CO} 1828, 1860, 1872, 1898 cm^{-1}) were gradually replaced by others attributable to Mn$_2$(CO)$_{10}$ (ν_{CO} 2044, 2009, 1979 cm^{-1}) and to a new transition-metal carbonyl fullerene compound, Na[Mn(CO)$_4$(η^2-C$_{60}$)] (ν_{CO} 2025, 1938, 1900

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cm^{-1}). Under these conditions, Na[Mn(CO)$_4$(η^2-C$_{60}$)] was formed in up to 50% yield and, after unreacted C$_{60}$ was removed by filtration and hexanes were layered over the solution to induce precipitation, could be isolated as somewhat air-stable, black crystals, soluble in THF. The electronic spectrum (THF) exhibited absorptions at 222, 260, 332, 450 (br), and 730 (br) nm, typical of many fullerene compounds,[3] but none in the near-IR region, where fullerides are known to absorb.[2] The compound Na[Mn(CO)$_4$C$_{60}$] was also prepared photochemically by irradiation (Hanovia lamp) of a mixture of Na[Mn(CO)$_5$] and C$_{60}$ in THF. Indeed, yields up to 90% could be obtained this way since, after 36 h, all of the Mn$_2$(CO)$_{10}$ had also been converted to product.

Although this new fullerene complex could not be obtained analytically pure as the sodium salt, its stoichiometry in THF solution was initially established by electrospray mass spectrometry (ES-MS), which has been extensively used to investigate negatively charged fullerene[6] and organometallic species.[7] The principal ion at 887 Da/e, with an appropriate isotope distribution, was observed at low cone voltages (0−25 V), while increasing the cone voltage to 50−75 V resulted in loss of CO and the formation of [Mn(CO)$_3$C$_{60}$]$^-$, [Mn(CO)$_2$C$_{60}$]$^-$, and [Mn(CO)C$_{60}$]$^-$ daughter ions. Facile identification of principal ions at low cone voltages but successive decarbonylations with increasing cone voltages is typical of ES-MS of transition-metal carbonylate anions.[7] The ^{13}C NMR spectrum of Na[Mn(CO)$_4$C$_{60}$] exhibited 13 sp^2 resonances of relative intensity 2 and 3 of relative intensity 1 in the range δ 175−136 in addition to an sp^3 resonance of relative intensity 1 at δ 85.8, similar to many η^2-C$_{60}$ metal compounds.[3] Carbonyl resonances were not observed, presumably because of significant quadrupolar broadening by the manganese.[8] Further evidence of coordination was obtained by the observation of a complex Raman spectrum of a type typical of a number of η^2-C$_{60}$−metal compounds in which the symmetry of the fullerene has been reduced from I_h to C_{2v}.[3]

Although crystals of Na[Mn(CO)$_4$(η^2-C$_{60}$)] suitable for X-ray crystallographic analysis could not be obtained, appropriate crystals of the analogous bis(triphenylphosphoranylidene)ammonium (PPN) salt were obtained via the photochemical route. Thus, photolysis for 48 h of a solution of PPN[Mn(CO)$_5$][9] in THF containing a suspension of C$_{60}$ (1:1 molar ratio) yielded a deep green solution, the IR spectrum of which exhibited *only* the absorptions attributed above to the [Mn(CO)$_4$(η^2-C$_{60}$)]$^-$ anion. The deep green solution was filtered and then layered with hexanes under argon, yielding eventually shiny black crystals of PPN[Mn(CO)$_4$C$_{60}$]. The X-ray crystal structure of PPN[Mn(CO)$_4$C$_{60}$][10] (Figure 1) shows that the C$_{60}$ is coordinated in an η^2-fashion via a six−six ring junction to the manganese, essentially as has been observed for many other η^2-C$_{60}$ metal complexes.[3] Analogous to many isoelectronic η^2-alkene compounds of the type Fe(CO)$_4$(η^2-alkene)[11] and as anticipated for the isoelectronic neutral compounds M(CO)$_4$(η^2-C$_{60}$) (M = Fe,[12a] Ru[12b]), the new complex may be considered to be a trigonal-bipyramidal complex in which the fullerene ligand occupies an equatorial site with the coordinated CC bond parallel to the plane created by the equatorial carbonyl ligands. However, in contrast to compounds of the type Fe(CO)$_4$(η^2-alkene), in which the OC$_{eq}$−Fe−CO$_{eq}$ angles are 104−117°,[11] the OC$_{eq}$−Mn−CO$_{eq}$ (C(102)−Mn(1)−C(101)) angle of [Mn(CO)$_4$(η^2-C$_{60}$)]$^-$ is 96.6(19)°, i.e., much closer to the bond angle expected for an octahedral complex. This result is consistent with there being much greater back-donation from the anionic manganese to the fullerene, perhaps to the point where the anion might be better considered a complex of manganese(I) with the [C$_{60}$]$^{2-}$ anion. Unfortunately, at the current state of refinement, the esd's for the fullerene carbon atoms are too large for meaningful comparisons of the Mn−C, C−O and C−C bond distances to be made.

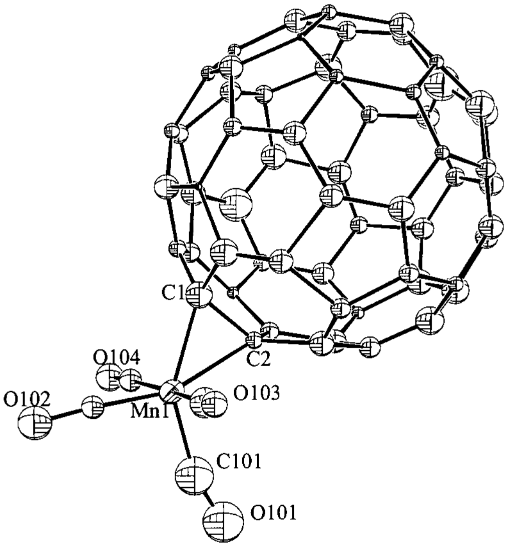

Figure 1. Molecular structure of the [Mn(CO)$_4$(η^2-C$_{60}$)]$^-$ anion showing the atom-labeling scheme for the inner coordination sphere of the manganese.

A reasonable mechanism of the thermal formation of [Mn(CO)$_4$(η^2-C$_{60}$)]$^-$ would involve initial electron transfer from [Mn(CO)$_5$]$^-$ to C$_{60}$ as in eq 1. The 17-electron

$$[\mathrm{Mn(CO)_5}]^- + \mathrm{C_{60}} \rightarrow \mathrm{Mn(CO)_5} + \mathrm{C_{60}}^- \qquad (1)$$

Mn(CO)$_5$ is known to be extremely substitution-labile[13]

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[10] Crystal data for PPN[Mn(CO)$_4$C$_{60}$]: black plate (0.015 × 0.10 × 0.15 mm); data collected at −100 °C; monoclinic, $P2_1/n$, a = 9.9169(17) Å, b = 17.082(3) Å, c = 38.157(6) Å, β = 94.55(2)°, V = 6443.5(19) Å^3, Z = 2; 37 559 reflections measured ($2\theta < 42°$), of which 6763 were unique and 3217 were observed (2.5σ); final residuals R = 19.2%, R_w = 13.6%, GOF = 5.08.

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and should undergo substitution of CO by the anionic fulleride ion, as in eq 2. Indeed, this process may well

$$\mathrm{Mn(CO)_5 + C_{60}{}^- \rightarrow [Mn(CO)_4(C_{60})]^- + CO} \qquad (2)$$

be assisted by coupling of the unpaired electrons on $\mathrm{Mn(CO)_5}$ and $\mathrm{C_{60}{}^-}$, a process which certainly occurs at some stage, since the product appears to be diamagnetic. Intermediacy of the 17-electron intermediate $\mathrm{Mn(CO)_5}$ seems confirmed by the formation of $\mathrm{Mn_2(CO)_{10}}$, the product expected from coupling of $\mathrm{Mn(CO)_5}$ radicals.[13] The photolytic synthesis is thus of particular interest because $\mathrm{Mn_2(CO)_{10}}$ was formed as an apparent intermediate but was converted to $[\mathrm{Mn(CO)_4}(\eta^2\text{-}\mathrm{C_{60}})]^-$ by continued photolysis after all of the $[\mathrm{Mn(CO)_5}]^-$ was gone. While $\mathrm{Mn_2(CO)_{10}}$ is stable during the thermal process and is one of the two major reaction products, it is known to undergo photolytic cleavage to the substitutionally labile $\mathrm{Mn(CO)_5}$.[13] Thus, any $\mathrm{Mn_2(CO)_{10}}$ formed during the photochemical process is converted to monomer and reacts further with the $\mathrm{C_{60}{}^-}$ already in solution to produce more of the final product, $[\mathrm{Mn(CO)_4}(\eta^2\text{-}\mathrm{C_{60}})]^-$.

The photoinduction of the chemistry of eq 1 is also noteworthy. It is well-established that outer-sphere interactions between the mild oxidant $\mathrm{C_{60}}$ and a wide variety of reducing agents generate new optical transitions involving charge transfer from the electron donor to the fullerene and that irradiation at the frequency of a charge-transfer band leads to electron transfer.[14] While we have not yet identified a charge-transfer band in the deeply colored, air-sensitive solutions containing $\mathrm{C_{60}}$ and $[\mathrm{Mn(CO)_5}]^-$, it is certain that the latter reagent is consumed much more quickly under photochemical than under thermal conditions. Thus, a charge-transfer process seems operative.

Comparisons of the IR spectra of the PPN and sodium salts of $[\mathrm{Mn(CO)_5}]^-$ in the carbonyl stretching region reveal subtle but interesting differences. While we find that the solution (THF) IR spectra of PPN$[\mathrm{Mn(CO)_5}]$ (1894, 1861 $\mathrm{cm^{-1}}$) and Na$[\mathrm{Mn(CO)_5}]$ (see above) are different because of significant contact ion pairing only in the latter, the corresponding IR spectra of the PPN and sodium salts of $[\mathrm{Mn(CO)_4}(\eta^2\text{-}\mathrm{C_{60}})]^-$ are identical. The latter observation seems to imply an absence of $\mathrm{Na^+{-}OCMn}$ ion pairing in THF solutions of the compound Na$[\mathrm{Mn(CO)_4}(\eta^2\text{-}\mathrm{C_{60}})]$, unusual for solutions of alkali-metal salts of carbonylate anions.[15] Thus, as suggested above, one must conclude that the negative charge is not localized on the $\mathrm{Mn(CO)_4}$ fragment of the $[\mathrm{Mn(CO)_4}(\eta^2\text{-}\mathrm{C_{60}})]^-$ anion but must rather be extensively delocalized onto the fullerene ligand, consistent with the general finding that $\mathrm{C_{60}}$ behaves as an electron-deficient alkene.[3] Consistent with this interpretation, the complex is inert to thermal substitution of $\mathrm{C_{60}}$ by $\mathrm{PPh_3}$, in strong contrast to many known neutral η^2-$\mathrm{C_{60}}$ compounds from which $\mathrm{C_{60}}$ is readily displaced.[3b,12b] Analogous reactions of $\mathrm{C_{60}}$ with other carbonylate anions, including clusters, are being pursued. If, as seems likely, carbonylate fullerene compounds are generally stable to $\mathrm{C_{60}}$ dissociation, thermal decarbonylation should provide a general route to transition-metal fulleride compounds analogous to the above-mentioned $\mathrm{NaCoC_{60}}$.

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Supporting Information Available: Crystallographical details, including figures showing complete numbering schemes for the cation and anion and a thermal ellipsoid diagram and tables of positional and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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