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New methods for the synthesis of transition-metal fullerene complexes*

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Abstract: Buckminsterfullerene, C_{60}, is readily reduced on exposure to solutions of strongly reducing transition-metal carbonylate anions to give the radical anion fulleride C_{60}^- and the corresponding highly reactive, 17-electron neutral compounds. Three secondary reaction paths have been identified, depending on the nature of the reactants and the reaction conditions. (1) With Na^+ and PPN^+ salts of $[Mn(CO)_5]^-$, thermal substitution of a CO on the metal radical by the C_{60}^- results in formation of the anionic, η^2-fullerene complex $[Mn(C_{60})(CO)_4]^-$. (2) With salts of $[Co(CO)_4]^-$, the thermal reaction results in formation of a novel transition-metal fulleride $NaCoC_{60}$ while (3) with $Na[CpFe(CO)_2]$ and $[CpM(CO)_3]^-$ (M = Mo, W), the 17-electron intermediates couple to form the 18-electron dimers, $[CpFe(CO)_2]_2$ and $[CpM(CO)_3]_2$. In contrast, photochemical reactions of C_{60} with salts of $[Mn(CO)_5]^-$, $[Co(CO)_4]^-$, and $[CpM(CO)_3]^-$ result in excellent yields of the complexes $[Mn(C_{60})(CO)_4]^-$, $[Co(C_{60})(CO)_3]^-$ and $[CpM(C_{60})(CO)_2]^-$, respectively; analogous complexes of C_{70} may be made similarly. The new complexes have been characterized crystallographically, by IR, ^{13}C NMR, and/or Raman spectroscopy and by electrospray mass spectrometry.

INTRODUCTION

Although C_{60} (**A**) forms many fulleride *salts* M_nC_{60} (M = Li, Na, K, Rb) by direct reaction with alkali metal vapors [1], very few simple transition-metal fullerides are known. Instead, the majority of C_{60} transition-metal complexes contain the neutral C_{60} coordinated in η^2-fashion to a metal in complexes of the type (η^2-ML_n, **B**) (Fig. 1) [2].

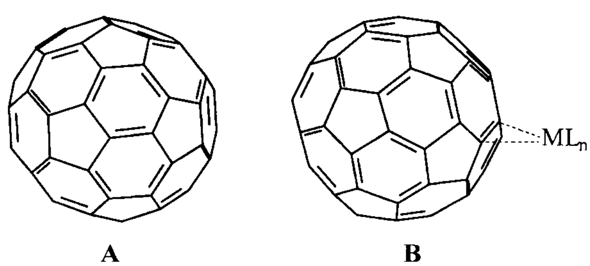

Fig. 1

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A NEW ROUTE TO TRANSITION-METAL CARBONYL C_{60} COMPOUNDS

General routes to transition-metal fullerides are desirable, as such materials could have very interesting properties arising from varying d electron configurations, nuclearities, etc. C_{60} has a high electron affinity (2.6–2.8 eV) and should readily oxidize carbonylate salts such as $Na[Co(CO)_4]$ (eq. 1).

$$C_{60} + Na[Co(CO)_4] \rightarrow NaC_{60} + \cdot Co(CO)_4 \qquad (1)$$

The Co-containing product is a 17-electron, metal-centered radical which is known to be substitution labile, and one might anticipate that the C_{60}^- radical ion would substitute a CO to give a spin-paired complex $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$. We have shown, however, that refluxing a tetrahydrofuran (THF) solution of $Na[Co(CO)_4]$ with a suspension of C_{60} for several hours results in the formation of black, insoluble $NaCoC_{60}(THF)_3$ [3a]. One or more carbonyl containing intermediates with ν(CO) at 1992, 1966, and 1920 cm^{-1} were noted, but could not be identified at the time.

Rather different results were found with $Na[Mn(CO)_5]$, which reacts with C_{60} in refluxing THF to give a green solution containing approximately 50% yields of $[Mn(CO)_5]_2$ and $Na[Mn(CO)_4(\eta^2\text{-}C_{60})]$ [3b]. Although the similarity of the ν(CO) [2025, ~2015 (sh), 1938, 1900 cm^{-1}] to those of $\eta^5\text{-}C_5H_5Mn(CO)_3$ (2025, 1938 cm^{-1}) suggested that the new compound might be a neutral species, electrospray mass spectrometry (ES MS) showed that it is anionic (molecular ion at m/e 887 for ^{55}Mn), and the structure was confirmed crystallographically to be as shown (Fig. 2).

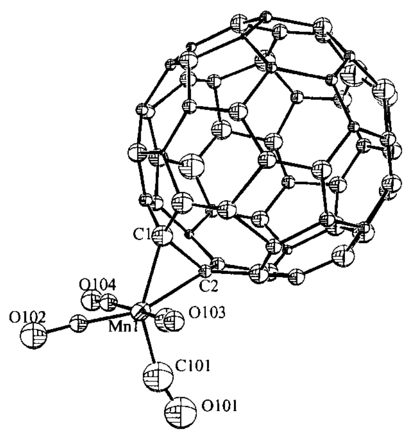
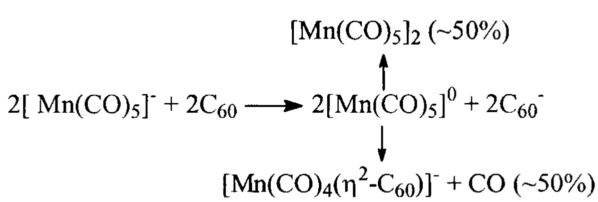


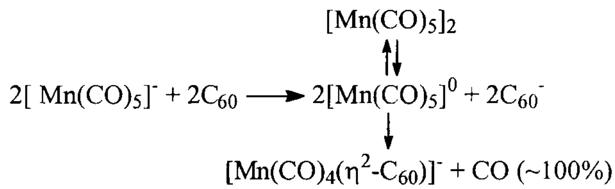
Fig. 2

The IR data suggest that the C_{60} in $PPN[Mn(CO)_4(\eta^2\text{-}C_{60})]$ is an excellent π-acceptor and, as a result, this new η^2-fullerene complexes exhibits unusually high stability with respect to both air oxidation (solutions are stable in air for hours), C_{60} dissociation, and thermal substitution by phosphines.

The reaction of $Na[Mn(CO)_5]$ with C_{60} probably proceeds as in Scheme 1. However, $[Mn(CO)_5]_2$ readily undergoes photolytic homolysis to $Mn(CO)_5$ radicals, and therefore a photochemical approach gives better yields (Scheme 2).



Scheme 1



Scheme 2

Anticipating that the photochemical route might generally give better yields, we returned to the cobalt system to find that the green complex $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$ could indeed be prepared in high yield (by IR). Although this complex has not been isolated pure, it was identified by ES MS (molecular ion at e/m 863 for ^{59}Co) and IR spectroscopy (ν(CO) at 1992 and 1920 cm^{-1}, compared with 1885 cm^{-1} for $Na[Co(CO)_4]$). The ν(CO) at 1992 and 1920 cm^{-1} are identical to two of the ν(CO) of intermediates formed when $[Co(CO)_4]^-$ was refluxed with C_{60}, and therefore $[Co(CO)_3C_{60}]^-$ is a precursor in the thermal synthesis of $NaCoC_{60}(THF)_3$. The intermediate is thus stable at room temperature.

Rather different results are obtained with the Group 6 cyclopentadienyl carbonylate anions $[CpM(CO)_3]^-$ (M = Mo, W), for which the thermal reactions in THF gave only the ultimate products of electron transfer, $[CpM(CO)_3]_2$. Under photolytic conditions, however, good yields (IR) of the complexes $[CpMo(CO)_2(\eta^2\text{-}C_{60})]^-$ were obtained as the PPN salts. The stoichiometries of these new complexes were established by ES MS (strongest molecular ions at e/m 939 and 1025, respectively, with appropriate isotope distributions), while the IR spectra exhibited ν(CO) at 1900, 1818 cm^{-1} (Mo) and 1894, 1809 cm^{-1} (W). The analogous chemistry of $[CpFe(CO)_2]^-$ yielded only $[CpFe(CO)_2]_2$.

We find that the photochemical route also works very well with C_{70}, the complexes $[Mn(CO)_4(\eta^2\text{-}C_{70})]^-$, $[Co(CO)_3(\eta^2\text{-}C_{70})]^-$, $[CpMo(CO)_2(\eta^2\text{-}C_{70})]^-$, and $[CpW(CO)_2(\eta^2\text{-}C_{70})]^-$ all forming in high yields and being characterized by ^{1}H NMR spectroscopy and by ES MS (molecular ions of $[Mn(CO)_4(\eta^2\text{-}C_{70})]^-$, $[Co(CO)_3(\eta^2\text{-}C_{70})]^-$, $[CpMo(CO)_2(\eta^2\text{-}C_{70})]^-$ and $[CpW(CO)_2(\eta^2\text{-}C_{70})]^-$ being observed at m/e 1007, 983, 1059 and 1145). Interestingly, the mass spectrum of the tungsten complex also exhibited a strong manifold of peaks clustered around m/e 725 with each pair separated by 0.5 units. Thus, the ion is to be identified as the doubly charged, ditungsten adduct $[\{CpW(CO)_2\}_2(\eta^2\text{-}C_{70})]^{2-}$. The IR spectra were all similar to those of the corresponding C_{60} complexes, although that of the tungsten system is quite complicated because of the presence of two species, one of which may exhibit geometrical isomerism.

ACKNOWLEDGMENTS

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REFERENCES

1. (a) M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund. *Science of Fullerenes and Carbon Nanotubes*, Academic Press, New York (1996); (b) M. J. Rosseinsky. *Chem. Mat.* **10**, 2665 (1998).
2. (a) W. Sliwa. *Transition Met. Chem.* **21**, 583 (1996); (b) H. H. Stephens and M. L. H. Green. *Adv. Inorg. Chem.* **44**, 1 (1997); (c) L. Balch and M. M. Olmstead. *Chem. Rev.* **98**, 2123 (1998).
3. (a) D. K. Patel, D. M. Thompson, M. C. Baird, L. K. Thompson, K. F. Preston. *J. Organomet. Chem.* **546**, 607 (1997); (b) M. Bengough, D. M. Thompson, M. C. Baird. *Organometallics* **18**, 2950 (1999).