Anionic Fullerene-60 Complexes of Manganese(−I), Cobalt(−I), and Rhenium(−I): Thermal and Photoinduced Electron Transfer Processes between Metal Carbonylate Anions and C_{60}

David M. Thompson, M. Bengough, and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Received May 16, 2002

Thermal and photochemical reactions of THF solutions of the carbonylate salts A[Mn(CO)$_5$], A[Co(CO)$_4$], and A[Re(CO)$_5$] (A = Na, PPN) with suspensions of C_{60} result in electron transfer to give $[C_{60}]^-$ and the transient 17-electron, metal-centered radicals Mn(CO)$_5$, Co(CO)$_4$, and Re(CO)$_5$, respectively. However, the ensuing secondary processes vary significantly, depending on the metal and the reaction conditions. With manganese and rhenium, self-coupling of M(CO)$_5$ (M = Mn, Re) to give the metal−metal bonded dimers M$_2$(CO)$_{10}$ and coupling of M(CO)$_5$ with $[C_{60}]^-$ to give the η^2-C_{60} complexes A[Mn(CO)$_4$(η^2-C_{60})] both occur under thermal and photochemical conditions. In contrast, the photochemical processes ultimately result also in complete homolysis of the dimers and regeneration of the metal-centered radicals, which then combine with fulleride ion $[C_{60}]^-$ still remaining in solution to form more of the η^2-C_{60} complexes. In the case of cobalt, no Co$_2$(CO)$_8$ is formed, but the η^2-C_{60} complex [Co(CO)$_3$(η^2-C_{60})]$^-$ is produced. While the latter is thermally unstable in refluxing THF, undergoing decarbonylation to the previously reported mixed metal fulleride compound NaCoC$_{60}$·3THF, it is thermally stable under photochemical conditions at room temperature. Spectroscopic evidence suggests that much of the negative charge in [Mn(CO)$_4$(η^2-C_{60})]$^-$ is delocalized onto the fullerene ligand; as a result, the η^2-C_{60}−Mn bond is unusually strong and the complex [Mn(CO)$_4$(η^2-C_{60})]$^-$ is very stable, exhibiting little of the chemistry associated with either neutral η^2-C_{60} complexes or the analogous [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] exohedral 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 a weakly conjugated, electron-deficient alkene ligand.[3] While a few incompletely characterized transition metal fulleride compounds are known,[2c−n] none have as of yet 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 capable of reducing C_{60} to radical anions $[C_{60}]^{n-}$ and have demonstrated that the reaction of Na[Co(CO)$_4$] with C_{60} in refluxing THF results in the formation of an insoluble, bimetallic fulleride compound NaCoC$_{60}$·3THF.[4] Although the latter could not be characterized structurally, it exhibits 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 organome-

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10.1021/om020396i CCC: $22.00
Publication on Web 09/24/2002

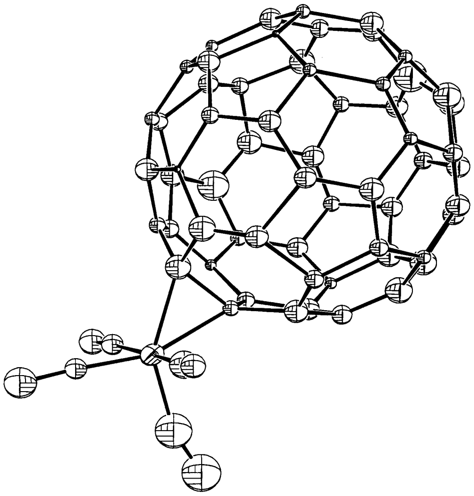

Figure 1. Molecular structure of the anion of PPN[Mn(CO)$_4$(η^2-C_{60})].

tallics have also appeared,[5] and we are investigating the reactions of a variety of metal carbonylate complexes with C_{60}. We have in a communication[6a] and a conference proceeding[6b] reported that the carbonylate anion [Mn(CO)$_5$]$^-$ does indeed reduce C_{60} and have reported the crystal structure of PPN[Mn(CO)$_4$(η^2-C_{60})], a product of this reaction and the first well-characterized fullerene complex of a metal in a negative oxidation state. The structure of the complex anion is shown in Figure 1, where it is seen that the C_{60} coordinates in conventional η^2-fashion. We now report fully on the η^2-C_{60} complexes formed during reactions of C_{60} with the carbonylate complexes A[Mn(CO)$_5$], A[Co(CO)$_4$], and A[Re(CO)$_5$] (A = Na, PPN).

Experimental Section

All reactions were carried out using standard Schlenk line techniques or in Vacuum Atmospheres or Mbraun gloveboxes. Argon and nitrogen were purified by passing through a column of BASF catalyst heated to 140 °C and subsequently through a second column containing 5 Å molecular sieves. Solvents were purified by distillation from a drying agent under a blanket of nitrogen or argon. In most cases Na wire was used as the drying agent, the exceptions being dichloromethane and acetonitrile, for which CaH_2 and P_2O_5 were used, respectively.

Infrared (IR) spectra were recorded on a Bruker IFS 25 FTIR spectrometer, and negative ion mode electrospray mass spectrometry (henceforth ESMS)[7] experiments on a VG Quattro with nitrogen as the nebulizing gas. Typical concentrations of the species being studied were 1−5 mM, and the capillary voltage, cone voltage, lens parameters, ionization energy and ramp, position of the source, flow rate of the sample, and time of acquisition were all varied in order to optimize the intensity of the peak being studied. Low cone voltages $<$ 30 V were normally used to observe parent ions in solution, and higher cone voltages (up to 150 V) to observe fragmentation products. High-resolution ESMS experiments were carried out on a Micromass Q-TOF-2 quadrupole time-of-flight mass spectrometer. Mass-to-charge ratios reported below refer in all cases to the strongest peak in what are always complex distributions of isotopomers. ^{13}C NMR were recorded on a Bruker AM-500 spectrometer and are referenced on the basis of comparisons with the solvent resonances. Near-IR spectra (800−1300 nm) were run on a Cary 17 UV−vis spectrophotometer; UV−vis spectra (190 nm-820 nm), on a HP 8452A diode array spectrophotometer.

Chemicals were generally obtained from Aldrich, Fisher, or Strem, while C_{60} was obtained from MER Corp. The compounds Na[Co(CO)$_4$],[8a] Na[Mn(CO)$_5$],[8b] PPN[Mn(CO)$_5$],[8c] and PPN[Co(CO)$_4$][8d] were prepared as in the literature. We were unable to prepare pure Na[Re(CO)$_5$] using the methods described in the literature, which involves stirring a solution of $Re_2(CO)_{10}$ in diethyl ether or THF over sodium amalgam.[8e,f] Complex (by IR) orange mixtures were invariably obtained, and it seemed likely that Na[Re(CO)$_5$] was reacting with $Re_2(CO)_{10}$ to form polynuclear anionic clusters.[8e] We therefore developed a method that maintained a low concentration of $Re_2(CO)_{10}$ in the presence of Na[Re(CO)$_5$]. A solution of 2.0 g of $Re_2(CO)_{10}$ (3.1 mmol) in 70 mL of THF was added dropwise over 45 min to a flask containing 80 g of 1% sodium amalgam. The dominant carbonyl absorptions in the IR spectrum of the resulting yellow solution were those characteristic of Na[Re(CO)]$_5$ (1830, 1864, 1907 cm^{-1}).[8e,f] The solution was filtered through Celite and treated with 50 mL of pentanes to give a yellow precipitate of the product. The solid was filtered, washed with pentanes (3 × 25 mL), and dried under reduced pressure.

The compound NaC_{60} was prepared following a variation on the literature procedure.[9] C_{60} (260 mg, 0.36 mmol), Na metal (7 mg, 0.33 mmol), and naphthalene (50 mg, 0.39 mmol) were stirred together in 50 mL of THF under argon. The solution quickly developed a deep burgundy color, and ESMS monitoring revealed the expected peak at 720 Da/e. In addition, a near-IR spectrum exhibited the characteristic absorption at 1076 nm.[2a,b] The solution was filtered and the solvent was removed from the filtrate under reduced pressure to give the black product, which was washed with toluene and dried.

Thermal Reactions of A[Mn(CO)$_5$], A[Co(CO)$_4$], and A[Re(CO)$_5$] (A = Na, PPN) with C_{60}. In a typical reaction, 100 mg of C_{60} (0.14 mmol) was added to a solution containing 0.14 mmol of A[Co(CO)$_4$], A[Mn(CO)$_5$], or A[Re(CO)$_5$] in 100 mL of THF under argon. The solution was refluxed, IR spectra being recorded immediately and thereafter every half hour or more. Workup procedures generally involved cooling the reaction mixture followed by filtration. Addition of hexanes to the filtrate resulted in precipitation of the product, which was washed with toluene and hexanes and then dried under reduced pressure.

Photochemical Reactions of A[Mn(CO)$_5$], A[Co(CO)$_4$], and A[Re(CO)$_5$] (A = Na, PPN) with C_{60}. In a typical

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reaction, 100 mg of C_{60} (0.14 mmol) was added to a solution containing 0.14 mmol of A[Mn(CO)$_5$], A[Co(CO)$_4$], or A[Re(CO)$_5$] in 100 mL of THF under argon. A Hanovia lamp, placed inside a water-cooled quartz tube, was situated 10−12 cm away from the reaction vessel, and the stirred reaction mixture was photolyzed for several hours while being monitored as above by IR spectroscopy and ESMS. Workup procedures were generally as above.

Photochemical Reactions of $Mn_2(CO)_8$ and $Co_2(CO)_8$ with NaC_{60}. A solution of 100 mg of NaC_{60} (0.13 mmol) and 0.065 mmol of $Mn_2(CO)_{10}$ or $Co_2(CO)_8$ in 100 mL of THF was photolyzed as above for several hours while being monitored by IR spectroscopy and ESMS. Workup procedures were as described above. Yields of Na[Mn(CO)$_4$(C_{60})] and Na[Co(CO)$_3$(C_{60})] were 36 mg (29%) and 45 mg (37%), respectively; the products were characterized by IR spectroscopy and ESMS.

Reactions of A[Mn(CO)$_4$(C_{60})] and A[Co(CO)$_3$(C_{60})] (A = Na, PPN) with Tertiary Phosphines. Solutions of 25−50 mg of A[Mn(CO)$_4$(C_{60})] or A[Co(CO)$_3$(C_{60})] (A = Na, PPN) in 100 mL of THF were treated with a slight excess of PMe_2Ph or PPh_3 and then stirred for 3 h at 20 °C. IR monitoring showed that in neither case had reaction occurred, and the reaction mixtures were refluxed for 3 h and then photolyzed as above for 12 h. Throughout this process, IR spectroscopy showed slow loss of starting materials but no evidence for new carbonyl compounds of any kind. In a separate experiment PPN[Mn(CO)$_4$(η^2-C_{60})] was also found to be inert to PMe_2Ph in refluxing THF in the presence of anhydrous trimethylamine oxide.

Reaction of PPN[Mn(CO)$_4$(C_{60})] with MeI. A solution of 50 mg of PPN[Mn(CO)$_4$(η^2-C_{60})] and 1 mL of CH_3I in 100 mL of THF was refluxed, the progress of the reaction being monitored by IR spectroscopy and ESMS. After several hours, the initial ν_{CO} of the starting material were replaced by new ν_{CO} at 1929, 1972, 1995, and 2068 cm^{-1} and the ESMS revealed a strong peak at 421 Da/e with an isotope distribution consistent with [Mn(CO)$_4$I$_2$]$^-$. The pale amber colored solution was filtered, and a black precipitate was separated from the supernatant. The solvent was removed from the supernatant to give a mixture containing PPN[Mn(CO)$_4$I$_2$], which was identified by ESMS and IR spectroscopy (ν_{CO} = 1929, 1972, 1995, and 2068 cm^{-1}) (see below). The black precipitate was insoluble in THF, toluene, benzene, and acetone and was not investigated further.

Results and Discussion

Syntheses and Properties of A[Mn(CO)$_4$(η^2-C_{60})] (A = Na, PPN). The thermal reaction of equimolar amounts of C_{60} and Na[Mn(CO)$_5$] in refluxing THF was monitored by IR spectroscopy for 18 h. The solution turned deep green, and ν_{CO} of [Mn(CO)$_5$]$^-$ (1895, 1861, 1828 cm^{-1}) decreased in intensity while those of $Mn_2(CO)_{10}$ (2044, 2010, 1979 cm^{-1}) and of the complex anion [Mn(CO)$_4$(η^2-C_{60})]$^-$ (2023, 1938, 1900, cm^{-1})[6a] appeared and steadily increased in intensity. ESMS revealed that the peak of [Mn(CO)$_5$]$^-$ (195 Da/e) disappeared and that the peak of [C_{60}]$^-$ (720 Da/e) appeared, grew, and then decreased in intensity; a peak at 887 Da/e, attributable to [Mn(CO)$_4$(η^2-C_{60})]$^-$, grew in over the course of the reaction and was the only anionic product present at the end of the reaction (Figure 2a). Identification of the new species as [Mn(CO)$_4$(η^2-C_{60})]$^-$ was strengthened by comparison of its isotope distribution (Figure 2b) with the calculated isotope pattern (Figure 2c). On workup, black Na[Mn(CO)$_4$(η^2-C_{60})] was obtained in 26% yield; while seemingly rather stable thermally and, surprisingly, somewhat stable even in air, the compound could not be obtained analytically pure nor could crystallographically useful crystals be obtained.

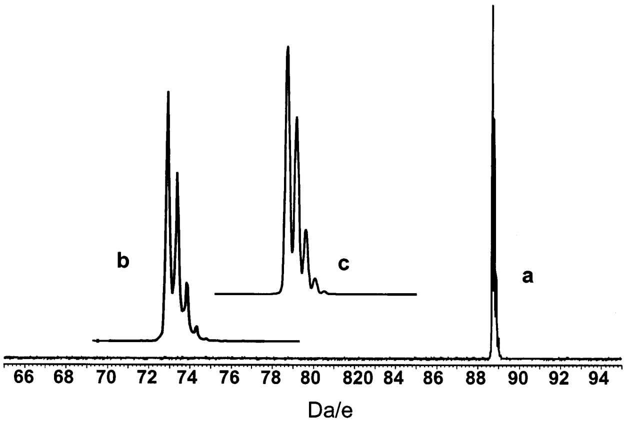

Figure 2. Mass spectrum of PPN[Mn(CO)$_4$(η^2-C_{60})]: (a) full spectrum; (b) experimental isotope distribution; (c) calculated isotope distribution.

In an effort to obtain better crystals, the reaction of PPN[Mn(CO)$_5$] with C_{60} was investigated. The reaction was monitored by IR spectroscopy and ESMS as described above, and PPN[Mn(CO)$_4$(η^2-C_{60})] was obtained in 23% yield. This compound was better obtained by photolysis of equimolar amounts of C_{60} and PPN[Mn(CO)$_5$] in THF at room temperature. Monitoring by IR spectroscopy and ESMS showed that the [Mn(CO)$_5$]$^-$ disappeared completely within 3 h, forming $Mn_2(CO)_{10}$ and PPN[Mn(CO)$_4$(η^2-C_{60})], while continued photolysis (up to 48 h) resulted in a slower loss of the ν_{CO} of $Mn_2(CO)_{10}$ and an increase in the intensity of ν_{CO} of PPN[Mn(CO)$_4$(η^2-C_{60})]. The latter was eventually obtained in 93% yield. As expected, photolysis of Na[Mn(CO)$_5$] with C_{60} proceeded in a similar fashion to form Na[Mn(CO)$_4$(η^2-C_{60})].

It was unfortunately found to be impossible to obtain analytically pure material; carbon analyses of several samples were variable, as is often the case with fullerene complexes.[3b] However, the identity of the [Mn(CO)$_4$(η^2-C_{60})]$^-$ anion was verified unambiguously by a high-resolution ESMS study of a THF solution of isolated PPN[Mn(CO)$_4$(η^2-C_{60})]. The molecular ion was observed at 886.9160 Da/e, differing by only 1.7 mDa (1.9 ppm) from the theoretical mass of 886.9177 Da/e. In addition, as noted previously,[6a] sufficiently good crystals were obtained that a crystal structure could be obtained by layering a THF solution with hexanes (see below).

A ^{13}C NMR spectrum of PPN[Mn(CO)$_4$(η^2-C_{60})] was recorded in THF-d_8, and the chemical shifts of all peaks are listed in Table 1. Resonances at δ 134.7, 133.6, 130.5, and 128.4 are attributed to the phenyl ring carbons of the PPN$^+$ cation on the basis of comparison with the ^{13}C NMR spectrum of the chloride salt. To aid in assignments, the relative intensities of the fullerene resonances are presented arbitrarily as ratios of the intensity of the peak at δ146.27. The reduction of symmetry from the I_h of C_{60} results in many of the fullerene carbon atoms becoming nonequivalent, and hence, a complex ^{13}C NMR spectrum is observed. While complete assignments of the resonances are not possible, the number and relative intensities of those between δ 135 and 176 can be used to determine the symmetry of the anion.[3b] There are 17 peaks in the spectrum, and the ^{13}C NMR spectrum of a fullerene complex with C_{2v} symmetry is expected to exhibit 17 ^{13}C resonances.[3b]

Table 1. ^{13}C NMR Data for PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$]

chemical shift of peak (ppm)	relative intensity	assignment
128.40 (doublet)		PPN^+
130.52 (multiplet)		PPN^+
133.40 (multiplet)		PPN^+
134.74		PPN^+
85.81		$sp^3\text{-}C_{60}$
136.32	1.82	$sp^2\text{-}C_{60}$
142.26	1.96	$sp^2\text{-}C_{60}$
142.75	2.07	$sp^2\text{-}C_{60}$
143.33	1.78	$sp^2\text{-}C_{60}$
143.43	2.16	$sp^2\text{-}C_{60}$
144.39	1.69	$sp^2\text{-}C_{60}$
145.97	1.91	$sp^2\text{-}C_{60}$
146.20	1.85	$sp^2\text{-}C_{60}$
146.27	1.00[a]	$sp^2\text{-}C_{60}$
146.48	2.21	$sp^2\text{-}C_{60}$
146.64	1.90	$sp^2\text{-}C_{60}$
146.83	0.95	$sp^2\text{-}C_{60}$
147.36	1.54	$sp^2\text{-}C_{60}$
148.33	0.69	$sp^2\text{-}C_{60}$
151.22	1.98	$sp^2\text{-}C_{60}$
174.39	1.86	$sp^2\text{-}C_{60}$

[a] Arbitrarily assigned.

Table 2. ^{55}Mn NMR of Organomanganese Complexes

compound	chemical shift	reference
$KMnO_4$	0	10
PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$]	−1844	this work
$Mn(CF_3CO)(CO)_5$	−1850	10
$Mn(CH_3CO)(CO)_5$	−1895	10
$Mn_2(CO)_{10}$	−2325	10
$MnH(CO)_5$	−2578	10
Na[$Mn(CO)_5$]	−2780	10

The ^{55}Mn NMR spectrum of a THF solution of PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] exhibited a single resonance at δ −1843.8 (relative to $KMnO_4$), and a comparison of this chemical shift with those of other manganese complexes[10] is made in Table 2. It is interesting to note that the ^{55}Mn chemical shift of PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] is much more similar to those of complexes of Mn(I) than of Mn(−I), although it is clear from the data that conclusions regarding oxidation state cannot be made on the basis of such data.

The UV−vis spectrum of PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] in CH_2Cl_2 exhibited absorption bands at 221, 260, 332, and 450 nm, the latter being relatively broad. The spectrum is thus very similar to that of C_{60} in hexanes, which exhibits absorptions at 215, 270, and 335 nm with a broad band between 440 and 640 nm.[11] A near-IR spectrum run on this solution revealed no absorptions between 900 and 1400 nm, where fulleride anions absorb strongly.[2a,b]

Molecular Structure of and Bonding in [$Mn(CO)_4(\eta^2\text{-}C_{60})$]$^-$. As we have shown previously,[6a] the structure of PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] contains a C_{60} ligand coordinated to the metal via a [6−6] ring junction at an equatorial position in a trigonal bipyramidal complex (Figure 1). The same type of structure is generally observed in complexes of the type $Fe(CO)_4(\eta^2\text{-alkene})$[12] and is postulated as well for the isoelectronic, neutral fullerene complexes $M(CO)_4(\eta^2\text{-}C_{60})$ (M = Fe, Ru).[13] The question arises as to whether the [$Mn(CO)_4(\eta^2\text{-}C_{60})$]$^-$ anion is better regarded as a complex of manganese(0) with a coordinated [C_{60}]$^-$ or as a complex of manganese(−I) with a coordinated C_{60}. The latter mode of bonding seems to be implied by the near-IR and UV−vis data, and we feel this to be an appropriate description of the bonding in this complex anion. However, the X-ray structural data shed no light and the IR data are surprisingly ambiguous.

Table 3. Carbonyl Stretching Frequencies of Manganese Carbonyl Complexes

complex	ν(CO) cm^{-1} (average)
PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$]	2025, ~2015 (sh), 1938, 1900 (1970)
PPN[$Mn(CO)_5$]	1894, 1861 (1878)
$Mn_2(CO)_{10}$	2044, 2009, 1979 (2011)
$\eta^5\text{-}C_5H_5Mn(CO)_3$	2025, 1938 (1982)
$\eta^3\text{-}C_3H_5Mn(CO)_4$	2068, 1989, 1974, 1958 (1997)

Indeed, before the ESMS spectrum was obtained and well before the crystal structure was available, the IR evidence seemed to suggest that the new compound was a neutral species related to $\eta^5\text{-}C_5H_5Mn(CO)_3$ or $\eta^3\text{-}C_3H_5\text{-}Mn(CO)_4$ rather than to [$Mn(CO)_5$]$^-$. In Table 3 is a comparison of ν_{CO} of PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] with those of several carbonyl complexes of manganese in the formal oxidation states 0, I, and −I. As can be seen, ν_{CO} of PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] are more similar to those of complexes containing Mn(0) or Mn(I) than those of the Mn(−I) complex PPN[$Mn(CO)_5$]. The implied possibility of η^3- or η^5-modes of coordination of the C_{60} to the manganese was initially quite exciting, as these modes of coordination are unknown for fullerenes.[3] However, the crystal structure of PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] ultimately showed unambiguously that there is nothing unprecedented structurally in the complex anion.

Considering, therefore, the C_{60}−Mn bonding on the basis of conventional η^2-coordination of a neutral C_{60} to a [$Mn(CO)_4$]$^-$ moiety, it is clear that there must be significant π back-donation from the formally Mn(−I) to the C_{60}. The latter is widely regarded as a weakly conjugated, electron-deficient alkene,[3] and it seems from comparisons of the IR data that its π acceptor properties in [$Mn(CO)_4(\eta^2\text{-}C_{60})$]$^-$ actually exceed those of an equatorial CO in [$Mn(CO)_5$]$^-$.[14a]

Returning to the ESMS study of a THF solution of isolated PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$], in addition to the molecular ion observed at low cone voltages, we also found that increasing the cone voltage to ~30 V resulted in the appearance of a new peak at 835 Da/e and with an isotope distribution consistent with [$Mn(CO)_3(\eta^2\text{-}C_{60})$]$^-$.

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[10] Pregosin, P. S. In *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991; p 90.

[11] Leach, S.; Vervloet, M.; Despres, A.; Brehert, E.; Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Chem. Phys.* **1992**, *160*, 451.

[12] Deeming, A. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Chapter 31.3, and references therein.

[13] (a) Douthwaite, R. E.; Green, M. L. H.; Stephens, A. H. H.; Turner, J. F. C. *J. Chem. Soc., Chem. Commun.* **1993**, 1522. (b) Raasinkangas, M.; Pakkanen, T. T.; Pakkanen, T. A. *J. Organomet. Chem.* **1994**, *476*, C6.

[14] (a) Support for this conclusion may also be gleaned indirectly from a comparison of the IR spectra of THF solutions of Na[$Mn(CO)_5$], PPN[$Mn(CO)_5$], Na[$Mn(CO)_4(\eta^2\text{-}C_{60})$], and PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$]. While the IR spectrum of PPN[$Mn(CO)_5$] exhibits the anticipated two ν_{CO}, that of Na[$Mn(CO)_5$] also exhibits a third broad peak at ~1830 cm^{-1}, a result of lowering of the symmetry because of Na−OC ion pairing in solution between a carbonyl ligand and the sodium ion.[14b] In contrast, the IR spectra of Na[$Mn(CO)_4(\eta^2\text{-}C_{60})$] and PPN[$Mn(CO)_4(\eta^2\text{-}C_{60})$] are essentially identical, implying an absence of strong Na−OC ion pairing in Na[$Mn(CO)_4(\eta^2\text{-}C_{60})$]. A reasonable conclusion is that the negative charge is sufficiently delocalized onto the fullerene that Na−OC ion pairing is negligible. (b) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

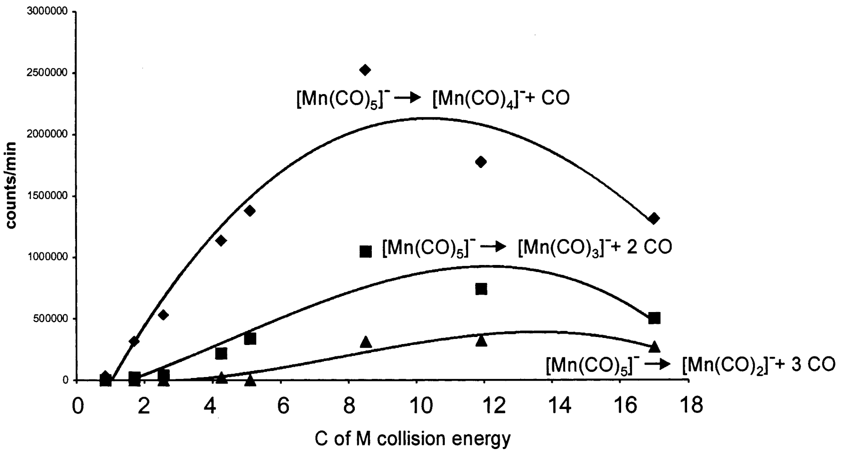

Figure 3. Intensity of $[Mn(CO)_5]^-$ daughter ions as a function of center of mass collision energy with Ar as determined by CID.

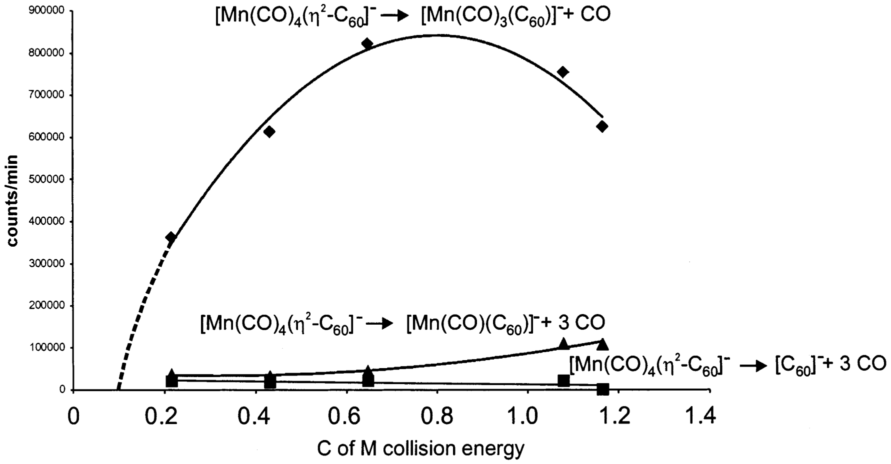

Figure 4. Intensity of $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ daughter ions as a function of center of mass collision energy with Ar as determined by CID.

Further increasing the cone voltage to ~60 V also resulted in the appearance of peaks at 803 and 720 Da/e with isotope patterns consistent with $[Mn(CO)(C_{60})]^-$ and $[C_{60}]^-$, respectively. Successive decarbonylation of metal carbonylate complexs with increasing cone voltage is an established phenomenon,[7c] and the loss of one or more CO ligands from $[Mn(CO)_4(C_{60})]^-$ is to be anticipated.

In view of the conclusions, discussed above, that there is less π back-donation to the carbonyl ligands in $[Mn(CO)_4(C_{60})]^-$ than in $[Mn(CO)_5]^-$, it follows that the metal–carbonyl bonds should be weaker in $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ than in $[Mn(CO)_5]^-$. To gain further insight into the matter, ESMS collision-induced dissociation (CID)[15] experiments were performed on these two complex ions. In these experiments a specific ion is selected using the first quadropole of the mass spectrometer and is passed through with a specific energy into a collision cell containing argon gas; the daughter ions from the collision are then analyzed in a second quadrupole. By plotting the intensity of peaks attributable to specific daughter ions versus the center of mass (C of M) collision energy and extrapolating the data back toward zero intensity, a threshold energy for the dissociation process can be determined.

Figures 3 and 4 show plots of the intensities of the daughter ions versus the center of mass collision energy for $[Mn(CO)_5]^-$ and $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$, respectively. The extrapolated threshold energies for the first carbonyl ligand dissociation were found to be ~0.1 eV for $[Mn(CO)_4(C_{60})]^-$ and ~1 eV for $[Mn(CO)_5]^-$, and thus the energy required to dissociate a carbonyl ligand from $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ in the gas phase is significantly less than that required to accomplish the same dissociation from $[Mn(CO)_5]^-$. Thus the mass spectrometry data concur qualitatively with the IR data, which suggest that there are weaker Mn–CO bonds in the fullerene complex.

Synthesis and Properties of A[Co(CO)$_4$] (A = Na, PPN). In an attempt to learn more about the mode of formation of the previously reported $NaCoC_{60}{\cdot}3THF$,[4] a mixture of equimolar amounts of $Na[Co(CO)_4]$ and C_{60} was refluxed in THF while the progress of the reaction was monitored using IR spectroscopy. As with the manganese system, the ν_{CO} of $Na[Co(CO)_4]$ slowly disappeared as new, weak ν_{CO} at 1920, 1966, and 1992 cm^{-1} appeared. Monitoring of the reaction by ESMS revealed that changes in the intensity of the ν_{CO} of the $[Co(CO)_4]^-$ anion correlated well with a decrease in the intensity of the peak of the $[Co(CO)_4]^-$ anion at 171 Da/e

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[15] (a) McLuckey, S. A. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 599. (b) Anderson, S. G.; Blades, A. T.; Klassen, J.; Kebarle, P. *Int. J. Mass Spectrom. Ion Processes* **1995**, *141*, 217. (c) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788. (d) Sunderlin, L. S.; Wang, D.; Squires, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 12060.

and the appearance of peaks at 720 and 863 Da/e, attributable respectively to $[C_{60}]^-$ and the new anionic complex $[Co(CO)_3(C_{60})]^-$. Although the intensity of the peak at 863 Da/e was generally relatively weak, we were able by focusing on that region and adjusting the cone voltage to maximize the peak intensity to observe an isotope distribution consistent with $[Co(CO)_3(C_{60})]^-$. Interestingly, at the cone voltage that optimized the intensity of this peak (43 V), we also observed a peak at 835 Da/e with an isotope distribution consistent with the formulation $[Co(CO)_2(C_{60})]^-$, and thus partial decarbonylation had occurred. After 4 h, all carbonyl intensity had disappeared and the previously reported $NaCoC_{60}\cdot 3THF$[4] was obtained.

The thermal reaction of $PPN[Co(CO)_4]$ with C_{60} proceeded similarly, a green solution of $PPN[Co(CO)_3(C_{60})]$ being obtained within 3 h, although further refluxing resulted again in complete loss of carbonyl intensity over 10 h. Workup as before resulted in a small amount of crude $PPN[Co(CO)_3(C_{60})]$, which could not be obtained analytically pure. However, a high-resolution ESMS study of a THF solution revealed a peak at 862.9245 Da/e, differing by only 7.6 ppm from the calculated value of 862.9179 Da/e and thus confirming the identity of the species.

Given the superiority of the photochemical over the thermal procedure with the manganese system, a brief study was also made of the photochemical reactions of equimolar amounts of $A[Co(CO)_4]$ (A = Na, PPN) with C_{60} in THF. IR and ESMS monitoring of the reaction of $PPN[Co(CO)_4]$ showed that ν_{CO} of $[Co(CO)_4]^{-1}$ steadily lost intensity, while those of $[Co(CO)_3(C_{60})]^-$ grew in and gained substantially in intensity over 48 h. ESMS monitoring of the reaction revealed the presence of the anticipated peak at 863 Da/e when the peaks at 1992 and 1920 cm^{-1} were present in the IR spectrum. Similarly photolysis of solutions of $Na[Co(CO)_4]$ in THF with C_{60} resulted in a loss of intensity from the carbonyl peaks attributable to $Na[Co(CO)_4]$ and the appearance of peaks attributable to $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$. Interestingly, the photochemical reaction of $Co_2(CO)_8$ with $Na[C_{60}]$ was also found to result in the formation of $[Co(CO)_3(C_{60})]^-$, identified via ESMS and IR spectroscopic monitoring.

In view of the close similarities between the manganese and cobalt systems, we believe that the fullerene in the latter is also coordinated in η^2-fashion. In contrast to manganese, analogous alkene complexes of cobalt have been reported previously and the IR spectrum of $Na[Co(CO)_3(\eta^2\text{-}C_{60})]$ in THF (ν_{CO} at 1920, 1966, and 1992 cm^{-1}) is comparable to those of the complexes $Na[Co(CO)_3(\eta^2\text{-alkene})]$ (alkene = maleic anhydride, dimethylmaleate, fumaronitrile), which exhibit ν_{CO} in the regions 1896−1904, 1910−1971, and 1992−2011 cm^{-1} in THF.[16] These results seem to confirm the nature of C_{60} as an electron-deficient alkene.[3]

The IR data also imply that the presence of C_{60} in both $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ and $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$ has a similar effect on the electron density on the metal. In Table 4 we compare ν_{CO} data for the two metals. As can be seen, not only are the average ν_{CO} of the two fullerene complexes very similar, but the changes in average frequency on going from the starting carbonylate anions to the fullerene products are almost identical, 70 and 76 cm^{-1}. Thus in both cases substitution apparently has a similar effect on the degree of π back-donation from the metal to the carbonyl ligand, and it seems reasonable to assume that C_{60} is coordinated to the two metals in the same way.

Table 4. Carbonyl Stretching Frequencies of PPN^+ Salts

species	ν_{CO} (cm^{-1})	ν_{CO} (average, cm^{-1})
$[Co(CO)_4]^-$	1886	1886
$[Co(CO)_3(\eta^2\text{-}C_{60})]^-$	1920, 1992	1956
$[Mn(CO)_5]^-$	1861, 1894	1878
$[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$	1900, 1938, 2023	1954

Synthesis and Properties of $Na[Re(CO)_4(\eta^2\text{-}C_{60})]$. A study of the rhenium system was initiated to complement our findings with manganese. A reaction of $Na[Re(CO)_5]$ with C_{60} in refluxing THF was monitored by IR spectroscopy and ESMS, and over several hours, ν_{CO} of the $Na[Re(CO)_5]$ were replaced by those of $Re_2(CO)_{10}$ in addition to several others. ESMS measurements revealed peaks at 720 and 838 Da/e, the former attributable to $[C_{60}]^-$, the latter apparently to the trinuclear species $[Re_3(CO)_{10}]^-$. Photolysis of a THF solution of $Na[Re(CO)_5]$ with C_{60} was also carried out, and again the ν_{CO} of $Na[Re(CO)_5]$ were replaced by a number of new peaks between 1850 and 2050 cm^{-1}, including those of $Re_2(CO)_{10}$, which appeared almost immediately. Interestingly, the ν_{CO} of both $Re_2(CO)_{10}$ and $[Re(CO)_5]^-$ disappeared within 48 h, while ESMS experiments revealed many peaks, including a strong peak at 1019 Da/e and exhibiting an isotope distribution consistent with $[Re(CO)_4(C_{60})]^-$. Other peaks in the spectrum at 895 and 867 are probably attributable to cluster anions such as $[Re_3(CO)_{12}]^-$ and $[Re_3(CO)_{11}]^-$, respectively. Increasing the cone voltage resulted in significant loss of intensity of these peaks and appearance of new peaks at 783 and 755 Da/e, tentatively attributed to $[Re_3(CO)_8]^-$ and $[Re_3(CO)_7]^-$, respectively. The species $[Re_3(CO)_{11}]^-$, $[Re_3(CO)_8]^-$, and $[Re_3(CO)_7]^-$ all appear to result from fragmentation of $[Re_3(CO)_{12}]^-$, a complex that does not appear to have been reported previously.[17] We suspect that all arise from secondary processes, possibly within the mass spectrometer, rather than directly from the initial electron-transfer process.

While we were not able to isolate $Na[Re(CO)_4(\eta^2\text{-}C_{60})]$, we were able to recover a solid that exhibited solubility in THF (green solution) and exhibited the same IR spectrum as that observed after 48 h of photolysis. A high-resolution ESMS study of this material revealed a peak at 1018.9423 Da/e, differing by 6.3 ppm from the theoretical mass of $[Re(CO)_4(\eta^2\text{-}C_{60})]^-$ (1018.93545 Da/e) and thus confirming the identity of this species. Interestingly, muliplets centered at ~658 and ~644 Da/e were also observed. The separations between these multiplets of only 14 Da/e in addition to separations within each multiplet of 0.5 Da/e suggest that these species are both doubly charged and differ only by one CO ligand. The mass-to-charge ratios of 658 and 644

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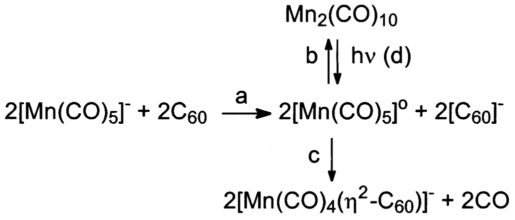
[16] Ungváry, F.; Gallucci, J.; Wojcicki, A. *Organometallics* **1991**, *10*, 3053.

[17] For summaries of rhenium carbonyl cluster anions, see: (a) Holloway, C. E.; Melnik, M. *Organomet. Chem. Rev.* **1988**, *20*, 249. (b) Henly, T. J. *Coord. Chem. Rev.* **1989**, *93*, 269. (c) Hillary, K. M.; Hughes, A. K.; Peat, K. L.; Wade, K. *Polyhedron* **1998**, *17*, 2803. (d) Hughes, A. K.; Wade, K. *Coord. Chem. Rev.* **2000**, *197*, 191.

Scheme 1. Proposed Mechanism for the Thermal and Photochemical Reactions of A[Mn(CO)$_5$] with C$_{60}$ (A = Na, PPN)



Da/e are those anticipated for $[Re_2(CO)_8(C_{60})]^{2-}$ and $[Re_2(CO)_7(C_{60})]^{2-}$, respectively, but the poor signal-to-noise ratios made assignment of these peaks tenuous.

While it is not possible to make an unambiguous identification of the ν_{CO} of $[Re(CO)_4(\eta^2\text{-}C_{60})]^-$, one would expect them to have frequencies and relative intensities similar to those of $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$. Assuming a slight shifting of IR-active carbonyl absorptions to lower frequencies on moving from first to third row metals,[18] we tentatively assign ν_{CO} at 2005, 1931, and 1891 cm^{-1} to $[Re(CO)_4(\eta^2\text{-}C_{60})]^-$, although there is, in fact, considerable overlap with absorptions of the polynuclear complexes. The assigned bands are quite different from those of the thermally unstable, neutral compound $C_{60}\text{-}\{Re(CO)_5\}_2$ (ν_{CO} 2134, 2130, 2036, 1993 cm^{-1}), prepared by reacting C$_{60}$ at low temperatures with the 17-electron, metal-centered radical Re(CO)$_5$, which was prepared via photolysis of $Re_2(CO)_{10}$.[19]

Mechanisms of the Reactions of A[Mn(CO)$_5$)], A[Co(CO)$_4$] (A = Na, PPN), and Na[Re(CO)$_5$)] with C$_{60}$. Mechanisms of Formation of η^2-C$_{60}$ Complexes. The high electron affinity of C$_{60}$ (2.65 eV[2a]) coupled with the strongly reducing nature of carbonylate anions[20] makes it likely that electron transfer from, for example, $[Mn(CO)_5]^-$ to C$_{60}$ takes place in the thermal reactions to generate the radical anion $[C_{60}]^-$ and the neutral 17-electron, metal-centered radical Mn(CO)$_5$ (step a of Scheme 1). The presence of the Mn(CO)$_5$ radical in solution would be expected to result in the formation of $Mn_2(CO)_{10}$ (step b of Scheme 1) since Mn(CO)$_5$ is known to dimerize at near diffusion-controlled rates.[21] In agreement with this, we do indeed observe $Mn_2(CO)_{10}$ as a major reaction product.

The formation of comparable amounts of $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ could conceivably involve direct substitution of a carbonyl ligand on $[Mn(CO)_5]^-$ by C$_{60}$, or even direct nucleophilic attack by the anion on the fullerene, as occurs with carbanions,[22] followed by loss of a CO. However, the reaction more likely involves substitution by $[C_{60}]^-$ of a carbonyl ligand on the Mn(CO)$_5$ radical (step c of Scheme 1), which is known to be very substitution labile.[23] This substitution reaction would probably also be facilitated by electron pairing as the two radicals combine. In this scenario, radical pairing of Mn(CO)$_5$ and $[C_{60}]^-$ is competitive with Mn(CO)$_5$ dimerization and results in the formation of $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$, as shown in Scheme 1.

Evidence for this mechanism is also inferred from the results of the photochemical syntheses of A[Mn(CO)$_4$(η^2-C$_{60}$)] (A = Na, PPN). It is known that $Mn_2(CO)_{10}$ is photosensitive, undergoing reversible homolysis to Mn(CO)$_5$ radicals on irradiation.[24] Thus the $Mn_2(CO)_{10}$ formed during the photochemical process should be converted to monomer (step d of Scheme 1), which can then react with the $[C_{60}]^-$ already in solution to produce a higher yield of the $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$. As indicated above, the $Mn_2(CO)_{10}$ formed within the first 3 h does indeed react further to give $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$, and isolated yields soared from ~25% in the thermal process to almost quantitative.

We note also that photoinduced charge transfer from the transition metal carbonylate anion to C$_{60}$ is a possible first step in the photochemical synthesis. Carbonylate anions have long been known to participate in photoinduced electron-transfer reactions,[25] and outer-sphere interactions between the mild oxidant C$_{60}$ and a wide variety of reducing agents have also been demonstrated to generate new optical transitions involving charge transfer from the electron donor to the fullerene.[26] Irradiation at the frequencies of these transitions results in electron transfer,[26] and it is possible that photoinduced charge-transfer phenomena explain the fact that all of the PPN[Mn(CO)$_5$] is consumed within 3 h in the photochemical reaction, while consumption of the anion requires 12 h in the thermal reaction. While no charge-transfer transitions were identified, that Mn(CO)$_5$ and $[C_{60}]^-$ can react directly was confirmed by an experiment in which $Mn_2(CO)_{10}$ and a solution of Na[C$_{60}$] in THF were photolyzed. Over the course of 8 h, ν_{CO} of $Mn_2(CO)_{10}$ disappeared while those of PPN[Mn(CO)$_4$(η^2-C$_{60}$)] grew in, demonstrating clearly that the $[C_{60}]^-$ radical anion can indeed substitute a CO ligand in the Mn(CO)$_5$ radical to form the $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ anion.

The stability of PPN[Mn(CO)$_4$(η^2-C$_{60}$)] during photolysis is interesting, as a control experiment showed that similar photolysis of a THF solution of $[Mn(CO)_5]^-$ resulted in loss of all ν_{CO} intensity over several hours. Fullerenes exhibit very strong absorptions in the UV–vis region,[26] however, and the presence of a coordinated fullerene may well create pathways other than CO dissociation for the relaxation of excited states of a complex carbonylate anion.

The reactions of A[Co(CO)$_4$] and A[Re(CO)$_5$] with C$_{60}$ presumably also involve initial electron transfer fol-

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[20] (a) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877. (b) Lai, C.-K.; Feighery, W. G.; Zhen, Y.; Atwood, J. D. *Inorg. Chem.* **1989**, *28*, 3929. (c) Corraine, M. S.; Atwood, J. D. *Organometallics* **1991**, *10*, 2315. (d) Lai, C. K.; Corraine, M. S.; Atwood, J. D. *Organometallics* **1992**, *11*, 582.

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lowed by CO substitution to give $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$ and $[Re(CO)_4(\eta^2\text{-}C_{60})]^-$, respectively. The former is thermally unstable in refluxing THF as the sodium salt and decarbonylates to yield the fulleride, $NaCoC_{60}\cdot 3THF$,[4] but its synthesis via the photolysis of $Co_2(CO)_8$ in the presence of $Na[C_{60}]$ clearly demonstrates that the $[C_{60}]^-$ anion can react with the $Co(CO)_4$ radical to form $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$. As the 17-electron radical $Co(CO)_4$ is known to dimerize readily to $Co_2(CO)_8$,[21] it is not clear why the latter is not formed as an intermediate. However, this dimerization process is an order of magnitude slower than dimerization of $Mn(CO)_5$,[21] and it may be that self-coupling is just not kinetically competitive with $Co(CO)_4{-}[C_{60}]^-$ coupling. The reaction of $Na[Re(CO)_5]$ with C_{60} proceeds similarly to the manganese system, but identification of the ν_{CO} of $[Re(CO)_4(\eta^2\text{-}C_{60})]^-$ is complicated by the concomitant formation of polynuclear carbonylate anions. While crystallographically useful crystals of the rhenium complex could not be obtained, the high-resolution MS studies confirmed unambiguously its identity and it seems reasonable to assume that the C_{60} is bound as in $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$, i.e. via a [6−6] ring junction.

Some Chemistry of $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$. All of the ($\eta^2$-fullerene)metal carbonylate salts described above are insoluble in pentane, hexanes, benzene, toluene, acetone, thiophene, benzonitrile, and acetonitrile, but exhibit limited solubility in THF and CH_2Cl_2 (5−10 mg/mL) to give very deep green solutions. We have therefore investigated a few reactions of the most available complex, $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$, with representative nucleophilic and electrophilic reagents.

Although PPh_3 reacts readily at room temperature with $Ru(CO)_4(\eta^2\text{-}C_{60})$ to give $Ru(CO)_4PPh_3$ and C_{60},[13b] we find that the isoelectronic $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ anion is inert to substitution in refluxing THF; $[Co(CO)_3(C_{60})]^-$ is similarly inert to thermal substitution. Presumably the negative charge on the metal anions increases the back-donation of electron density to the fullerene, resulting in stronger metal−fullerene bonds than is the case with the neutral ruthenium(0) compound.

It has been reported that the photochemical reaction of $[Mn(CO)_5]^-$ with PPh_3 results in dissociative phosphine substitution of one of the carbonyl ligands to yield $[Mn(CO)_4(PPh_3)]^-$.[7c] Under identical reaction conditions, however, we were unable to induce photochemical CO substitution by PPh_3 on any of the complexes $A[Mn(CO)_4(\eta^2\text{-}C_{60})]$ or $A[Co(CO)_3(\eta^2\text{-}C_{60})]$ (A = Na, PPN). The metal−CO bonds are relatively weak in the latter complexes, and it seems that the presence of a coordinated fullerene somehow permits relaxation of the absorbed energy via nondissociative pathways. However, the possibility of the added steric encumbrance of C_{60} discouraging PPh_3 coordination also seemed plausible, and a less sterically hindered phosphine, PMe_2Ph, was tried; again no substitution was observed.

Phosphine substitution of carbonyl ligands in neutral metal carbonyls having ν_{CO} greater than 2000 cm^{-1} can often be induced thermally by the addition of $O{=}N(CH_3)_3$.[27] The latter reacts with electron-poor carbonyl ligands to produce trimethylamine and carbon dioxide, thus generating a vacant site on the metal at which an incoming ligand can coordinate. While this type of reaction cannot generally be applied to metal carbonylate complexes because of the negative charges and the increased metal carbonyl bond strengths, the ν_{CO} of $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ are in the range of typically active neutral carbonyls, and we therefore attempted to induce CO substitution in this way. Again, we were unable to induce substitution.

The anionic $[Mn(CO)_5]^-$ is a good nucleophile and reacts with MeI to form $MeMn(CO)_5$ and I^-.[28a] However, the analogous chemistry of $PPN[Mn(CO)_4(\eta^2\text{-}C_{60})]$ with CH_3I was quite different, as IR monitoring revealed that the thermal reaction resulted in a new anionic species with ν_{CO} at 2068, 1995, 1972, and 1929 cm^{-1} and a peak in the mass spectrum at 421 Da/e. The latter exhibited an isotope pattern consistent with $[Mn(CO)_4I_2]^-$, and $[Bu_4N][Mn(CO)_4I_2]$ was synthesized for purposes of comparison according to a procedure described previously.[28b] The IR spectrum of the latter complex compared well with ν_{CO} observed in the IR spectrum of the reaction between $PPN[Mn(CO)_4(\eta^2\text{-}C_{60})]$ and CH_3I, although other ν_{CO} were also observed and thus the reaction was complex. There was also a black precipitate recovered from the reaction, but this did not exhibit solubility in THF, toluene, benzene, or acetone and was not examined further. If MeI does indeed react with $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ to give an iodo-manganese rather than a methyl-manganese species, i.e., in the opposite sense of the reaction of MeI with $[Mn(CO)_5]^-$, which gives $MeMn(CO)_5$ and iodide ion,[28a] then a fullerene product should be $[C_{60}Me]^-$, a known compound soluble in THF.[29] We did not detect $[C_{60}Me]^-$, and thus the course of the reaction remains somewhat mysterious. Reactions of $PPN[Mn(CO)_4(\eta^2\text{-}C_{60})]$ with trifluoroacetic acid were also investigated, but the results were erratic and the reactions were not pursued further.

Summary. Thermal and photochemical reactions of the carbonylate salts $A[Mn(CO)_5]$, $A[Co(CO)_4]$, and $A[Re(CO)_5]$ (A = Na, PPN) with C_{60} result in all cases in electron transfer to give $[C_{60}]^-$ and the transient 17-electron, metal-centered radicals $Mn(CO)_5$, $Co(CO)_4$, and $Re(CO)_5$, respectively. Subsequent self-coupling of $M(CO)_5$ (M = Mn, Re) then gives the metal−metal bonded dimers $M_2(CO)_{10}$ competitively with coupling of $M(CO)_5$ with $[C_{60}]^-$, which gives the η^2-C_{60} complexes $A[Mn(CO)_4(\eta^2\text{-}C_{60})]$. Interestingly, the photochemical processes ultimately result also in complete homolysis of the dimers and regeneration of the metal-centered radicals, which then combine with the $[C_{60}]^-$ still remaining in solution to form more of the η^2-C_{60} complexes. In the case of cobalt, no $Co_2(CO)_8$ is formed, but the thermally labile η^2-C_{60} complex $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$ is produced and decarbonylation in refluxing THF gives the previously reported mixed fulleride compound $NaCoC_{60}\cdot 3THF$. Much of the negative charge in $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ (and the cobalt and rhenium analogues) is delocalized onto the fullerene ligand; as a result, the η^2-C_{60}−Mn bond is unusually strong and the complex $[Mn(CO)_4(\eta^2\text{-}C_{60})]^-$ is very stable, exhibiting little of the

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chemistry associated with either neutral η^2-C_{60} complexes or the analogous $[Mn(CO)_5]^-$.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for a Research Grant to M.C.B. and a Graduate Fellowship to D.M.T., and ALCAN for a Graduate Fellowship to D.M.T. We also thank Prof. J. A. Stone, Mr. T. Hunter, and Dr. I. Galetich for assistance with the mass spectrometry measurements, and Prof. Gang Wu for assistance in obtaining the ^{55}Mn NMR spectrum.

OM020396I