Anionic Cyclopentadienyl C_{60} Complexes of Molybdenum and Tungsten; The Strange Case of Iron

David M. Thompson,[a] Marni Jones,[a] and Michael C. Baird*[a]

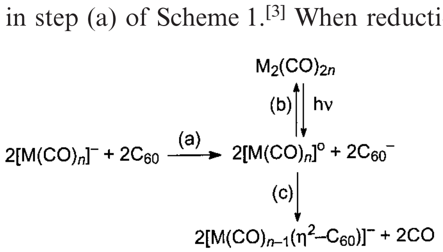
Keywords: Fullerenes / Molybdenum / Tungsten / Iron

Thermal and photochemical reactions of the carbonylate salts $A[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, $A[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$ and $A[(\eta^5\text{-}C_5H_5)W(CO)_3]$ (A = Na, PPN) in THF with C_{60} result in all cases in electron transfer to give $[C_{60}]^-$ and the transient 17-electron, metal-centered radicals $CpFe(CO)_2$, $CpMo(CO)_3$ and $CpW(CO)_3$, respectively. Subsequent self-coupling of the three metal-centred radicals then results in the formation of the metal-metal bonded dimers $[CpFe(CO)_2]_2$, $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$. In contrast, while the mixture of $Na[C_{60}]$ and $[CpFe(CO)_2]_2$ does not react further under photochemical conditions, photolysis of mixtures of $Na[C_{60}]$ and both $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$ ultimately results in complete homolysis of the dimers and regeneration of the corresponding metal-centered radicals, which then combine with the $[C_{60}]^-$ remaining in solution to form the η^2-C_{60} complexes $A[CpMo(CO)_2(\eta^2\text{-}C_{60}]$ and $A[CpW(CO)_2(\eta^2\text{-}C_{60}]$.

Introduction

Molecular transition metal-fullerene compounds generally fall into two main classes, endohedral compounds in which the metal atom is confined within a fullerene molecule,[1] and η^2-transition metal complexes in which the fullerene behaves essentially as a weakly conjugated, electron-deficient alkene ligand η^2-bonded to the metal via a [6-6] ring junction.[2] Most known examples of η^2-complexes are neutral compounds in which the fullerene has either added to a neutral precursor, thus increasing the coordination number about the metal, or has displaced a ligand such as CO or a phosphane.[2] We have recently described a third synthetic methodology, an approach which results in the formation of unusually stable anionic η^2-fullerene complexes.[3]

It is well-known that C_{60} contains a low lying, triply degenerate LUMO and is therefore readily reduced,[4] and we have found that the carbonylate anions $[M(CO)_n]^-$ (M = Co, $n = 4$; M = Mn, Re, $n = 5$) are sufficiently reducing in THF solution that they convert C_{60} to the radical anion $[C_{60}]^-$ as in step (a) of Scheme 1.[3] When reduction is carried out in refluxing THF with $A[M(CO)_5]$ (A = Na, PPN; M = Mn, Re), the rates at which the 17-electron intermediates $M(CO)_5$ couple [step (b) of Scheme 1] and undergo CO substitution [step (c) of Scheme 1] are similar and comparable amounts of $M_2(CO)_{10}$ and the stable complexes $A[Mn(CO)_4(\eta^2\text{-}C_{60})]$ are formed.[3b−3d] However, under photolytic conditions, the 18-electron dimers $M_2(CO)_{10}$ undergo dissociation back to the radicals [reverse of step (b)] which then react with the $[C_{60}]^-$ remaining in solution to give higher yields of the η^2-C_{60} products.[3b−3d] In contrast, with $A[Co(CO)_4]$ (A = Na, PPN), no $Co_2(CO)_8$ is formed in either the thermal or the photochemical reactions, possibly because the rate of dimerization of the $Co(CO)_4$ radical is slow relative to the rate of CO substitution by $[C_{60}]^-$.[3d] Interestingly, the η^2-fullerene complex $[Co(CO)_3(\eta^2\text{-}C_{60})]^-$ is thermally rather labile, and the sodium salt $Na[Co(CO)_3(\eta^2\text{-}C_{60})]$ decomposes in refluxing THF to give the unusual mixed-metal fulleride compound $NaCoC_{60}\cdot 3THF$.[3a,3d]



Scheme 1

In view of the rich variety of chemistry observed with these three carbonylate anions, we have extended our studies to anionic cyclopentadienyl analogues of iron, molybdenum and tungsten, $A[(\eta^5\text{-}C_5H_5)M(CO)_n]$ (A = Na, PPN; M = Fe, $n = 2$; M = Mo, W, $n = 3$); these are found to exhibit analogous but different patterns of reactivity.

Results and Discussion

As an extension of our earlier research on reactions of the carbonylate anions $[Co(CO)_4]^-$ $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$ with C_{60},[3] we have now investigated the analogous reactions of C_{60} with the anionic complexes

---

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

$[CpFe(CO)_2]^-$, $[CpMo(CO)_3]^-$ and $[CpMo(CO)_3]^-$. These anions are all highly reducing,[7] and we anticipated chemistry rather similar to that outlined in Scheme 1, that is single-electron transfer processes followed by dimerization of the resulting metal-centered radicals and/or combination of the metal-centered radicals with the $[C_{60}]^-$ radical anion. Sodium salts were utilized in all cases because of their ease of preparation, while PPN salts were also utilized in the case of molybdenum and tungsten in unsuccessful attempts to obtain suitable crystals of the new η^2-C_{60} complexes for crystallographic purposes, as we had done previously with the manganese system.[3b]

Reactions of $A[CpFe(CO)_2]$ ($A = Na^+$, PPN^+) with C_{60}

The thermal reactions of $A[CpFe(CO)_2]$ ($A = Na^+$, PPN^+) proceeded extremely rapidly. The first IR spectrum run following the addition of C_{60} to a THF solution of either salt (recorded within 1−2 min) revealed only the ν_{CO} bands of $[CpFe(CO)_2]_2$ with intensities similar to those of the starting $CpFe(CO)_2{}^-$, while ES-MS revealed a strong peak at 720 Da/e and with an isotope distribution consistent with $[C_{60}]^-$. Consistent with the presence of $[C_{60}]^-$ in solution, a near IR spectrum of a THF solution exhibited a peak at 1078 nm.[4] Refluxing these solutions over several hours resulted in no further changes to any of the spectra, and we were able to selectively precipitate $A[C_{60}]$ from the THF solutions by adding a small amount of pentane.

The reactions appear to involve extremely facile initial electron transfer from $[CpFe(CO)_2]^-$ to C_{60} and subsequent dimerization of the $CpFe(CO)_2$ radicals [Equation (1) and (2)].

$$[CpFe(CO)_2]^- + C_{60} \rightarrow CpFe(CO)_2 + [C_{60}]^- \qquad (1)$$

$$CpFe(CO)_2 \rightarrow 0.5[CpFe(CO)_2]_2 \qquad (2)$$

It was initially thought that $[CpFe(CO)(C_{60})]^-$ was perhaps not being formed because the rate of $CpFe(CO)_2$ radical dimerization is very nearly diffusion controlled[8] and, possibly, much higher than the rate of CO substitution by $[C_{60}]^-$. However, since photolysis of $[CpFe(CO)_2]_2$ is known to result in metal-metal bond homolysis, it was anticipated that continued photolysis would provide a source of $CpFe(CO)_2$ radicals which would be able to react with $[C_{60}]^-$ at least to some extent.[8]

To our surprise, however, the photochemical reactions of $A[CpFe(CO)_2]$ ($A = Na^+$, PPN^+) with C_{60} proceeded in an analogous fashion to the thermal reactions, the only product detected in IR spectra being, again, the dimer $[CpFe(CO)_2]_2$ in high yield. Subsequent photolyses run for up to 96 h revealed no changes to the IR spectra. Tandem ES-MS measurements revealed the strong peak of C_{60}^- at 720 Da/e.

It seems possible that the Cp ring provides steric hindrance and prevents coordination of fulleride to the relatively small iron. While other complexes have been reported containing both metal-fullerene and metal-Cp bonds,[2] there are no examples of the smaller first row transition metals showing both ligands coordinated. Thus the steric argument seems reasonable.

Reactions of $A[CpM(CO)_3]$ ($M = Mo$, W; $A = Na^+$, PPN^+) with C_{60}

Thermal reactions of $A[CpMo(CO)_3]$ ($A = Na^+$, PPN^+) with C_{60} in refluxing THF resulted in a gradual loss (over 3 h) of the ν_{CO} bands of $[CpMo(CO)_3]^-$ and the appearance of the ν_{CO} bands of $[CpMo(CO)_3]_2$.

The intensities of the product peaks were in both cases similar to those of the starting carbonylate anion before reaction. The presence of $[C_{60}]^-$ in the solutions was confirmed by observation of a peak at 720 Da/e in the ES mass spectrum and a peak at 1074 nm in the near NIR spectrum.[4] As with the iron system, continued refluxing of the solutions resulted in no further changes to any of the spectra, and thus the reactions were as in Equation (3) and (4).

$$[CpMo(CO)_3]^- + C_{60} \rightarrow CpMo(CO)_3 + [C_{60}]^- \qquad (3)$$

$$CpMo(CO)_3 \rightarrow 0.5[CpMo(CO)_3]_2 \qquad (4)$$

In contrast, photolysis of THF solutions of $A[CpM(CO)_3]$ ($A = Na$, PPN) in the presence of C_{60} yielded much more interesting results. In the case of $A[CpMo(CO)_3]$, the ν_{CO} bands of $[CpMo(CO)_3]^-$ were replaced over the course of about 3 h by two sets of ν_{CO} bands, those at 1911, 1956 and 2012 cm^{-1} attributable to $[CpMo(CO)_3]_2$, and two new ν_{CO} bands at 1818 and 1900 cm^{-1}. After 48 h, the latter pair of peaks dominated the IR spectrum.

ESMS monitoring of these reactions at times when the ν_{CO} bands of $[CpMo(CO)_3]_2$ and the new pair at 1900 and 1818 cm^{-1} were present in the IR spectrum revealed peaks at 720 and 939 Da/e with isotope distributions consistent with attributions to $[C_{60}]^-$ and $[CpMo(CO)_2(C_{60})]^-$, respectively. As the reaction continued and the intensities of the ν_{CO} band of $[CpMo(CO)_3]_2$ decreased, the intensity of the peak at 720 Da/e in the ESMS also decreased. When only the ν_{CO} bands at 1818 and 1900 cm^{-1} were present, photolysis was discontinued and the reaction mixtures were worked up as above to give $A[CpMo(CO)_2(C_{60})]$. The latter complexes are soluble in THF, and IR spectra of their THF solutions revealed the two ν_{CO} bands at 1800 and 1900 cm^{-1}. Furthermore, ESMS revealed a single peak at 939 Da/e, consistent with the isotope distribution anticipated for $[CpMo(CO)_2(C_{60})]^-$ (Figure 1).

On this basis, the course of the photochemical process clearly involves electron transfer and molybdenum-centered radical coupling, as in Equation (3) and (4), but the latter is reversed photochemically[9] and gives rise to coupling of molybdenum-centered and fulleride radicals, as in Equation (5) [$M = Mo$].

$$CpM(CO)_3 + [C_{60}]^- \rightarrow [CpM(CO)_2(C_{60})]^- + CO \qquad (5)$$

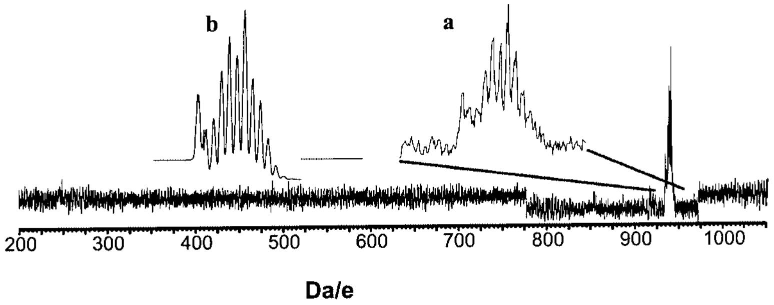


Figure 1. Negative-ion mode ES mass spectrum of PPN[$CpMo(CO)_2(C_{60})$]: (a) observed; (b) calculated

Interestingly, it was also observed that increasing the cone voltage from 10 mV to 30−50 mV resulted in loss of intensity from the peak at 939 Da/e and gain in intensity of a peak at 909 Da/e, a new peak with a position and isotope distribution consistent with [$CpMo(CO)(C_{60})$]$^-$. As has been established previously,[5c] successive decarbonylation of transition metal carbonylates with increasing cone voltage is a general phenomenon and this result was anticipated. Further increasing the cone voltage above 50 mV resulted in the observation of a peak at 720 Da/e with an isotope distribution consistent with [C_{60}]$^-$. No anionic daughter ions of the type [$CpMo(CO)_x$]$^-$ (x = 1−2) were observed.

A ^1H NMR spectrum of the complex was recorded in [D_8]THF, and exhibited a singlet at δ = 5.65 ppm attributable to the Cp ring protons. A ^{13}C NMR spectrum of PPN[$CpMo(CO)_2(C_{60})$] was also recorded in [D_8]THF, and the chemical shifts of the resonances are listed in Table 1, where the approximate relative intensities of the sp^2-hybridized carbon resonances are also given. As with the ^{13}C NMR spectra of other transition metal fullerene complexes,[2b] rigorous assignments of the sp^2-carbon resonances are not possible, although the numbers and intensities of the peaks between δ = 135 and 180 ppm can be used to determine the symmetry of the anion. Resonances in this region at δ = 134.7, 133.6, 130.5 and 128.4 ppm are attributed to the phenyl ring carbons on the PPN$^+$ cation on the basis of comparison with the spectrum of the chloride salt. Of the remaining 18 resonances, one (δ = 125.99 ppm) is readily attributed to the Cp ring carbons, and 17 to fullerene cage carbons. A fullerene bound to a metal by a [6-6] ring junction in an olefinic coordination mode (C_{2v} symmetry) should exhibit 17 ^{13}C resonances, one for the two coordinated (sp^3-hybridized) carbons and 16 attributable to the sp^2-carbons,[2b] and thus the ^{13}C NMR spectroscopic data are consistent with a structure of C_{2v} symmetry.

The near-IR spectra of solutions of A[$CpMo(CO)_2(\eta^2\text{-}C_{60})$] revealed no absorptions in the range 800−1400 nm, results consistent with observations made previously for A[$Mn(CO)_4(\eta^2\text{-}C_{60})$].[3d] Despite many attempts to obtain X-ray quality crystals, none of the crystals obtained proved to be amenable to solution by X-ray crystallography. Confirmation of the correct elemental composition was provided, however, by high resolution ESMS experiments on PPN[$CpMo(CO)_2(C_{60})$]; a peak at 938.9491 Da/e was observed, differing by 14.7 mDa (15.7 ppm) from the theoretical mass of 938.9344 Da/e.

Table 1. ^{13}C NMR spectroscopic data for PPN[$CpMo(CO)_2(\eta^2\text{-}C_{60})$]

Chemical shift of peak (δ)	Relative intensity[a]	Assignment
93.36		sp^3-C_{60}
125.99		Cp
128.40		PPN$^+$
130.53		PPN$^+$
133.39		PPN$^+$
134.74		PPN$^+$
136.60	1.60	sp^2-C_{60}
142.01	2.00	sp^2-C_{60}
142.64	1.96	sp^2-C_{60}
143.37	3.44	sp^2-C_{60}
144.20	2.29	sp^2-C_{60}
145.77	1.26	sp^2-C_{60}
145.90	2.29	sp^2-C_{60}
146.19	1.86	sp^2-C_{60}
146.39	2.16	sp^2-C_{60}
146.43	2.18	sp^2-C_{60}
146.50	1.00	sp^2-C_{60}
147.41	2.36	sp^2-C_{60}
148.08	0.97	sp^2-C_{60}
151.48	1.98	sp^2-C_{60}
156.89	0.77	sp^2-C_{60}
179.32	1.61	sp^2-C_{60}

[a] The relative intensities were calculated arbitrarily as ratios of the intensity of the peak at δ = 146.50 ppm. The intensities calculated in this way are approximate at best and are probably only valid for carbons in the general environment (sp^2 carbons)

The thermal and photochemical reactions of A[$CpW(CO)_3$] (A = Na$^+$, PPN$^+$) with C_{60} in THF parallel those of molybdenum. Reactions in refluxing THF were monitored by IR spectroscopy and ESMS, and the sole products were [$CpW(CO)_3$]$_2$ (in high yield) and A[C_{60}]. These products presumably arise as postulated in Equation (3) and (4) for molybdenum, and involve initial electron transfer from [$CpW(CO)_3$]$^-$ to C_{60} to give the $CpW(CO)_3$ radical and the [C_{60}]$^-$ radical anion followed by dimerization of $CpW(CO)_3$

In contrast, the photochemical reactions of A[$CpW(CO)_3$] (A = Na$^+$, PPN$^+$) with C_{60} in THF resulted in the slow but clean formation of A[$CpW(CO)_2(C_{60})$] (A = Na$^+$, PPN$^+$), via the same intermediates — the $CpW(CO)_3$

radical and the $[C_{60}]^-$ radical anion — observed in the thermal reactions. The photochemical reactions were monitored by IR spectroscopy and ESMS, and the ν_{CO} bands of A$[CpW(CO)_3]$ were found to be replaced initially by the ν_{CO} bands of $[CpW(CO)_3]_2$, and then by the ν_{CO} bands of $[CpW(CO)_2(C_{60})]^-$ (1809, 1894 cm^{-1}) over several hours. Tandem ESMS measurements revealed peaks at 720 Da/e and 1025 Da/e with intensities linked to the intensities of the carbonyl absorptions of $[CpW(CO)_3]_2$ and those at 1809 and 1894 cm^{-1}, respectively.

When only the ν_{CO} bands at 1809 and 1894 cm^{-1} were evident in the IR spectrum (96 h for the Na^+ salt, 48 h for the PPN^+ salt), photolysis was discontinued and the black product was precipitated from the solution by the addition of pentane and identified by IR spectroscopy and ESMS. The latter exhibits a peak at 1025 Da/e with an isotope pattern consistent with $[CpW(CO)_2(C_{60})]^-$ (Figure 2). Increasing the cone voltage from 10 to 30−50 V resulted in the appearance of a peak at 997 Da/e$^-$ with an isotope distribution consistent with $[CpW(CO)(C_{60})]^-$. Further increasing the cone voltage beyond 50 V resulted in the observation of the peak of $[C_{60}]^-$ at 720 Da/e.

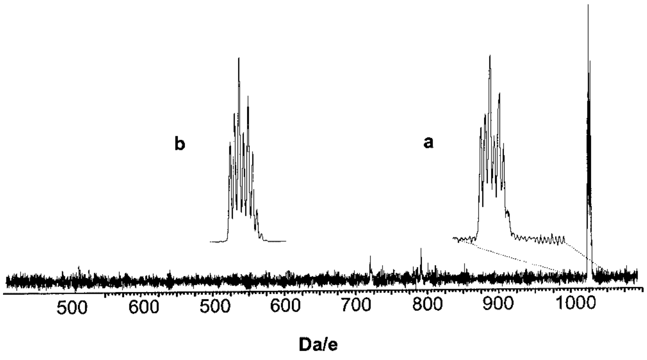


Figure 2. Negative-ion mode ES mass spectrum of PPN$[CpW(CO)_2(C_{60})]$: (a) observed; (b) calculated

Although we could again obtain crystals by layering THF solutions with pentane, the X-ray diffraction pattern generated by the crystals gave insufficient data for a structure solution. However, a ^1H NMR spectrum was obtained (δ_{Cp} = 5.56 in $[D_8]$THF), and confirmation of the elemental composition for PPN$[CpW(CO)_2(C_{60})]$ was provided by high resolution ESMS experiments in which a peak at 1024.9689 Da/e was observed, differing by 11.0 mDa (10.8 ppm) from the theoretical mass of 1024.9799 Da/e.

Thus the photochemical reactions of PPN$[CpW(CO)_3]$ and PPN$[CpW(CO)_3]$ with C_{60} both proceed as in Equations 3−5 and result in the formation of the complexes PPN$[CpM(CO)(C_{60})]$ (M = Mo, W) via a mechanism similar to those found for the manganese and cobalt complexes reported previously.[3b−3d] Given that no $[CpM(CO)_2(C_{60})]^-$ is observed in the thermal reactions, it seems that the rate of metal-centered radical dimerization is considerably higher than the rate of $[C_{60}]^-$ substitution. However, photolysis provides a constant supply of $CpM(CO)_3$ radicals through dimer homolysis, and the apparently irreversible nature of $[C_{60}]^-$ substitution for CO leads to an accumulation of $[CpM(CO)_2(C_{60})]^-$. By further analogy with PPN$[Mn(CO)(C_{60})]$, for which η^2-coordination of the fullerene has been established crystallographically,[3b] we presume that the molybdenum and tungsten complexes should also be formulated as η^2-complexes with the C_{60} coordinated via a [6-6] ring junction, as in Figure 3.

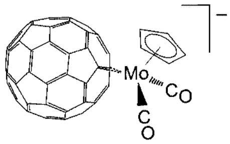


Figure 3. Proposed Structure of the $[CpMo(CO)_2(C_{60})]^-$ anion

Conclusions

Thermal and photochemical reactions of the carbonylate salts A$[(\eta^5\text{-}C_5H_5)M(CO)_n]$ (A = Na, PPN; M = Fe, n = 2; M = Mo, W, n = 3) with C_{60} result in all cases in electron transfer to give $[C_{60}]^-$ and the transient 17-electron, metal-centered radicals $CpFe(CO)_2$ or $CpM(CO)_3$. Subsequent self-coupling of $CpFe(CO)_2$ and $CpM(CO)_3$ then gives the metal-metal bonded dimers $[CpFe(CO)_2]_2$ and $[CpM(CO)_3]_2$. Interestingly, while the mixture of Na$[C_{60}]$ and $[CpFe(CO)_2]_2$ does not react further under photochemical conditions, photolysis of the mixtures of Na$[C_{60}]$ and $[CpM(CO)_3]_2$ ultimately results also in complete homolysis of the dimers and regeneration of the metal-centered radicals, which then combine with the $[C_{60}]^-$ remaining in solution to form the η^2-C_{60} complexes A$[CpM(CO)_2(\eta^2\text{-}C_{60}]$.

Experimental Section

All reactions were carried out using standard Schlenk line techniques or under Vacuum Atmospheres or MBraun glove boxes. Argon and nitrogen were purified by passing over a column of BASF catalyst heated to 140 °C and subsequently over a second column containing 5 Å molecular sieves. Solvents were purified by distillation over 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)[5] experiments on a VG Quattro spectrometer 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.

^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer and were referenced internally to the known residual ^{1}H signal in the deuterated solvent relative to TMS. ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer, and were internally referenced relative to the solvent resonances. Near-IR spectra in the region 800−1300 nm were run on a Cary 17 UV/Vis spectrophotometer, and UV/Vis spectra in the region 190 nm−820 nm on a HP 8452A Diode Array Spectrophotometer.

Unless explicitly stated otherwise, all chemicals were obtained from Aldrich, Fisher or Strem and were used as received. C_{60} was obtained from MER Corporation. The compounds Na[(η^5-C_5H_5)Fe(CO)$_2$],[6a] Na[(η^5-C_5H_5)Mo(CO)$_3$][6a] and Na[(η^5-C_5H_5)W(CO)$_3$][6a] were prepared as in the literature.

PPN[(η^5-C_5H_5)Fe(CO)$_2$]: This compound was prepared utilizing a modification of a reported procedure.[6b] A solution of [(η^5-C_5H_5)Fe(CO)$_2$]$_2$ (2.0 g) in 30 mL of THF was stirred over 80 g of 1% sodium amalgam for 30 min. The resulting red supernatant was then cannulated into a 250 mL flask and a solution containing an excess of [PPN]Cl in dry CH_3CN was added. The solution was stirred vigorously for 30 min, by which time a white precipitate of NaCl was evident. The solution was separated from the solid by filtration through Celite and the solvent was removed under reduced pressure to give PPN[(η^5-C_5H_5)Fe(CO)$_2$] as a deep red solid.[6b]

PPN[(η^5-C_5H_5)M(CO)$_3$] (M = Mo, W): These compounds were prepared from the corresponding sodium salts as described for the iron analogue except that dichloromethane was used as a solvent for the [PPN]Cl; yellow products were obtained. The products were characterized by ^{1}H NMR and IR spectroscopy. For PPN[(η^5-C_5H_5)Mo(CO)$_3$], ν_{CO} = 1782, 1895 cm^{-1} (CH_2Cl_2).[6a] For PPN[(η^5-C_5H_5)W(CO)$_3$], ν_{CO} = 1775, 1892 cm^{-1} (CH_2Cl_2).[6a]

Thermal Reactions of A[CpFe(CO)$_2$] (A = Na, PPN) with C_{60}: C_{60} (100 mg, 0.14 mmol) was added to a solution of Na[CpFe(CO)$_2$] (0.40 g, 0.14 mmol) in 10 mL of THF. The solution immediately turned a deep red color, and an IR spectrum recorded within 2 min revealed only the ν_{CO} bands of [CpFe(CO)$_2$]$_2$ at 1782 and 1992 cm^{-1}. The reaction was refluxed for 3 h, but no further changes occurred in the carbonyl region. The solution was filtered through Celite, 25 mL of hexanes was added to the filtrate and a black solid precipitated from the red solution. The black solid was filtered and characterized as NaC_{60} on the basis of an absorption at 1078 nm in the NIR[4] and a peak at 720 Da/e in the ES mass spectrum (both THF solutions). Removal of the solvent from the red solution under reduced pressure yielded [CpFe(CO)$_2$]$_2$, identified by IR spectroscopy (1782 and 1992 cm^{-1} in THF). Very similar observations were made with PPN[CpFe(CO)$_2$].

Thermal Reactions of A[CpMo(CO)$_3$] (A = Na, PPN) with C_{60}: A solution of Na[CpMo(CO)$_3$] (37 mg, 0.14 mmol) in 10 mL of THF was treated with C_{60} (100 mg, 0.14 mmol) and the mixture was refluxed. The color of the solution quickly turned deep red and the ν_{CO} bands of [CpMo(CO)$_3$]$^-$ were gradually replaced by those of [CpMo(CO)$_3$]$_2$ (1911, 1956, and 2012 cm^{-1}) over 3 h. ESMS monitoring revealed the presence of a peak at 720 Da/e. After 4 h of refluxing, no further changes to the carbonyl region of the IR spectrum were evident and the solution was filtered. The filtrate was treated with 25 mL of pentane to give a black precipitate of NaC_{60}, identified as above by ESMS and near IR spectroscopy (characteristic peak at 1078 nm[4]). [CpMo(CO)$_3$]$_2$ was recovered by removing solvent from the filtrate under reduced pressure (ν_{CO} 1911, 1956, 2012 cm^{-1}). The compounds PPN[CpMo(CO)$_3$] and A[CpW(CO)$_3$] (A = Na, PPN) reacted similarly.

Photochemical Reactions of A[CpFe(CO)$_2$] (A = Na, PPN) with C_{60}: C_{60} (100 mg, 0.14 mmol) was added to a solution of Na[CpFe(CO)$_2$] (0.40 g, 0.14 mmol) in 10 mL of THF. The solution immediately turned deep red, and an IR spectrum recorded immediately revealed only the ν_{CO} bands of [CpFe(CO)$_2$]$_2$ at 1782 and 1992 cm^{-1}. 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 96 h. During this time no further changes in the IR occurred while ESMS revealed only a peak at 720 Da/e. Workup procedures were as described above for the thermal reactions, and again yielded only NaC_{60} and [CpFe(CO)$_2$]$_2$. Similar results were obtained with PPN[CpFe(CO)$_2$].

Photochemical Reactions of A[CpMo(CO)$_3$] (A = Na, PPN) with C_{60}. Syntheses of A[CpMo(CO)$_3$(η^2-C_{60})]: A solution of Na[CpMo(CO)$_3$] (37 mg, 0.14 mmol) in 10 mL THF was treated with C_{60} (100 mg, 0.14 mmol) and the mixture was photolyzed as above. The solution quickly turned deep red, and the ν_{CO} bands of Na[CpMo(CO)$_3$] decreased over 3 h as ν_{CO} bands at 1818, 1900, 1911, 1956, and 2012 cm^{-1} appeared and gained in intensity. On further photolysis, the solution turned brown as the ν_{CO} bands at 1818 and 1900 cm^{-1} continued to gain intensity while those at 1911, 1956, and 2012 cm^{-1}, attributable to [CpMo(CO)$_3$]$_2$, decreased. ESMS monitoring of the solution revealed peaks at 720 and 937 Da/e which increased in intensity over the first 3 hours, but the latter thereafter gained intensity at the expense of the former. Increasing the cone voltage in any ESMS experiment resulted in a loss of intensity from the peak at 937 Da/e$^-$, an increase in the intensity of the peak at 720 Da/e and the appearance of a new peak 909 Da/e. The reaction was halted after 96 h, the solution was then filtered through Celite and pentane was added to the now green filtrate to precipitate Na[CpMo(CO)$_2$(η^2-C_{60})]. This was washed with pentane and dried under reduced pressure; yield 77 mg (58%). The compound was characterized by IR spectroscopy (ν_{CO} 1818, 1900 cm^{-1} in THF) and ESMS (937 Da/e, THF).

The synthesis of PPN[CpMo(CO)$_3$(η^2-C_{60})] proceeded similarly and was carried out several times; it was typically finished within 36 h to give amber-green solutions of the product in 70−90% isolated yield (140−180 mg). PPN[CpMo(CO)$_2$(η^2-C_{60})] was characterized by ESMS (939 Da/e) as well as IR (ν_{CO} 1818, 1900 cm^{-1}), ^{1}H NMR (δ_{Cp} = 5.65 in [D$_8$]THF) and ^{13}C NMR spectroscopy (Table 1; in [D$_8$]THF). The near IR spectrum (THF) exhibited no absorptions between 800 and 1400 nm, but the UV/Vis spectrum (THF) exhibited absorptions at 336, 400−600 (broad band) and 583 nm. While crystals of this compound were obtained by layering THF solutions with hexanes, they did not give useful elemental analyses and were not of sufficient quality for X-ray crystallographic analysis. However the anion was characterized unambiguously by high resolution ESMS; 938.9491 Da/e; calc. 938.9344; difference 15.7 ppm.

Photochemical Reactions of A[CpW(CO)$_3$] (A = Na, PPN) with C_{60}. Syntheses of A[CpW(CO)$_3$(η^2-C_{60})]: These reactions were carried out as described for the molybdenum analogues and proceeded similarly. Combining Na[CpW(CO)$_3$] with C_{60} resulted in the formation of a red solution, loss of intensities of the ν_{CO} bands of Na[CpW(CO)$_3$] (1744, 1793 and 1895 cm^{-1}) over 3 h and appearance of ν_{CO} bands at 1809, 1894, 1904, 1953, and 2010 cm^{-1}. On further photolysis, the ν_{CO} bands at 1809 and 1894 cm^{-1}, attributed to [CpW(CO)$_2$(η^2-C_{60})]$^-$, continued to gain intensity while the ν_{CO} bands (of [CpW(CO)$_3$]$_2$) at 1904, 1953, and 2010 cm^{-1} grew weaker. ESMS monitoring of the reaction revealed peaks at 720 Da/e and 1025 Da/e which increased in intensity over the first

3 h, at which point that at 720 Da/e began to lose intensity in favor of the peak at 1025 Da/e, attributed to $[CpW(CO)_2(\eta^2\text{-}C_{60})]^-$. The reaction was stopped after 96 h, and the solution was then filtered through Celite and worked up as above to give 67 mg of $Na[CpW(CO)_2(\eta^2\text{-}C_{60})]$ (46% yield).

A similar procedure was used to synthesize $PPN[CpW(CO)_2(\eta^2\text{-}C_{60})]$ from $PPN[CpW(CO)_3]$ in yields ranging from 141−198 mg (65−91%). The product was characterized using IR (ν_{CO} 1809, 1894 cm^{-1}), ^1H NMR ($\delta = 5.56$ ppm in $[D_8]$THF) and near IR (no absorptions in the region 800−1400 nm) spectroscopy and ESMS (1025 Da/e). Although crystals were obtained by layering THF solutions with hexanes, they did not give useful elemental analyses and were not of sufficient quality for X-ray crystallographic analysis. Therefore the anion was characterized unambiguously as such by high resolution ESMS: 1024.9689 Da/e; calcd. 1024.9799; difference 10.8 ppm.

Acknowledgments

We thank the Natural Sciences and Engineering Research Council for a Research Grant to MCB and a Graduate Fellowship to DMT, and ALCAN for a Graduate Fellowship to DMT. We also thank Prof. J. A. Stone, Mr. T. Hunter and Dr. I. Galetich for assistance with the mass spectrometry measurements.

---

[1] [1a] D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries, C. C. Yannoni, *Nature (London)* **1993**, *366*, 123. [1b] I. Holleman, M. G. H. Boogaarts, G. Meijer, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 543. [1c] F. T. Edelmann, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 981. [1d] S. Nagase, K. Kobayashi, T. Akasaka, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2131.

[2] [2a] W. Śliwa, *Transition Met. Chem.* **1996**, *21*, 583. [2b] A. H. H. Stephens, M. L. H. Green, *Adv. Inorg. Chem.* **1997**, *44*, 1. [2c] A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123.

[3] [3a] D. K. Patel, D. M. Thompson, M. C. Baird, L. K. Thompson, K. F. Preston, *J. Organomet. Chem.* **1997**, *546*, 607. [3b] M. Bengough, D. M. Thompson, M. C. Baird, *Organometallics* **1999**, *18*, 2950. [3c] D. M. Thompson, J. McLeod, M. C. Baird, *Pure Appl. Chem.* **2001**, *273*, 287. [3d] D. M. Thompson, M. Bengough, M. C. Baird, *Organometallics*, in press.

[4] [4a] M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, 1996. [4b]M. J. Rosseinsky, *Chem. Mat.* **1998**, *10*, 2665.

[5] For information on electrospray mass spectrometry and applications to organometallic and fullerene chemistry, see: [5a] S. J. Gaskell, *J. Mass Spectrom.* **1997**, *32*, 677. [5b] R. Colton, A. D'Agostino, J. C. Traeger, *Mass Spectrom. Rev.* **1995**, *14*, 79. [5c] W. Henderson, B. K. Nicholson, L. J. McCaffrey, *Polyhedron* **1998**, *17*, 4291. [5d] W. Henderson, J. S. McIndoe, B. K. Nicholson, P. J. Dyson, *J. Chem. Soc., Dalton Trans.* **1998**, 519. [5e] M. Ferrer, R. Reina, O. Rossell, M. Seco, G. Segales, *J. Organomet. Chem.* **1996**, *515*, 205. [5f] G. Khairallah, J. B. Peel, *Chem. Commun.* **1997**, 253. [5g] M. P. Barrow, X. Feng, J. I. Wallace, O. V. Boltalina, R. Taylor, P. J. Derrick, T. Drewello, *Chem. Phys. Lett.* **2000**, *330*, 267.

[6] [6a] R. Faltynek, M. S. Wrighton, *J. Am. Chem. Soc.* **1978**, *100*, 2701. [6b] J. K. Ruff, W. J. Schlientz, *Inorg. Synth.* **1976**, *15*, 85.

[7] [7a] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877. [7b] C.-K. Lai, W. G. Feighery, Y. Zhen, J. D. Atwood, *Inorg. Chem.* **1989**, *28*, 3929. [7c] M. S. Corraine, J. D. Atwood, *Organometallics* **1991**, *10*, 2315. [7d] C. K. Lai, M. S. Corraine, J. D. Atwood, *Organometallics* **1992**, *11*, 582.

[8] [8a] J. V. Caspar, T. J. Meyer, *J. Am. Chem. Soc.* **1980**, *102*, 7794. [8b] B. D. Moore, M. B. Simpson, M. Poliakoff, J. J. Turner, *J. Chem. Soc., Chem. Commun.* **1984**, 972.

[9] [9a] M. S. Wrighton, D. S. Ginley, *J. Am. Chem. Soc.* **1975**, *97*, 4246. [9b] J. L. Hughey, C. B. Bock, T. J. Meyer, *J. Am. Chem. Soc.* **1975**, *97*, 4440. [9c] R. M. Laine, P. C. Ford, *Inorg. Chem.* **1977**, *16*, 388.

Received August 6, 2002
[I02453]