Electrochemical Studies of C_{60}−Triosmium Complexes: First Evidence for a C_{60}-Mediated Electron Transfer to the Metal Center

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In recent years the organometallic chemistry of C_{60} has attracted much attention concerning the effect of metal coordination on the physical and chemical properties of C_{60}.[1] The electrochemistry of C_{60} itself has been extensively studied, and free C_{60} is known to be a fairly electronegative carbon cluster being reducible up to C_{60}^{6-}.[2] However, little is known about the electrochemical properties of organometallic C_{60} derivatives, although a few examples have appeared for $(\eta^5\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_{60})$[3] and $[(Et_3P)_2M]_n(\eta^2\text{-}C_{60})$ (M = Ni, Pd, Pt; $n = 1-4$)[4] complexes, which revealed C_{60}-localized sequential reductions. Some of us have recently characterized C_{60}-triosmium complexes,[5] $Os_3(CO)_{11}(\eta^2\text{-}C_{60})$ (**1**),[6] $Os_3(CO)_{10}(PPh_3)(\eta^2\text{-}C_{60})$ (**2**), and $Os_3(CO)_9(PPh_3)_2(\eta^2\text{-}C_{60})$ (**3**). We herein report cyclic voltammetric and IR spectroelectrochemical studies of complexes **1**−**3**, which provide the first examples of a C_{60}-mediated electron transfer to the metal centers.

Typical cyclic voltammograms (CV's) and proposed overall electrochemical pathways of **1** are shown in Figure 1 and Scheme 1, respectively. Half-wave potentials ($E_{1/2}$) of **1**−**3** and other known C_{60} complexes are summarized in Table 1. The fast scan CV (a) exhibits two reversible reduction waves at $E_{1/2} = -1.08$ and -1.31 V. The first reduction wave at $E_{1/2} = -1.08$ V of **1** is slightly more negative than that of free C_{60} at -1.05 V, which is consistent with the metal-to-C_{60} π-back-donation as was shown in other previous C_{60}-metal complexes[3,4] (see Table 1). The direct metal center reductions of $Os_3(CO)_{12}$ (**4**) and $Os_3(CO)_{11}(\eta^2\text{-dmfu})$[7] (**5**, dmfu = *trans*-$MeO_2CHC{=}CHCO_2Me$) have been observed at far more negative potentials, -2.02 V for **4** and -1.71 V for **5** under conditions identical to those for **1**. These results indicate that reduction of **1** by one electron occurs *via* the coordinated C_{60} ligand. However, the second reduction wave at -1.31 V unusually appears at a more positive potential than that of the free C_{60} at -1.41 V. If an electron in $\mathbf{1}^-$ is localized at the C_{60} ligand, the second reduction potential should be also more negative than that of free C_{60}. This unusual opposite potential shift suggests that the electron density of the C_{60} ligand in anion $\mathbf{1}^-$ is less than that of free C_{60}^-. This implies that the first electron accepted *via* the C_{60} ligand in $\mathbf{1}^-$ is delocalized to the triosmium center with its strong π-acid carbonyl ligands (see Scheme 1). Anionic species $\mathbf{1}^-$ with electron delocalization to the osmium center, therefore, undergoes easier reduction *via* the C_{60} ligand than free C_{60}^- to afford $\mathbf{1}^{2-}$. Species $\mathbf{1}^{2-}$ undergoes slow decomposition, because the slow scan CV (b) reveals only one oxidation peak at -1.02 V which is attributed to the oxidation of free C_{60}^-.

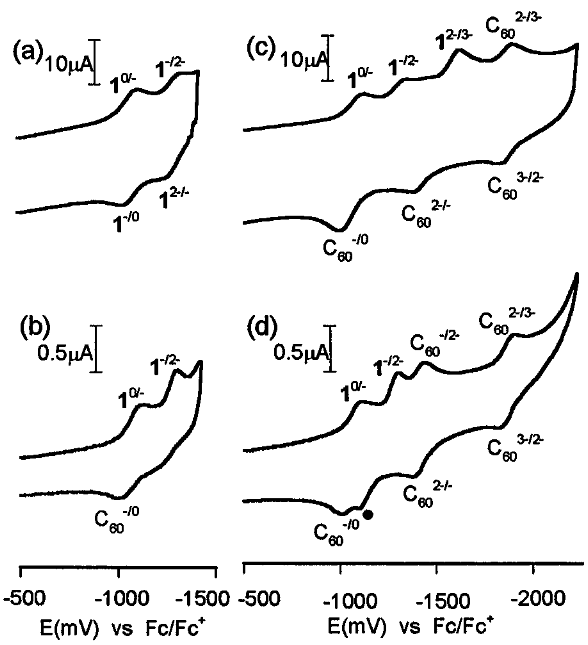
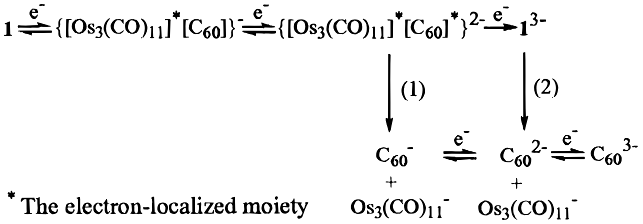


Figure 1. Cyclic voltammograms of **1** at a platinum electrode (1.6 mm diameter disk) in a dry deoxygenated mixed solvent (0.1 M $[(n\text{-}Bu)_4N]ClO_4$ in 4:1 dichloromethane (DM)−toluene (Tol)): $E_\lambda = -1.42$ V for (a) and (b), -2.22 V for (c) and (d); scan rate = 20.48 V/s for (a) and (c), 0.10 V/s for (b) and (d). A peak[8] indicated by ● is due to an irreversible oxidation of either $Os_3(CO)_{11}^-$ or an unknown species derived from $Os_3(CO)_{11}^-$.

Scheme 1



The CV's of (c) and (d) in Figure 1 at the two different scan rates have been recorded by changing the switching potential from -1.42 to -2.22 V to study further stepwise reductions of **1**. The reduction peak of $\mathbf{1}^{2-/3-}$ is observed at a potential of -1.61 V in the fast scan CV (c), while it is not observable in the slow scan CV (d), in which case $\mathbf{1}^{2-}$ has already decomposed

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(1) (a) Bowser, J. R. *Adv. Organomet. Chem.* **1994**, *36*, 57. (b) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992**, *25*, 134.

(2) (a) Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (b) Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 781. (c) Fhou, F.; Jehoulet, C.; Bard, A. J. *J. Am. Chem. Soc.* **1992**, *114*, 11004.

(3) Koefod, R. S.; Xu, C.; Lu, W.; Shapley, J. R.; Hill, M. G.; Mann, K. R. *J. Phys. Chem.* **1992**, *96*, 2928.

(4) Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 7807.

(5) Park, J. T.; Cho, J.-J.; Song, H. *J. Chem. Soc., Chem. Commun.* **1995**, 15.

(6) A single-crystal structure of $\mathbf{1}\cdot CH_2Cl_2$ has been obtained and will be reported elsewhere. The η^2-C_{60} ligand occupies an equatorial position.

(7) (a) The fumarate ligand has been proposed to have a similar electron-withdrawing property to that of free C_{60} by Shapley and co-workers: Shapley, J. R.; Du, Y.; Koefod, R. S. *Proceedings of Korea-U.S. Inorganic Chemistry Conference*; 1993, 9. (b) Complex **3**: ^1H NMR ($CDCl_3$, 25 °C) δ 3.87 (d, 1H, $^3J_{HH} = 8.9$ Hz), 3.78 (s, 3H), 3.69 (s, 3H), 3.61 (d, 1H, $^3J_{HH} = 8.9$ Hz); IR (C_6H_{12}) ν(CO) 2123 (m), 2070 (s), 2065 (sh), 2037 (vs), 2017 (s), 2005 (m), 1991 (w), 1967 (vw) cm^{-1}.

(8) This unknown oxidation peak shifts to more positive potentials at intermediate scan rates and finally merges into a single peak with the $C_{60}^{-/0}$ peak at -1.02 V. Note that the peak current of $C_{60}^{-/0}$ in the CV (c) is larger than those of $C_{60}^{2-/-}$ and $C_{60}^{3-/2-}$ owing to the merger of the two oxidation peaks.

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Table 1. Half-Wave Potentials ($E_{1/2}$ vs $E°_{Fc/Fc^+}$) of C_{60} and M(η^2-C_{60}) Complexes[a]

complex	$E_{1/2}{}^{0/-1}$	$E_{1/2}{}^{-1/-2}$	$E_{1/2}{}^{-2/-3}$	solvent	ref
C_{60}	−1.05 (−1.08)	−1.41 (−1.44)	−1.87 (−1.90)	DM/Tol	*c*
1	−1.08 (−1.12)	−1.31 (−1.34)	*b* (−1.61)	DM/Tol	*c*
2	−1.16 (−1.18)	−1.44 (−1.49)	*b* (−1.68)	DM/Tol	*c*
3	−1.19 (−1.21)	−1.53 (−1.56)	*b* (−1.76)	DM/Tol	*c*
C_{60}	−1.00	−1.39	−1.81	DM	3
Ir(η^5-C_9H_7)(CO)(η^2-C_{60})	−1.08	−1.43		DM	3
C_{60}	−0.86	−1.44	−2.00	THF	4
$(Et_3P)_2Pt(\eta^2\text{-}C_{60})$	−1.20	−1.73	−2.27	THF	4
$(Et_3P)_2Pd(\eta^2\text{-}C_{60})$	−1.18	−1.69	−2.23	THF	4
$(Et_3P)_2Ni(\eta^2\text{-}C_{60})$	−1.20	−1.74	−2.32	THF	4

[a] The cathodic peak potentials (E_{pc}) at the scan rate of 20.48 V/s are in parentheses. [b] Half-wave potentials could not be obtained due to very fast decomposition of **1**$^{3-}$ − **3**$^{3-}$. [c] This work.

producing C_{60}^- and $Os_3(CO)_{11}^-$ as shown in eq 1 of Scheme 1. The other two possible decomposition pathways of **1**$^{2-}$ producing $C_{60}{}^n$ ($n = 0, -2$) are excluded on the basis of the current intensity ratio (*ca.* 1:1) of the peaks due to **1**$^{-/2-}$ and $C_{60}{}^{-/2-}$ in CV (d). In the slow scan CV (d), all **1**$^{2-}$ decomposed to generate free C_{60}^-, which is responsible for both the third reduction peak ($C_{60}{}^{-/2-}$) at −1.44 V and the fourth reduction peak ($C_{60}{}^{2-/3-}$) at −1.90 V. The fourth reduction peak at a potential of −1.90 V is observed for both slow and fast scan rates, which is due to the reduction of $C_{60}{}^{2-}$ to $C_{60}{}^{3-}$ and is indicative of fast decomposition of **1**$^{3-}$. Decomposition of **1**$^{3-}$ to $C_{60}{}^{2-}$ and $Os_3(CO)_{11}^-$ appears to be the predominant pathway as shown in eq 2 of Scheme 1. A similar analogy to the previous decomposition mechanism of **1**$^{2-}$ excludes the other three possible decomposition pathways of **1**$^{3-}$ producing $Os_3(CO)_{11}{}^{n-}$ ($n = 0, 2, 3$). Furthermore, the fact that the reduction (−1.61 V) of **1**$^{2-}$ is much easier than that (−1.90 V) of $C_{60}{}^{2-}$ strongly supports the conclusion that the electron density in **1**$^{2-}$ is also delocalized to the triosmium center (see Scheme 1). The three oxidation peaks at potentials of −1.83, −1.38, and −1.02 V in both CV's of (c) and (d) are due to the three stepwise oxidation of $C_{60}{}^{3-}$ back to C_{60}.

The cyclic voltammetric data of **2** and **3** are listed in Table 1. The first reduction potentials of both **2** and **3** have been observed shifted to more negative potentials relative to **1** by 0.08 and 0.11 V, respectively, reflecting the electron-donating nature of the phosphine ligands. The second reduction potentials of **2** and **3** are more negative than that of free C_{60}. The third reduction peak potentials of both **2** (−1.68 V) and **3** (−1.76 V) are more positive than that of free C_{60} (−1.90 V), revealing that a similar C_{60}-mediated electron transfer occurs in these complexes.

Definitive evidence for the C_{60}-mediated electron transfer to the triosmium center was obtained by both an IR spectroelectrochemical study of **1** and characterization[9] of $[NiCp'_2]^+$**1**$^-$ (**6**, Cp′ = η^5-C_5Me_5). The IR spectrum of **1**$^-$ obtained by the IR spectroelectrochemical study is rather poorly defined, presumably, because of the instability of **1**$^-$ during the spectroelectrochemical experiment. Nevertheless the general features of the IR spectrum of **1**$^-$ are similar to **1** but shifted to lower energies compared to that of **1**. In order to obtain a clear IR spectrum of **1**$^-$, complex **6** has been prepared and characterized. The carbonyl region IR spectrum of **6** is now well defined and quite similar to that of **1**$^-$. The carbonyl bands of **6**[9] are also shifted to lower energies by *ca.* 40−50 cm^{-1} compared to those of **1** [2123 (s), 2076 (s), 2058 (m), 2038 (vs), 2015 (m), 2005 (m) cm^{-1} in THF], reflecting the electron density in **1**$^-$ is localized at the metal centers. Reduction of triosmium carbonyl complexes by one electron typically results in a change in ν_{CO} on the order of ∼50 cm^{-1}.[10] If an electron is localized on the C_{60} ligand, a small shift in ν_{CO} (∼10 cm^{-1}) is expected.[3] The IR spectroelectrochemical study of **2**$^-$ reveals a similar change but very poorly defined spectrum, and thus an electron transfer mechanism analogous to that of **1**$^-$ seems to occur. However, the IR spectrum of **3**$^-$ during the spectroelectrochemical study remains the same as that of **3**. This observation, together with the CV data, indicates that appreciable electron delocalization takes place only after the second reduction of **3** due to the donor effect of the two phosphine ligands. The IR spectroelectrochemical data of the dianions **1**−**3** could not be obtained, because reductions of **1**−**3** at a potential just negative of the respective second wave resulted in extensive decomposition.[4]

In conclusion, we have demonstrated that a C_{60}-mediated electron transfer to the metal center takes place in C_{60}-triosmium carbonyl complexes, **1**−**3**, which may afford a possible electron transfer pathway in C_{60}-derived materials. Intense efforts are currently underway in our laboratory to explore the electron transfer mechanism in C_{60}-triosmium complexes.

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Supporting Information Available: Summaries of both cyclic voltammetric and IR spectroelectrochemical experiments of **1** and a figure showing both IR spectra of **1**$^-$ obtained by an IR spectroelectrochemical study of **1** and from complex **6** (2 pages). Ordering information is given on any current masthead page.

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(9) (a) The synthesis and structure of $[NiCp'_2]^+[C_{60}]^-$ have been recently reported: Wan, W. C.;Liu, X.; Sweeney, G. M.; Broderick, W. E. *J. Am. Chem. Soc.* **1995**, *117*, 9580. (b) Complex **6**: ^{1}H NMR (THF-d_8, 24 °C) δ 105.0 (br, s); IR (THF) ν(CO) 2073 (s), 2029 (s), 1994 (vs), 1986 (sh), 1973 (m), 1949 (m) cm^{-1}. Anal. Calcd for $C_{91}H_{30}O_{11}$-$NiOs_3$: C, 56.68; H, 1.57. Found C, 56.13; H 1.76. (c) Note that the methyl proton resonance (δ 105.0) of paramagnetic **6** is shifted downfield by *ca.* 140 ppm compared to that of Cp'_2Ni (δ 244.6), implying the monocationic nature of $[NiCp'_2]^+$.

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