

by  $R^{*+}$ .<sup>11b</sup> On the basis of these results, it was proposed<sup>11</sup> that CcP turnover involves an initial one-electron reduction of  $R^{*+}$  in compound I, leaving the oxyferryl heme intact. Subsequently, an intramolecular et reaction regenerates  $R^{*+}$ , which can then be reduced by another electron equivalent. Intramolecular et was presumed to occur *only* during transient turnover because of a rate-limiting conformational transition which stabilizes the oxyferryl heme relative to  $R^{*+}$ .

In disagreement with the above mechanism, we have obtained direct kinetic evidence using laser flash photolysis<sup>12</sup> that one-electron reduction of compound I by cyt  $c^{2+}$  involves simultaneous oxyferryl heme reduction and cyt  $c$  oxidation, consistent with an initial *direct* reduction of the oxyferryl center.<sup>13</sup> This was confirmed in a stopped-flow study by Summers and Erman,<sup>3</sup> who additionally reported<sup>3</sup> a transient ascribed to partial reoxidation ( $\sim 20\%$ ) of ferric CcP by  $R^{*+}$  ( $k = 5 \text{ s}^{-1}$ ).

Inasmuch as the product of the one-electron reduction of compound I by cyt  $c^{2+}$  is clearly a ferric CcP<sup>3,12</sup> which still retains one oxidizing equivalent, it should be possible in a laser photolysis experiment to observe reoxidation of the heme, occurring via et between the heme and  $R^{*+}$ . We have attempted to detect this as follows (cf. refs 12c, d for details of the experimental protocol). Reduction of compound I by horse cyt  $c^{2+}$  occurs upon laser flash photolysis of a solution containing 5-deazaluminoflavin *N*-3-propanesulfonate, EDTA, cyt  $c^{3+}$ , and compound I. This results from rapid in situ reduction of cyt  $c^{3+}$  by deazaflavin semiquinone ( $k = 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), which subsequently reduces compound I.<sup>14</sup> Inasmuch as compound I is present in large excess over the deazaflavin semiquinone, and thus the cyt  $c^{2+}$  generated by the laser flash ( $\leq 1 \mu\text{M}$ ), its reduction occurs only by one electron equivalent.<sup>14</sup> Furthermore, we have determined that the stoichiometry of cyt  $c^{2+}$  oxidized to oxyferryl heme reduced is 1:1, within our experimental error. Figure 1 shows laser-induced transients at 557 nm (an isosbestic point for cyt  $c$ ) and 445 nm (as close to the Soret peak as possible because of deazaflavin absorption) obtained on a 1-s time scale. The initial rapid loss of absorbance at both wavelengths corresponds to one-electron reduction of the oxyferryl heme by cyt  $c^{2+}$ . A value for  $k_{\text{obsd}}$  of  $560 \text{ s}^{-1}$  (Figure 1c) is in good agreement with previous measurements by ourselves,<sup>12</sup> and by Summers and Erman<sup>3</sup> under similar conditions. Note that *no* return of absorbance occurred at either wavelength on a 1-s time scale, demonstrating that the oxyferryl heme was *not* regenerated by an et process.<sup>15</sup> Based on the rate constants determined by Ho et al.<sup>11</sup> and Summers and Erman,<sup>3</sup> a 1-s time scale should have allowed the detection of reoxidation of the ferric heme by  $R^{*+}$ . We conclude, on the basis of the previously demonstrated stability of the oxyferryl heme in the absence of the  $R^{*+}$  site,<sup>11</sup> and the presently observed lack of et from the ferric heme to  $R^{*+}$  on a catalytically relevant time scale, that during catalysis electrons enter compound I in a sequential fashion leading to an initial reduction of the oxyferryl heme and subsequent reduction of  $R^{*+}$ . Furthermore, there is presently no need to invoke the occurrence of et between the heme and  $R^{*+}$  at any stage of catalytic turnover.

(12) (a) Hazzard, J. T.; Poulos, T. L.; Tollin G. *Biochemistry* **1987**, *26*, 2836-2848. (b) Hazzard, J. T.; Moench, S. J.; Erman, J. E.; Satterlee, J. D.; Tollin, G. *Biochemistry* **1988**, *27*, 2002-2008. (c) Miller, M. A.; Hazzard, J. T.; Mauro, J. M.; Edwards, S. L.; Simons, P. C.; Tollin, G.; Kraut, J. *Biochemistry* **1988**, *27*, 9081-9088. (d) Hazzard, J. T.; Tollin, G. *Arch. Biochem. Biophys.* **1991**, *287*, 1-7.

(13) It is also kinetically possible that initial reduction of  $R^{*+}$  occurs, followed by extremely rapid ( $>2000 \text{ s}^{-1}$ ) et from the reduced amino acid side chain to the oxyferryl heme. However, such a rapid et process has never been observed.

(14) We have previously shown<sup>12a,c</sup> that the direct reduction of compound I by 5-deazariboflavin semiquinone is quite sluggish, relative to reduction of cyt  $c^{3+}$ . Also, under our experimental conditions, all the flavin triplet generated by the flash is quenched by EDTA, and all the flavin semiquinone is scavenged by cyt  $c^{3+}$ . The EDTA radical which is formed is known to be unstable and rapidly converts to stable products (cf. Traber et al. *Biochemistry* **1982**, *21*, 1687-1693). Even if some of this species is available for reaction with compound I, it is highly unlikely that this would occur with the same molecule that reacts with cyt  $c$ .

(15) Increasing the ionic strength to 70 mM had no effect on the kinetics, suggesting that cyt  $c^{3+}$  complexation of CcP was not a factor.

## Organometallic Chemistry with Buckminsterfullerene. Preparation and Properties of an Indenyliridium(I) Complex

Robert S. Koefod, Mark F. Hudgens, and John R. Shapley\*

School of Chemical Sciences and the  
Materials Research Laboratory  
University of Illinois, Urbana, Illinois 61801

Received August 21, 1991

Shortly after the initial recognition of  $C_{60}$  in a molecular beam,<sup>1</sup> the intriguing prospects raised by its interaction with metal atoms were under consideration.<sup>2</sup> However, the more recent development of a straightforward macroscopic preparation of  $C_{60}$ <sup>3</sup> has truly opened the door to exploration of its coordination chemistry.<sup>4</sup> The first isolated transition-metal derivative was an osmate ester,<sup>5a</sup> and a related derivative provided the first atomic-scale X-ray crystallographic data for the  $C_{60}$  framework.<sup>5b</sup> The platinum derivative  $(\text{Ph}_3\text{P})_2\text{Pt}(\eta^2\text{-}C_{60})$  was the first complex with a direct metal-carbon bond to be defined crystallographically,<sup>6a</sup> and more recently a hexasubstituted derivative has been isolated and similarly analyzed.<sup>6b</sup> We report the preparation, isolation, and characterization of an iridium(I) complex of  $C_{60}$  together with some observations on the stability of the complex toward typical organometallic reagents (see Scheme 1). This information adds to the basis for further development of metal-mediated modifications of  $C_{60}$ .

A combination of the cyclooctene complex  $(\eta^5\text{-}C_9H_7)\text{Ir}(\text{CO})(\eta^2\text{-}C_8H_{14})$ <sup>7</sup> (19 mg, 0.042 mmol) and  $C_{60}$  (30 mg, 0.042 mmol) was heated in dichloromethane under reflux for 8 h. The IR spectrum of the solution during this period showed that the carbonyl stretch of the initial iridium complex at  $1954 \text{ cm}^{-1}$  was replaced by a single new band at  $1998 \text{ cm}^{-1}$ . The solvent was evaporated, and the black solid residue was washed with pentane and dried in vacuo (25 mg, 58%). Formulation of the product as  $(\eta^5\text{-}C_9H_7)\text{Ir}(\text{CO})(C_{60})$  (**1**) is supported by microanalysis (Anal. Calcd for  $C_{70}H_9\text{OIr}$ : C, 79.62; H, 0.67. Found: C, 79.26; H, 0.80; C, 79.83; H, 0.99), by an appropriate parent ion multiplet<sup>8</sup> in the field-desorption mass spectrum ( $m/z$  1056, <sup>193</sup>Ir), and by the <sup>1</sup>H NMR spectrum in  $\text{CDCl}_3$  solution [ $\delta$  7.65 (m, 2 H), 7.48 (m, 2 H), 6.89 (tr, 1 H,  $J = 2.7 \text{ Hz}$ ), 5.97 (d, 2 H,  $J = 2.7 \text{ Hz}$ )]. Compound **1** forms dark green (vide infra) solutions in aromatic and chlorinated solvents, but it is insoluble in pentane, acetone, and acetonitrile. We have not yet been able to obtain crystals suitable for X-ray crystallographic analysis.

We formulate compound **1** as  $(\eta^5\text{-}C_9H_7)\text{Ir}(\text{CO})(\eta^2\text{-}C_{60})$  because its <sup>1</sup>H NMR signals for the protons in the five-membered ring of the indenyl ligand correspond better with those of analogous olefin complexes, for example,  $(\eta^5\text{-}C_9H_7)\text{Ir}(\text{CO})(\eta^2\text{-}C_8H_{14})$ ,<sup>7</sup> than with those of compounds containing a lower hapticity indenyl ring, such as  $(\eta^3\text{-}C_9H_7)\text{Ir}(\text{PMe}_3)_3$ <sup>9</sup> and  $[(\eta^1\text{-}C_9H_7)\text{Ir}(\text{CH}_3)(\text{PPh}_3)_2(\text{CN}^t\text{Bu})_2]^+$ .<sup>10</sup> Since there is no evidence for isomers in the <sup>1</sup>H

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.

(3) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(4) Very recently, evidence has been reported for a  $\text{Fe}^+-C_{60}$  complex in the gas phase: Roth, L. M.; Huang, Y.; Schwedler, J. T.; Cassidy, C. J.; Ben-Amotz, D.; Kahr, B.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 6298.

(5) (a) Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Shibato, Y.; Saykally, R. J. *J. Org. Chem.* **1990**, *55*, 6250. (b) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312.

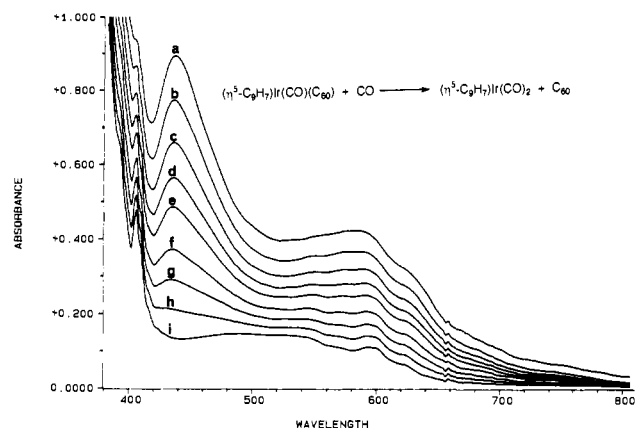
(6) (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160. (b) Fagan, P. J., personal communication. Fagan, P. J.; Calabrese, J. C.; Malone, B. *J. Am. Chem. Soc.*, in press.

(7) Szajek, L. P.; Lawson, R. J.; Shapley, J. R. *Organometallics* **1991**, *10*, 357.

(8) Parent ion multiplet relative intensities ( $m/z$ , found, calcd): 1054, 51, 51; 1055, 41, 39; 1056, 100, 100; 1057, 73, 70; 1058, 26, 26; 1059, 7, 6.

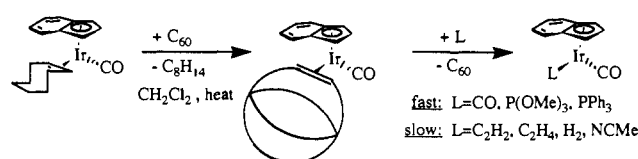
(9) Merola, J. S.; Kacmarcik, R. T.; Engen, D. V. *J. Am. Chem. Soc.* **1986**, *108*, 329.

(10) Habib, A.; Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Organometallics* **1989**, *8*, 1225.



**Figure 1.** Absorption spectra recorded after the exposure of compound **1** in dichloromethane solution to carbon monoxide: (a) 5 s, (b) 15 s, (c) 25 s, (d) 35 s, (e) 45 s, (f) 65 s, (g) 85 s, (h) 120 s, (i) 10 min.

#### Scheme I



NMR spectrum of **1**, we presume that the iridium center is bound to the “double-bond site” of  $C_{60}$ , i.e., exo to the five-membered rings, as found for both the osmate ester<sup>5b</sup> and platinum<sup>6a</sup> derivatives. The CO stretching frequency of the indenyliridium compounds provides a probe of electron density at the metal center,<sup>11</sup> and the marked shift to higher frequency in the  $C_{60}$  derivative **1** is a good indicator of the electron-withdrawing character of  $C_{60}$  as an olefinic ligand; this was deduced previously on chemical grounds.<sup>6a</sup>

The cyclic voltammogram of complex **1** ( $CH_2Cl_2$ , 0.05 M  $[NBu_4][PF_6]$ , 100 mV/s) provides a direct indication of charge transfer upon complex formation. Two quasi-reversible reduction waves are seen at  $-0.75$  and  $-1.10$  V (ferrocene internal reference<sup>12</sup>) compared to  $-0.63$  and  $-1.03$  V for  $C_{60}$  under the same conditions.<sup>13</sup> Since the voltammogram of  $(\eta^5-C_9H_7)Ir(CO)(\eta^2-C_8H_{14})$  shows no evidence of electroactivity to ca.  $-1.5$  V, the addition of electrons to complex **1** appears to be largely localized on the  $C_{60}$  ligand. The negative shift of ca. 100 mV in the reduction potentials is consistent with a more negative  $C_{60}$  moiety after binding to the iridium center.

The visible absorption spectrum of complex **1** contains a strong band at 436 nm ( $\epsilon$  ca.  $8000 \text{ cm}^{-1} \text{ L M}^{-1}$ ) as well as generally stronger absorption throughout the visible region compared to  $C_{60}$  alone. Changes in color of solutions of **1** provide a convenient way to monitor its susceptibility to reactions, especially those leading to displacement of  $C_{60}$  (see Scheme I). Thus, exposure of a solution of the complex to an excess of CO,  $P(OMe)_3$ , or  $PPh_3$  leads to a rapid (ca. 1 min) change in color from green to the characteristic mauve of  $C_{60}$ ; the known derivatives  $(\eta^5-C_9H_7)Ir(CO)(L)$ , which are pale yellow to colorless compounds, can be observed by their IR ( $\nu_{CO}$ ) bands.<sup>11</sup> Figure 1 shows the spectral changes for a saturated solution of CO in dichloromethane at room

temperature. Under these conditions ( $10^{-4}$  M complex, ca. 0.2 M CO), the pseudo-first-order rate constant is  $0.02 \text{ s}^{-1}$ . Significantly, exposure of solutions of complex **1** to a second class of potential reactants, e.g.,  $C_2H_4$ ,  $C_2H_2$ ,  $H_2$ , and  $NCCH_3$ , does not lead to any color change over the course of 5–10 min. Quantitative monitoring of the solution indicates small absorbance changes in the case of ethylene ( $<5\%$  in 5 min), but it is clear that any reaction with ethylene, despite the known stability of the substitution product,<sup>7</sup> is more than 100 times slower than the reaction with carbon monoxide. We take these reactivity differences, in which smaller and/or more nucleophilic ligands are favored, to indicate an associative path for the substitution reaction, as has been seen for other reactions involving indenyl metal complexes.<sup>14</sup>

A number of interesting questions regarding the effect of metal substitution on the properties of the  $C_{60}$  framework can be formulated, and we are exploring some of these with complex **1**. Interestingly, we have not been able to observe any similar reaction with  $C_{70}$ ,<sup>15</sup> implying that  $C_{70}$  is a significantly poorer ligand.

**Acknowledgment.** This research was supported by the National Science Foundation through Grant DMR 89-20538 to the Materials Research Laboratory of the University of Illinois. M.F.H. acknowledges a scholarship from the Harold Snyder Fund at the University of Illinois. We thank Professor W. Pirkle for the loan of a chromatography column used in the  $C_{60}/C_{70}$  separation and Chris Welch for extensive help in its use. We appreciate the interest of Drs. Richard Milberg and Steve Mullen of the School of Chemical Sciences Mass Spectrometry Center in this project as well as their expertise in obtaining useful mass spectra. We also thank Chad Hansen for his help in the preparation and purification of  $C_{60}$ .

(14) For leading references, see: (a) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307. (b) Turaki, N. N.; Huggins, J. M.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 424. (c) Reference 10.

(15) UV-vis spectra clearly show that  $[(\eta^5-C_5H_5)Ru(NCCH_3)_3]PF_6$  and  $C_{60}$  interact when combined in dichloromethane, presumably with release of one or more  $NCCH_3$  ligands (compare ref 6a). However, no similar interaction with  $C_{70}$  (80–90% pure) is observed. Koefod, R. S.; Shapley, J. R., unpublished observations.

## Multiplicity of Forms of Cyclopentanol and Other Five-Membered Rings in the Solid State

Joseph B. Lambert,\*<sup>1</sup> Liang Xue, and Suzanne C. Howton

Department of Chemistry, Northwestern University  
2145 Sheridan Road, Evanston, Illinois 60208

Received January 24, 1991

The rapid internal motions of five-membered rings have made them a difficult subject for study by solution NMR.<sup>2</sup> Rapid pseudorotation at all available temperatures interconverts the envelope and twist forms and interchanges the substituent positions found on these two conformations. Solution NMR gives chemical shifts and coupling constants that are averages for all the various forms.<sup>3</sup> Individual conformers cannot be examined by X-ray methods, unless a single form happens to crystallize exclusively and does not undergo motion in the crystal. For the power of NMR to be brought to bear on simple five-membered rings, it will have to be done on the solid state. Variable-temperature studies with high-speed magic angle spinning and cross polarization have been able to slow conformational and other rate processes on the NMR time scale,<sup>4</sup> but the method has not been applied

(11) (a) Ma, L.; Szajek, L. P.; Shapley, J. R. *Organometallics* **1991**, *10*, 1662. (b) Szajek, L. P. Ph.D. Thesis, University of Illinois, 1991.

(12) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(13) (a) Values of  $-0.61$  and  $-1.00$  V vs NHE with ferrocene as internal reference have been reported by the following: Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634. (b) Values of  $-0.33$  and  $-0.73$  V vs Ag/AgCl have been reported by the following: Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

(1) (1) This work was supported by the National Science Foundation (Grant No. CHE-8910841) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(2) Fuchs, B. *Top. Stereochem.* **1978**, *10*, 1–94.

(3) Lambert, J. B.; Papay, J. J.; Khan, S. A.; Kappauf, K. A.; Magyar, E. S. *J. Am. Chem. Soc.* **1974**, *96*, 6112–6118.