completely retained in each case.[2]

A representative experimental procedure is given by the reaction of benzaldehyde with geranylbarium reagent: To a suspension of anhydrous BaI_2[6] (435 mg, 1.1 mmol) in THF (5 mL) was added at room temperature a preformed lithium biphenylide, prepared from freshly cut lithium (16 mg, 2.3 mmol) and biphenyl (360 mg, 2.3 mmol) in THF (5 mL), and the reaction mixture was stirred for 30 min at room temperature. To the resulting brown suspension of barium powder in THF was slowly added a solution of geranyl chloride (170 mg, 0.98 mmol) in THF (1.5 mL) at -78 °C. After being stirred for 30 min, the mixture was treated with a solution of benzaldehyde (40 μL, 0.39 mmol) in THF (1 mL) at -78 °C and stirred for another 30 min at this temperature. To the mixture was added 1 N HCl, and the organic material was extracted with ether. The combined organic extracts were dried ($MgSO_4$) and concentrated, and the crude product was purified by column chromatography on silica gel (hexane–ethyl acetate, 5:1) to afford the homoallylic alcohol (86 mg, 90% yield); the α:γ and E:Z ratios were determined to be 92:8 and 98:2, respectively, by GC analysis.

The extraordinary α-selectivity and stereospecificity of the carbonyl addition of barium reagent provide an unprecedented route to homoallylic alcohols and are broadly applicable in organic synthesis.[9,10] Further work on the reaction with barium reagent is now being done.

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Intramolecular Electron Transfer from the Heme to the Radical Site Does Not Occur in Compound II of Yeast Cytochrome *c* Peroxidase during Catalytic Turnover†,‡

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Yeast cytochrome *c* peroxidase is a ferric heme containing enzyme which catalyzes the decomposition of H_2O_2 to H_2O, utilizing reduced cytochrome *c* (cyt c^{2+}) as an electron source.[1] Classically, the reaction is thought to proceed in three stages:[2,3]

$$\text{CcP} + H_2O_2 \rightarrow \text{compound I} + H_2O \quad (1)$$

$$\text{compound I} + \text{cyt } c^{2+} + 2H^+ \rightarrow \text{compound II} + \text{cyt } c^{3+} + H_2O \quad (2)$$

$$\text{compound II} + \text{cyt } c^{2+} \rightarrow \text{CcP} + \text{cyt } c^{3+} \quad (3)$$

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‡ The abbreviations used are as follows: CcP, yeast cytochrome *c* peroxidase; cyt c^{3+} and cyt c^{2+}, the ferric and ferrous oxidation states of cytochrome *c*; et, electron transfer.

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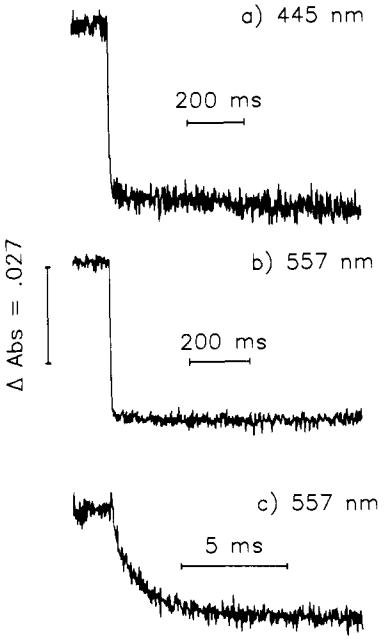

Figure 1. Laser flash generated transients for the reduction of compound I by cyt c^{2+}. Experiments were performed in a 4.2 mM phosphate buffer (pH 7.4) containing 0.5 mM EDTA and 0.1 mM 5-deazalumiflavin *N*-3-propanesulfonate; compound I (20 μM) was generated by titration of ferric CcP immediately prior to the flash experiment. The concentration of horse cyt c^{3+} was 20 μM for all traces.

Compound I is relatively stable[4] and contains two oxidizing equivalents.[2a,5] One of these is an oxyferryl heme[6], in which the iron atom has a formal oxidation state of 4+. The other is an organic free radical ($R^{\bullet+}$)[5b,7] localized on an amino acid residue(s) of somewhat controversial identity; however, the most likely candidate is Trp-191.[8] A transient porphyrin π-cation radical may be formed prior to transfer of the oxidizing equivalent to the amino acid side chain.[9]

The location of the oxidizing equivalent in compound II is also controversial.[2c,3] Stopped-flow measurements of ferrocyanide reduction suggest that $R^{\bullet+}$ reacts approximately five times faster than the oxyferryl site.[2c,10] When ferric CcP is reduced to the ferrous state and then oxidized with H_2O_2, a stable oxyferryl species without an oxidized amino acid side chain is produced.[11] Reaction of this species with F^- results in reduction of the heme Fe to the ferric state with a rate constant of 0.11 s^{-1}, due to intramolecular et from an unknown amino acid.[11b] A rate constant of 20 s^{-1} has been calculated for the oxidation of the ferric heme

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by $R^{\bullet+}$.[11b] On the basis of these results, it was proposed[11] that CcP turnover involves an initial one-electron reduction of $R^{\bullet+}$ in compound I, leaving the oxyferryl heme intact. Subsequently, an intramolecular et reaction regenerates $R^{\bullet+}$, 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 $R^{\bullet+}$.

In disagreement with the above mechanism, we have obtained direct kinetic evidence using laser flash photolysis[12] 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.[13] This was confirmed in a stopped-flow study by Summers and Erman,[3] who additionally reported[3] a transient ascribed to partial reoxidation (~20%) of ferric CcP by $R^{\bullet+}$ (k = 5 s^{-1}).

Inasmuch as the product of the one-electron reduction of compound I by cyt c^{2+} is clearly a ferric CcP[3,12] 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 $R^{\bullet+}$. 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-deazalumiflavin *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 M^{-1} s^{-1}), which subsequently reduces compound I.[14] Inasmuch as compound I is present in large excess over the deazaflavin semiquinone, and thus the cyt c^{2+} generated by the laser flash (≤1 μM), its reduction occurs only by one electron equivalent.[14] 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_{obsd} of 560 s^{-1} (Figure 1c) is in good agreement with previous measurements by ourselves,[12] and by Summers and Erman[3] 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.[15] Based on the rate constants determined by Ho et al.[11] and Summers and Erman,[3] a 1-s time scale should have allowed the detection of reoxidation of the ferric heme by $R^{\bullet+}$. We conclude, on the basis of the previously demonstrated stability of the oxyferryl heme in the absence of the $R^{\bullet+}$ site,[11] and the presently observed lack of et from the ferric heme to $R^{\bullet+}$ 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 $R^{\bullet+}$. Furthermore, there is presently no need to invoke the occurrence of et between the heme and $R^{\bullet+}$ at any stage of catalytic turnover.

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(14) We have previously shown[12a,c] 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

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Shortly after the initial recognition of C_{60} in a molecular beam,[1] the intriguing prospects raised by its interaction with metal atoms were under consideration.[2] However, the more recent development of a straightforward macroscopic preparation of C_{60}[3] has truly opened the door to exploration of its coordination chemistry.[4] The first isolated transition-metal derivative was an osmate ester,[5a] and a related derivative provided the first atomic-scale X-ray crystallographic data for the C_{60} framework.[5b] The platinum derivative $(Ph_3P)_2Pt(\eta^2\text{-}C_{60})$ was the first complex with a direct metal–carbon bond to be defined crystallographically,[6a] and more recently a hexasubstituted derivative has been isolated and similarly analyzed.[6b] 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 I). This information adds to the basis for further development of metal-mediated modifications of C_{60}.

A combination of the cyclooctene complex $(\eta^5\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_8H_{14})$[7] (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 cm^{-1} was replaced by a single new band at 1998 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 $(\eta^5\text{-}C_9H_7)Ir(CO)(C_{60})$ (**1**) is supported by microanalysis (Anal. Calcd for $C_{70}H_9OIr$: 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[8] in the field-desorption mass spectrum (m/z 1056, ^{193}Ir), and by the ^1H NMR spectrum in $CDCl_3$ solution [δ 7.65 (m, 2 H), 7.48 (m, 2 H), 6.89 (tr, 1 H, J = 2.7 Hz), 5.97 (d, 2 H, J = 2.7 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 $(\eta^5\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_{60})$ because its ^1H NMR signals for the protons in the five-membered ring of the indenyl ligand correspond better with those of analogous olefin complexes, for example, $(\eta^5\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_2H_4)$,[7] than with those of compounds containing a lower hapticity indenyl ring, such as $(\eta^3\text{-}C_9H_7)Ir(PMe_3)_3$[9] and $[(\eta^1\text{-}C_9H_7)Ir(CH_3)(PPh_3)_2(CN^tBu)_2]^+$.[10] Since there is no evidence for isomers in the ^1H

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