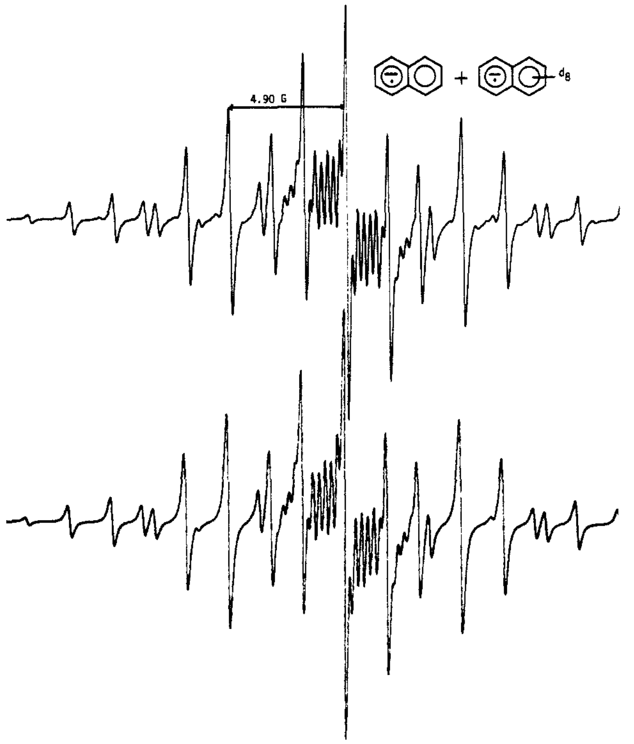

Figure 1. ESR spectrum at −2 °C of a solution of 3.4×10^{-3} M NP plus 2.1×10^{-2} M NP-d_8 in hexamethylphosphoramide (HMPA) reduced with a very deficient amount of potassium metal. The lower spectrum is a computer simulation that was generated by using a 1.0:1.8 ratio of $\mathrm{NP}^{-}\cdot$ to NP-$d_8^{-}\cdot$. The equilibrium constant in HMPA is well within experimental error of that found in THF. Coupling constants of 4.90 and 1.79 G were used for $\mathrm{NP}^{-}\cdot$ and 0.76 and 0.28 for NP-$d_8^{-}\cdot$. All of the ratios of unsubstituted to isotopically substituted anion radicals were obtained by using similar computer simulations. These simulations rigorously account for line broadening due to electron exchange.

of K per mol of hydrocarbon was carried out. The addition of water to this anion radical solution leads to the Birch reduction[11] of the NP and NP-d_8 that are in the reduced state. Since the concentration of $\mathrm{NP}^{-}\cdot$ is larger than that of NP-$d_8^{-}\cdot$, more $\mathrm{NPH_2}$ than $\mathrm{NPH_2}$-d_8 is formed. Even if this reduction involves protonation of the dianion rather than the radical anion this same argument holds. The isolated naphthalenes remaining after the water addition prove to contain an enhanced ratio of NP-d_8 to NP.

The analogous equilibrium for the benzene (BZ) system also yields an equilibrium constant that is well below unity ($K_{\mathrm{eq}} = 0.26 \pm 0.10$, reaction 2. Very similar results were observed from

$$\mathrm{BZ}^{-}\cdot,\mathrm{K}^+ + \mathrm{BZ}\text{-}d_6 \rightarrow \mathrm{BZ} + \mathrm{BZ}\text{-}d_6^{-}\cdot,\mathrm{K}^+ \qquad (2)$$

$$\Delta G° = 0.41 \pm 0.12 \text{ kcal/mol at } -120\ °\mathrm{C}$$

mixtures of benzene and BZ-$^{13}C_6$. The ESR spectrum of benzene containing six ^{13}C atoms (98.2% ^{13}C) can be readily generated via the reduction of BZ-$^{13}C_6$ in THF with K, and it consists of two heptets, one due to six protons with a coupling constant of 3.75 G and the other due to six ^{13}C's with a splitting of 2.70 G. The potassium reduction of 4.5:1 [BZ-$^{13}C_6$]/[BZ] mixtures yields ESR spectra consistent with a ratio of anion radicals [BZ-$^{13}C_6^{-}\cdot$]/[$\mathrm{BZ}^{-}\cdot$] of $^1/_2$. Thus, the decrease in solution EA is slightly less when the six neutrons are added to the carbon atoms.

$$\mathrm{BZ}^{-}\cdot,\mathrm{K}^+ + \mathrm{BZ}\text{-}^{13}C_6 \rightarrow \mathrm{BZ} + \mathrm{BZ}\text{-}^{13}C_6^{-}\cdot,\mathrm{K}^+ \qquad (3)$$

$$\Delta G° = 0.24 \pm 0.08 \text{ kcal/mol}$$

$$K_{\mathrm{eq}} = 0.45 \pm 0.12 \text{ at } -120\ °\mathrm{C}$$

The measured equilibrium constant for reaction 3 is very dependent upon small impurities of benzene in the solvent or metal due to the fact that the $\mathrm{BZ}^{-}\cdot$ lines exactly superimpose upon the most intense lines from the BZ-$^{13}C_6^{-}\cdot$. To varify the value of $\Delta G°$ for reaction 3, mixtures of BZ-$^{13}C_6$ and BZ-d_6 were reduced. The equilibrium constant for reaction 4 was found to be 0.51 ± 0.09.

$$\mathrm{BZ}\text{-}^{13}C_6^{-}\cdot,\mathrm{K}^+ + \mathrm{BZ}\text{-}d_6 \rightarrow \mathrm{BZ}\text{-}d_6^{-}\cdot,\mathrm{K}^+ + \mathrm{BZ}\text{-}^{13}C_6 \qquad (4)$$

The division of K_{eq} for reaction 2 by that of reaction 4 is equal to 0.51, thus providing an independent confirmation of K_{eq} for reaction 3.

Raman spectra[12] of anion radical systems indicate that the presence of an added electron could increase the zero point energy (ZPE) of the C–C stretch in $\mathrm{BZ}^{-}\cdot$ relative to that of BZ by as much as 25 cm^{-1}. Considering the fact that six such bonds are present this ZPE effect could account for up to 0.02 kcal/mol of the free energy of reaction 3.

From the work described here it appears that the presence of heavier isotopes in anion radical precursors significantly reduces their solution EA, which allows a means for isotope enrichment via the different reactivities of the reduced and unreduced materials. This reduction of solution EA is probably due to a combination of electronic, ZPE, and solvent/counterion effects. Further, studies into the mechanism of this effect are in progress.

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Remarkable Oxygen Affinity of a Mixed Valence Dicobalt Cofacial Porphyrin Co$^{\mathrm{III}}$Co$^{\mathrm{II}}$FTF4

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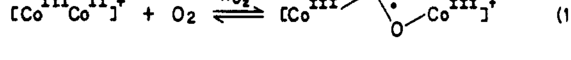
When the dicobalt cofacial porphyrin complex **1**, $\mathrm{Co_2}$FTF4 (Figure 1), is adsorbed on a graphite electrode in aqueous acid, it is an efficient catalyst for the four-electron reduction of dioxygen.[1] A dioxygen adduct is thought to be an important intermediate in the catalytic cycle.[1] We have shown that *in nonaqueous solutions* the mixed-valence (Co$^{\mathrm{III}}$Co$^{\mathrm{II}}$FTF4) complex of **1** forms a stable dioxygen adduct.[2] We now report the equilibrium affinity of this mixed-valence derivative for O_2. Our data reveal three major points: (a) the high equilibrium affinity is unprecedented for cobalt porphyrin derivatives, (b) axial ligands have no measured effect on the magnitude of the O_2 binding constant, and (c) water is a competitive inhibitor of O_2 binding.

The equilibrium constant, K_{O_2}, for oxygen complex formation in benzonitrile (BN) has been measured both spectrophotometrically and potentiometrically.[3]



$$[\mathrm{Co^{III}Co^{II}}]^+ + \mathrm{O_2} \xrightleftharpoons{K_{O_2}} [\mathrm{Co^{III}}\text{–O–O}^{\bullet}\text{–}\mathrm{Co^{III}}]^+ \qquad (1)$$

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(2) Le Mest, Y.; L'Her, M.; Courtot-Coupez, J.; Collman, J. P.; Evitt, E.; Bencosme, C. S. *J. Chem. Soc., Chem. Comm.* **1983**, 1286. Surprisingly, the Co$^{\mathrm{II}}$Co$^{\mathrm{II}}$ derivative does not show measurable O_2 binding in nonaqueous media.

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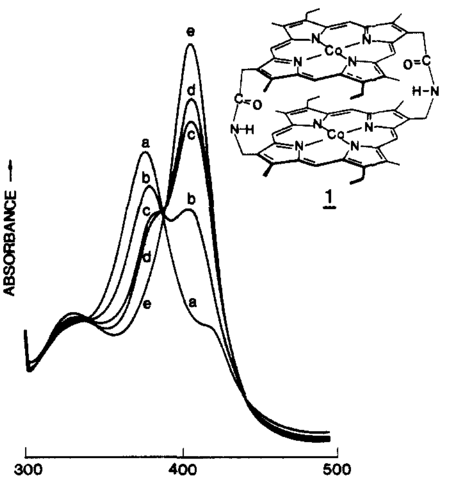

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Figure 1. UV-vis spectrum (Soret Band) evolution of a $Co^{III}Co^{II}FTF4$ solution in benzonitrile under varying partial pressures of dioxygen: (a) 0; (b) 0.7; (c) 2.7; (d) 6.6; (e) 10-760 torr.

The Soret region of the spectrum is shown in Figure 1 where it can be seen that increasing the O_2 partial pressure from 0 to 10 torr causes marked changes in the spectrum. The reaction is reversible; bubbling nitrogen through the solution restores the spectrum of the uncomplexed $Co^{III}Co^{II}FTF4$. When the O_2 partial pressure is greater than 10 torr, the equilibrium lies so far to the right that precise measurements are not possible. Analysis of these spectrophotometric data gives the binding constant $K_{O_2} = 10^{3.0\pm0.3}$ atm^{-1}.

Since the $Co^{II}Co^{II}FTF4$ derivative does not interact with dioxygen in benzonitrile unless a stronger axial ligand is present, potentiometry is also a suitable method for determining this O_2 binding constant. If reaction 1 is superimposed on the electron exchange between the two oxidation states of Co_2FTF4, then the zero current potential of a platinum electrode in a solution of the $Co^{II}Co^{II}$ and $Co^{III}Co^{II}FTF4$ derivatives in equal concentrations would vary as shown in eq 2 where E_1 is the potential of the

$$\Delta E = E_2 - E_1 = -0.059 \log [K_{O_2}pO_2] \qquad (2)$$

electrode in the solution under pure nitrogen, which is equivalent to the formal potential of the $Co^{III}Co^{II}/Co^{II}Co^{II}$ system, and E_2 is the potential at a given oxygen partial pressure pO_2. Experimentally, ΔE is found to vary linearly with log pO_2 when the dioxygen concentration in the gas mixtures is varied over the range 1-100% O_2. This potentiometric determination gives a K_{O_2} value consistent with the one measured by spectrophotometry: $K_{O_2} = 10^{3.0\pm0.1}$ atm^{-1}.

In order to see if the binding of a nitrogenous base to Co^{III} or to Co^{II} affects the dioxygen affinity, spectrophotometric measurements of the O_2 binding constant of $Co^{III}Co^{II}FTF4$ were carried out in the presence of *N*-methylimidazole (*N*-MeIm) at various ratios of *N*-MeIm/Co_2FTF4. In the presence of *N*-methylimidazole, the spectrophotometric method is less accurate since changes in the spectrum upon oxygen complexation are less pronounced. However, within experimental error, the K_{O_2} values measured are *identical* with those in the absence of the axial ligand, even in the presence of a large excess of *N*-MeIm (*N*-MeIm/Co_2FTF4 > 50). This suggests that the base binds with equal or approximately equal strength to the oxy and deoxy forms of the mixed-valence complex.

Table I. $P_{1/2}$ for Dioxygen Binding to Cobalt Porphyrins and to Models of Hemoproteins

compound	exptl conditns	$P_{1/2}$, torr[a]	ref
$Co^{III}Co^{II}FTF4$	BN, 0.1 M Bu_4NPF_6, 20 °C	0.8	*h*
$Co^{III}Co^{II}FTF4$(*N*-MeIm)[b]	BN, 0.1 M Bu_4NPF_6, 20 °C	0.8	*h*
$Co^{III}Co^{II}FTF4(H_2O)$[c]	BN, 0.1 M Bu_4NPF_6, 20 °C	38	*h*
CoMb[d]	pH 7 (0.1 M phosphate buffer), 25 °C	51	7
CoTpivPP(*N*-MeIm)[e]	toluene, 25 °C	140	6
CoPPIXDME(*N*-Im)[f]	toluene, 25 °C	17800	6, 8
Mb[g]	pH 7-7.4 (0.1 M phosphate buffer), 25 °C	0.37-10	9

[a] $P_{1/2} = K_{O_2}^{-1}$. [b] For $Co^{III}Co^{II}FTF4$/N-MeIm from 1/1 to 1/50. [c] $[H_2O]$ = 0.1 M. [d] Sperm whale or horse myoglobin. [e] (*meso*-α,α,α,α-tetra-*O*-Pivalamidoporphyrinato)cobalt(II) = "picket fence" porphyrin. [f] Cobalt(II) protoporphyrin(IX) dimethyl ester. [g] Myoglobin. [h] This work.

Experimental evidence shows that water binds to the Co^{III} center of the mixed-valence porphyrin.[4] Our measurements support the formation of a 1:1 adduct. The equilibrium constant K_{H_2O} was determined spectrophotometrically.

$$K_{H_2O} = \frac{[Co^{III}Co^{II}FTF4\cdot H_2O]}{[Co^{III}Co^{II}FTF4][H_2O]} = 10^{1.3\pm0.1}\ M^{-1}$$

A calculation of K_{O_2} in the presence of 0.1 M H_2O (K_{O_2}') gives a value for K_{O_2}' as follows:

$$K_{O_2}' = \frac{[Co^{III}Co^{II}FTF4\cdot O_2][H_2O]}{[Co^{III}Co^{II}FTF4\cdot H_2O]pO_2} = \frac{K_{O_2}}{K_{H_2O}}$$

The value we measure for K_{O_2}' is $10^{1.3\pm0.4}$ mol atm^{-1}. Competition for binding between dioxygen and water thus lowers the equilibrium affinity of the mixed-valence complex for dioxygen.

The unusually high oxygen affinity exhibited by the mixed-valence complex $Co^{III}Co^{II}FTF4$ is revealed by the equilibrium data shown in Table I. The mixed-valence complex **1** binds O_2 70 times more strongly than does cobalt-substituted myoglobin, CoMb, 175 times more strongly than the "picket fence" cobalt complex, and about as well as myoglobin (Mb) itself.[5] The origin of this tight binding is undoubtedly complexation of O_2 with both cobalt atoms. The most reasonable formulation is that of a superoxide ion bonded to two cobalt(III) centers. ESR measurements of the O_2 adduct derived from this mixed-valence complex exhibit hyperfine coupling to both cobalt atoms, demonstrating that the O_2 ligand is bound within the interporphyrin cavity.[2,10] It is known that the dioxygen ligand in Mb, and presumably in CoMb, is stabilized by a hydrogen bond to the "distal" imidazole.[11] A substitution-inert cobalt(III) center may serve as an especially effective Lewis acid, stabilizing the superoxide ligand. It will be interesting to see if this high O_2 affinity is sensitive to the interporphyrin separation (work in progress).

The possible role of this stable O_2 complex in the four-electron reduction of dioxygen remains unclear, in view of (1) our earlier electrochemical analysis of surface waves for the adsorbed catalyst

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(3) All experiments were conducted in an inert atmosphere box. The $Co^{III}Co^{II}FTF4$ complex is obtained by controlled-potential electrolysis of a $Co^{II}Co^{II}FTF4$ solution. Since reaction 1 is very sensitive to water it is necessary to dry the solvent by percolation through activated alumina and the gases by molecular sieves. Very dry gas mixtures were prepared by mixing known volumes of O_2 and N_2 in a flask.

(4) The UV-vis spectrum of a $Co^{II}Co^{II}FTF4$ solution in BN is unaffected by the addition of water. On the contrary, the UV-vis spectrum of the mixed-valence derivative $Co^{III}Co^{II}FTF4$ is modified by water and its ESR spectrum is not.

(5) When comparing the oxygen affinities of these various compounds one should keep in mind that they were measured in different media.

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in the presence and absence of oxygen, (2) uncertainties regarding the nature of axial bases (if any) supplied by the graphite surface, and (3) the competitive inhibition by water shown in the present work. However, the surprisingly high dioxygen affinity of **1** can give new insight into the factors that influence dioxygen binding to metal centers.

Acknowledgment. The support of this research by the CNRS (Centre National de la Recherche Scientifique), France, the National Science Foundation (Grant CHE83-18512), the National Institutes of Health (Grant NIHGM17880-14,15), and NATO (North Atlantic Treaty Organization) is gratefully acknowledged. The Bio-organic, Biomedical Mass Spectrometry Resource (A. L. Burlingame, Director), supported by NIH Division of Research Resources Grant RR 01614, is also gratefully acknowledged.

Registry No. 1, 89906-36-5; **1**·O_2, 89906-37-6; **1**·(*N*-MeIm), 99665-74-4; **1**·(H_2O), 99665-75-5; O_2, 7782-44-7.

Photochemical Carbonylation of Benzene by Iridium(I) and Rhodium(I) Square-Planar Complexes

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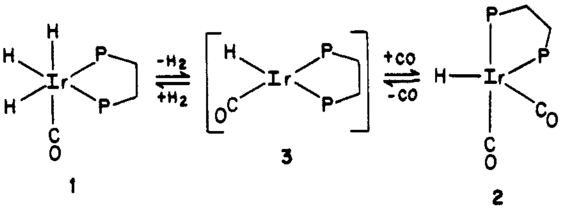
The photochemical behavior of d^8 square-planar complexes represents an area of current interest as evidenced by Ford's recent flash photolysis studies on $RhCl(CO)(PPh_3)_2$ and its well-known Ir analogue.[1-3] In these studies all intermediates and observed transients are thought to form via initial photodissociation of CO. In the absence of added substrate, the principal chemical reaction following the photolysis is recombination of $MCl(PPh_3)_2$ and CO, although for M = Rh, dimerization to $[MCl(PPh_3)_2]_2$ followed by slower carbonylation to starting complex is also noted. Flash photolysis of the Rh complex with either H_2 or C_2H_4 present gives spectral changes indicative of initial reaction of $RhCl(PPh_3)_2$ with substrate, but subsequent and rapid carbonylation leads to no net chemical change for the system. In this paper we report that photolysis of these complexes under long-term continuous irradiation leads to significant and new overall reaction chemistry. This chemistry, which is only observed upon photolysis, involves arene C–H functionalization and, in particular, the carbonylation of benzene to benzaldehyde. This observed C–H bond functionalization contrasts with the known oxidative carbonylation of arenes using Pd^{2+} in that no prior activation of the benzene ring is needed.[4] We are also able to show that the system is limited by the overall thermodynamics of the arene carbonylation reaction and not by the reactivity of the d^8 photocatalyst system.

The starting point for this work derives from a mechanistic proposal made previously in a report on benzene carbonylation using either $IrH_3(CO)(dppe)$ (**1**) or $IrH(CO)_2(dppe)$ (**2**) as the photocatalyst complex.[5] These coordinatively saturated complexes undergo exchange reaction (1) thermally or photochemically, presumably through the intermediacy of the four-coordinate species IrH(CO)(dppe) (**3**). Since benzene carbonylation was only observed upon photolysis, it was proposed that **3** was the photochemically active species for the system. A test of this proposal was performed based on the assumption that **3**, as a four-coordinate, 16-e^- species, would be yellow or orange and therefore absorb light at longer wavelengths than the two precursor complexes **1** and **2**. Two samples containing 6 mM solutions of $IrH(CO)_2(dppe)$ (**2**) in benzene under 600 torr of CO were photolyzed through a 366-nm cut-off filter. Under these conditions, **2** is the only observable complex in solution, but it exhibits no significant absorptions at λ greater than 320 nm. The first sample, which was maintained at room temperature, showed no benzaldehyde formation after 48 h of photolysis. The second sample was heated during photolysis to 75 °C at which temperature dissociation of CO from **2** is known to occur.[4] After 6 h of photolysis the second sample was analyzed by gas chromatography and found to contain 1.1×10^{-3} mmol (1.8 mM) of benzaldehyde. This result provides strong support that **3** is the photochemically active species in the previously reported benzene carbonylation system.[5]



(1)

The formation of benzaldehyde is also seen when benzene solutions of the chelated di(phosphine) complexes $IrH_3(CO)(dppp)$ (**4**) (dppp = 1,3-bis(diphenylphosphino)propane) and IrBr(CO)(dppe) (**5**) are irradiated under 600 torr of CO. Complex **4** is synthesized analogously to the procedure used for **1**[5] and, like **1**, undergoes thermal and photochemical exchange with CO and H_2, presumably through the 16-e^- species IrH(CO)(dppp). The four-coordinate complex **5** exists under CO in equilibrium with its five-coordinate carbonyl adduct $IrBr(CO)_2(dppe)$ and ν_{CO} for both species are observed in solution.[6]

The observation of benzene carbonylation promoted photochemically by four-coordinate species of general formula $IrX(CO)(P\frown P)$ prompted us to examine the photolysis of benzene solutions of Ir(I) and Rh(I) monodentate phosphine complexes under CO. We find that for $IrCl(CO)(PPh_3)_2$, $RhCl(CO)(PPh_3)_2$, and $RhH(CO)(PPh_3)_3$, PhCHO forms under long-tern continuous irradiation. The most extensively studied of these systems is $RhCl(CO)(PPh_3)_2$. In a typical experiment, a 7.2 mM solution of $RhCl(CO)(PPh_3)_2$ [3.0 mg of complex in 0.6 mL of benzene] was placed under 100 mm of CO and the tube was flame-sealed. The sample was irradiated at ambient temperature through Pyrex. Benzaldehyde was observed by ^1H NMR in a concentration of 0.15 mM after 2 h of photolysis.[7] The concentration continued to increase until it remained essentially constant at 15 mM after 40 h of photolysis. This final aldehyde concentration was further confirmed by GC analysis.[8]

In all runs the amounts of PhCHO formed are small, never exceeding 3 turnovers. This is consistent with the unfavorable thermodynamics for the reaction $C_6H_6 + CO = C_6H_5CHO$, for

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(7) (a) All proton spectra were recorded on a Bruker WH-400 400-MHz spectrometer. (b) Benzaldehyde (PhCHO) was observed by ^1H NMR by using a solvent peak suppression program. The reaction solvent was 20% C_6D_6 in C_6H_6, and the irradiated frequency was 7277.67 Hz.

(8) Benzaldehyde was detected on 10 ft of Apiezon L on Chromosorb W on a Hewlett-Packard 5730A GLC (FID) equipped with an HP 3380A automatic integrator. GLC conditions: injector port, 200 °C; oven, 150 °C; detector, 200 °C.

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