# Photoinduced Electron Transfer in Contact Ion Pairs

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Contact ion pair (CIP) formation is especially relevant to the reactivity of organic and organometallic nucleophiles and electrophiles in solution.[1,2] We felt that the intermolecular charge-transfer (CT) absorptions which commonly accompany the interaction of uncharged nucleophiles (donors) with electrophiles (acceptors)[3] could also provide the experimental means to assess CIP behavior.[4] Accordingly we examined the CT excitations from CIPs of carbonylmetallate anions in this study, since they are known to be effective nucleophiles with relatively low ionization potentials.[5]

Unlike the colorless alkali salts of cobalt tetracarbonyl anion, the cobalticenium salt[6] is deep red, both in the solid state and in nonpolar solvents. For example, the electronic spectrum of $Cp_2Co^+Co(CO)_4^-$ in $CH_2Cl_2$ (Figure 1A) shows the broad absorption band with $\lambda_{max}$ = 520 nm that is responsible for the red color together with the characteristic absorption band ($\lambda_{max}$ 412 nm) of the yellow cobalticenium cation.[7] Strikingly, the solution of $Cp_2Co^+\ Co(CO)_4^-$ in more polar solvents (e.g., MeCN) is pale yellow, and the absorption band at 520 nm is singularly absent. Equally strikingly, the addition of tetra-*n*-butylammonium perchlorate (TBAP) to a solution of $Cp_2Co^+Co(CO)_4^-$ in $CH_2Cl_2$ leads to the diminution of only the red band (Figure 1B). Both effects are readily ascribed to the displacement of the CIP and its associated charge-transfer band at 520 nm by polar solvents and by added salts,[4a,b,8] e.g.

$$Cp_2Co^+Co(CO)_4^- \xrightleftharpoons{MeCN} Cp_2Co^+//Co(CO)_4^-, \text{ etc.} \quad (1)$$

$$Cp_2Co^+Co(CO)_4^- + Bu_4N^+ClO_4^- \rightleftharpoons Cp_2Co^+ClO_4^- + Bu_4N^+Co(CO)_4^- \quad (2)$$

The structure of the CIP is given by the infrared spectrum of $Cp_2Co^+Co(CO)_4^-$ in solution as a spectral composite of the individual ionic components. However, on changing the solvent from MeCN to THF, the symmetry forbidden $A_1$ carbonyl band at 2005 $cm^{-1}$ increases in intensity without shifting, which together with the concomitant broadening of the strong $T_2$ band at 1890 $cm^{-1}$ suggests a structural perturbation of the tetrahedral $Co(CO)_4^-$ in nonpolar solvents.[9] Indeed X-ray crystallographic analysis of $Cp_2Co^+Co(CO)_4^-$ revealed the slight distortion of $Co(CO)_4^-$ from ideal $T_d$ to $C_{2v}$ symmetry.[10] More importantly the ORTEP diagram in Figure 2 establishes the nonbonded cation–anion interactions at ~4 Å. Such mean ionic separations in the red crystal of $Cp_2Co^+Co(CO)_4^-$ and the charge-transfer transition with $\lambda_{max}$ = 520 nm (obtained from the solid-state diffuse reflectance spectrum) are both related to those of the contact ion pair in solution (see Figure 1).[11]

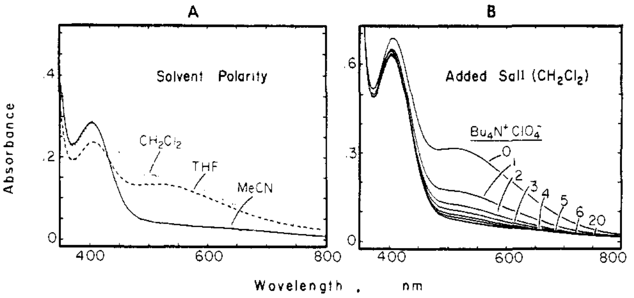

**Figure 1.** Solvent and salt effects on the CIP absorption spectrum: (A) 1 × $10^{-3}$ M $Cp_2Co^+Co(CO)_4^-$ in $CH_2Cl_2$, THF, and MeCN and (B) 2 × $10^{-3}$ M $Cp_2Co^+Co(CO)_4^-$ with 0, 1, 2, 3, 4, 5, 6, and 20 equiv of TBAP in $CH_2Cl_2$.

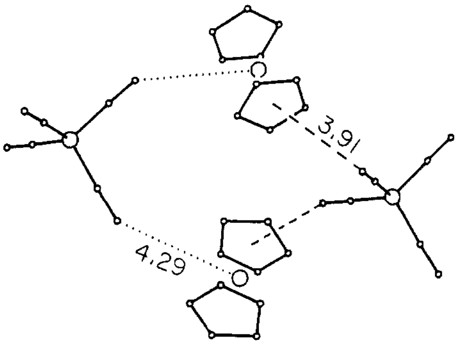

**Figure 2.** ORTEP packing diagram of $Cp_2Co^+Co(CO)_4^-$ showing closest nonbonded interionic distances (Å).

Electron transfer in the CIP can be induced by the specific excitation of its charge-transfer band, i.e.[12]

$$Cp_2Co^+(CO)_4^- \xrightleftharpoons{h\nu_{CT}} Cp_2Co^\bullet Co(CO)_4^\bullet \quad (3)$$

but it is reversible since no lasting change of either the IR or UV-vis spectrum is observed even upon prolonged irradiation of the THF solution at $\lambda$ > 520 nm. However, the back electron transfer of $Co(CO)_4^\bullet$ in eq 3 can be effectively obviated by added phosphines L. Thus the repetition of the experiment (eq 3) in the presence of either L = $PPh_3$ or $PMe_2Ph$ leads to the photoredox process in eq 4. The formation of the dimeric cobalt carbonyl

$$Cp_2Co^+Co(CO)_4^- \xrightarrow[L]{h\nu_{CT}} Cp_2Co + 1/2[Co_2(CO)_6L_2] + CO \quad (4)$$

with L = $PMe_2Ph$ in 85% yield undoubtedly results from the efficient scavenging of the 17-electron radical followed by dimerization, i.e.

$$Co(CO)_4^\bullet + L \xrightarrow[-CO]{k_s} Co(CO)_3L^\bullet \xrightarrow{k_d} 1/2[Co_2(CO)_6L_2] \quad (5a,b)$$

both steps of which are known to be rapid.[13] Such an effective

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(8) Compare (a) Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *102*, 7880. (b) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5235. (c) For eq 1, $K^{-1}$ = 88 in MeCN and >$10^4$ in THF and $CH_2Cl_2$ according to the method of Rose and Drago (Rose, N. J.; Drago, R. S. *J. Am. Chem. Soc.* **1959**, *81*, 6138).

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(10) Crystal data for $Cp_2Co^+Co(CO)_4^-$: $Co_2C_{14}H_{10}O_4$, $M$ = 360.1, monoclinic, space group $C2/c$, $a$ = 9.414 (2) Å, $b$ = 10.761 (2) Å, $c$ = 14.306 (3) Å, $\beta$ = 99.94 (2)°, $V$ = 1428 $Å^3$, $Z$ = 4, Nicolet R3m/V diffractometer, Mo K$\alpha$ ($\lambda$ = 0.71073 Å), $\mu$ = 23.27 $cm^{-1}$, 1118 reflections $I > 3\sigma(I)$ refined to $R$ = 0.037 ($R_w$ = 0.036), C–Co–C 107°, 111°.

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conversion of $Co(CO)_4^\bullet$ to $Co(CO)_3L^\bullet$ minimizes the energy wasting back electron transfer

$$Cp_2Co^\bullet + Co(CO)_3L^\bullet \xrightarrow{\text{slow}} Cp_2Co^+Co(CO)_3L^- \quad (6)$$

owing to the significantly enhanced oxidation potential of the phosphine-substituted radical.[14] Indeed the high quantum yield ($\Phi = 0.3$) for the photoredox process (eq 4) indicates that $Co(CO)_4^\bullet$ is scavenged by phosphine half as fast as it undergoes back electron transfer in eq 3. Furthermore the interception of $Co(CO)_4^\bullet$ must follow cage escape from $Cp_2Co^\bullet$ (see eq 3) since the ligand substitution of $17\epsilon$ carbonylmetal radicals ($k_s \sim 10^7$ M$^{-1}$ s$^{-1}$)[15] is generally slower than diffusive separation of radical pairs ($\tau \sim 10^{-9}$ s).[16]

When phosphites such as $L' = P(OMe)_3$ and $P(OPh)_3$ are employed as scavengers, the stoichiometry of the photoinduced process is

$$Cp_2Co^+Co(CO)_4^- \xrightarrow[L']{h\nu_{CT}} Cp_2Co^+Co(CO)_3L'^- + CO \quad (7)$$

which corresponds to an overall ligand substitution of the tetracarbonylcobalt anion. Such a transformation also derives from an initial CT excitation of the CIP in eq 3 and ligand substitution by phosphite (cf. eq 5). Independent experiments demonstrate that the subsequent thermal reduction of the phosphite-substituted carbonylcobalt dimer is rapid and quantitative, i.e.

$$2Cp_2Co + Co_2(CO)_6L'_2 \rightarrow 2Cp_2Co^+Co(CO)_3L'^- \quad (8)$$

The latter illustrates the ligand dependence of the redox properties of carbonylmetals since the *phosphine* analogues are inert, i.e.[19]

$$2Cp_2Co + Co_2(CO)_6L_2 \nrightarrow 2Cp_2Co^+Co(CO)_3L^- \quad (9)$$

These photoinduced processes of CIP thus provide a novel mode for the activation of ionic species in solution. We hope that further elaborations with a variety of other organometallic and organic ions will establish the generality of the charge-transfer methodology.

**Acknowledgment.** We thank J. D. Korp for crystallographic assistance and the National Science Foundation and Robert A. Welch Foundation for financial support.

**Supplementary Material Available:** Tables of bond distances and angles and anisotropic thermal parameters for $Cp_2Co^+Co(CO)_4^-$ (1 page); table of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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[16] (a) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129. (b) The unexpectedly slow rate of back electron transfer in spite of the driving force[14,17] may arise from a sizeable reorganization energy for $Co(CO)_4^\bullet$ resulting from a configurational change.[18]

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[19] (a) The irreversible cathodic CV peak potential for $Co_2(CO)_6[P(OPh)_3]_2$ is 300 mV more *positive* than that for $Co_2(CO)_6[PMe_2Ph]_2$. (b) It is also possible[14] that $Co(CO)_3[P(OPh)_3]^\bullet$ is reduced by $Cp_2Co^\bullet$ prior to dimerization in eq 5.

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# An Iron-Activated Alcohol Dehydrogenase: Metal Dissociation Constants and Magnetic and Spectroscopic Properties

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Two alcohol dehydrogenases (ADH) have been isolated from the fermenting bacterium *Zymomonas mobilis*.[1] One is a "normal" zinc enzyme while the second contains iron ($\alpha_4$; 150 000 Da). The presence of naturally occurring iron at the active center of an ADH or of any NAD$^+$-linked dehydrogenase has not been reported previously. In striking contrast to the four-coordinate $ZnN_2S_2$ site in horse liver ADH,[2] this communication shows the center to be a mononuclear six-coordinate high spin ferrous site bound to oxygen and nitrogen ligand atoms. Preliminary spectroscopic and magnetic properties of the active $Fe^{2+}$ and $Co^{2+}$ forms are presented as well as those of the inactive $Mn^{2+}$, $Fe^{3+}$, $Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ forms.

The Fe$^{II}$–ADH is not very stable as isolated ($t_{1/2}$, 2–5 h; 4 °C). Inclusion of $Co^{2+}$ in the isolation buffer provides $Co^{2+}$-substituted enzyme, Co–ADH, which is more stable and also active.[3] Treatment of Co–ADH with 1,10-phenanthroline leads to metal-free apoenzyme[3] which may be stored indefinitely at 77 K. $Fe^{2+}$ and $Co^{2+}$ reactivate apo–ADH completely[3] upon addition of a single equivalent, while $Zn^{2+}$ is ineffective under the same conditions.

Apparent dissociation constants determined by metal buffer or competition experiments[4] are listed below

| M: | $Mn^{2+}$ | $Fe^{2+}$ | $Fe^{3+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ |
|---|---|---|---|---|---|---|---|
| p$K_M$: | 7.4 | 7.5 | 5.8 | 7.8 | 8.3 | 8.5 | 9.0 |

All the bivalent metals are tightly bound with p$K_M$ increasing monotonically but slowly across the first transition series, a property generally associated with the presence of oxygen ligands.[5] The slope is even lower than those observed[6] for glyoxalase I and phosphoglucomutase, two enzymes thought to involve six-coordinate $N_2O_4$ coordination spheres.

The tight metal binding and availability of apoenzyme to act as reference and as diagmagnetic correction has facilitated spectral

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[3] Conditions: KMes (10 mM); pH 6.5. The specific activities of Fe-, Co-, and apo–ADH were 750, 300, and <3 IU mg$^{-1}$. Content (g atoms per subunit) of Fe, Co, and Zn, in the three forms were (0.96 ± 0.15, <0.05, <0.01), (<0.08, 1.16 ± 0.03, <0.01), and (<0.02, <0.05, <0.01), respectively. Enzyme concentrations in the range 0.6–1.2 mM were employed in the physical measurements.

[4] p$K_{Co}$ was determined employing nitrilotriacetic acid as metal buffer.[6a] The concentration of Co–ADH was estimated via the activity assay. $Fe^{2+}$ oxidized under the above conditions. p$K_M$ for the inactive M–ADH (M = $Mn^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$) were determined via competition with $Co^{2+}$. Complementary experiments in which total $Co^{2+}$ and then total $M^{2+}$ concentrations were kept constant were employed to maximize precision. The constant for $Fe^{2+}$ was established via competition with $Zn^{2+}$ and that for $Fe^{3+}$ via competition with $Fe^{2+}$.

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