

Treatment of metallacycle **2** with this phosphine and purification by column chromatography gave a 78% yield of **10** and its diastereomer having the opposite configuration at cobalt, as an air-stable orange paste. The Cp resonances of the two diastereomers were easily distinguishable by $^1\text{H NMR}$ (δ 4.42 and 4.49); this showed that they were formed in approximately equivalent amounts. Four recrystallizations from diethyl ether gave the less-soluble diastereomer (**10**; absolute configuration assigned by chemical correlation to **11**; see below) in 60% recovery and optically pure form as determined by NMR and by unchanged optical rotation upon further recrystallization. Treatment of this material with LDA followed by pivaldehyde as described above gave aldol **11** in 98% isolated yield. Inspection of the 250-MHz $^1\text{H NMR}$ spectrum of **11** showed only a single Cp resonance, again indicative of high diastereoface selectivity at the reacting ring carbon and high threo/erythro selectivity, as observed with this aldehyde in experiments with **3** and **4**.

In order to obtain a completely secure assignment of the absolute stereochemistry of **11** and therefore of the sense of the asymmetric induction observed in its formation, we determined its structure by X-ray diffraction. Details of the structure study are provided as supplementary material; an ORTEP drawing of the molecule, illustrating the absolute configuration at all chiral centers, is shown in Figure 1. As indicated in the drawing and assumed in the previous discussion, the aldol product is the threo isomer, and the hydroxyalkyl chain and the Cp ring are related in a cis manner.

We have carried out preliminary experiments aimed at developing ways to remove the metal moiety. Thus far we have found one efficient method, which involves oxidatively induced reductive elimination to cyclobutanone derivatives. For example, reaction of racemic **11** with 2 equiv of FeCl_3 afforded pure 2-(1-hydroxy-2,2-dimethylpropyl)cyclobutanone (**12**) in 70% yield. Carrying out this reaction on optically active **11** gave cyclobutanone **12**, optically pure by NMR analysis using chiral shift reagents.⁹

Our results suggest that other organo transition-metal acyl complexes should be similarly reactive, and we are planning to investigate a range of such systems. Experiments aimed at removing the cobalt from the complexes described in this paper to give acyclic, rather than cyclic, systems are also under way.

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Registry No. **2**, 74656-84-1; **3**, 74656-85-2; **3-d₁(R*,R*)**, 82837-81-8; **3-d₂(R*,S*)**, 82837-82-9; **4**, 82783-72-0; **5(R*,R*)**, 82783-73-1; **5(R*,S*)**, 82837-83-0; **6(R*,R*)**, 82783-74-2; **6(R*,S*)**, 82837-84-1; **7**, 82783-75-3; **8**, 82783-76-4; (+)-**9**, 2627-86-3; (-)-**10**, 82783-77-5; **10** diastereomer, 82837-85-2; (-)-**11**, 82783-78-6; **12**, 82783-79-7; MeOD, 1455-13-6; MeI, 74-88-4; EtI, 75-03-6; Me₂CO, 67-64-1.

Supplementary Material Available: Details of the preparation of metallacyclopentanones **3** from CpCo(CO)₂ (**1**), spectral and analytical data on metallacyclic products formed from enolate **4**, details of the structure determination of optically active metallacyclopentanone **11**, including atomic numbering scheme, crystal and data collection parameters, positional and thermal parameters, selected interatomic distances, selected interatomic

angles, selected torsional angles, general temperature factor expressions, crystal and orthonormal and least-squares planes, and observed and calculated data points (38 pages). Ordering information is given on any current masthead page.

Experimental Probe of Nonadiabatic Effects in Simple Electron-Transfer Reactions¹

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It has long been postulated that purely electronic or nonadiabatic effects (such as orbital symmetries, changes in spin multiplicity, donor-acceptor separation, etc.) play a significant role in determining the rates of electron-transfer reactions.² However, the predominant features of electron-transfer reaction patterns seem best attributable to Franck-Condon factors,³⁻¹⁵ but the precise values of these factors have proved elusive.¹⁶ The actual significance of purely electronic contributions has therefore remained equivocal.^{15,16}

Recent studies of the quenching of electronically excited transition-metal complexes¹⁷⁻¹⁹ have led us to an experimental

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(16) Franck-Condon factors based on experimental structural parameters seem consistently a little too small to account for the large barriers observed for Co(II)-Co(II) electron-transfer self-exchange.¹⁵ However, uncertainties in the knowledge of bond lengths, $\sim \pm 1$ pm in the best documented cases, lead to very large uncertainties in ΔG^{\ddagger}_{in} , since $\Delta G^{\ddagger}_{in} \propto \Delta X^2$. In a typical Co(II)-Co(II) couple, $\Delta X = 20 \pm 2$ pm, and this results in $\Delta G^{\ddagger}_{in} \approx 60 \pm 12$ kJ mol⁻¹.^{15c,d} Calculated values of ΔG^{\ddagger} run 5-30 kJ mol⁻¹ smaller than $\Delta G^{\ddagger}_{obsd}$, with the discrepancy similar in magnitude to the uncertainty in ΔG^{\ddagger}_{in} . In view of such large uncertainties, the differences between $\Delta G^{\ddagger}_{obsd}$ and $\Delta G^{\ddagger}_{calcd}$ (Franck-Condon terms) cannot be an accurate measure of the contribution of purely electronic factors. Even an electronic contribution of 10^4 to the observed rate constant could not be clearly defined by this approach.

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Table I. Summary of Kinetic Parameters for Anion Effects on the Reaction of Co(phen)_3^{3+} with Co(sep)^{2+} or $\text{Ru(NH}_3)_6^{2+}$

anion, X	K, M ⁻¹	10 ⁻⁴ k _x , M ⁻¹ s ⁻¹	
		Co(sep) ²⁺	Ru(NH ₃) ₆ ²⁺
CF ₃ SO ₃ ⁻		0.48 ± 0.01 ^b	0.93 ± 0.02 ^b
I ⁻	30 ± 5 ^{c,d}	1.8 ± 0.2	1.1 ± 0.1
NO ₂ ⁻	8 ± 2 ^c	7.5 ± 0.5	1.3 ± 0.1
ascorbate ⁻	35 ± 5 ^e	23 ± 3	2.5 ± 0.3

^a Temperature = 25 °C; I = 0.1 M LiCF₃SO₃. ^b Obtained experimentally at 0.1 M CF₃SO₃Li and treated as a fixed quantity, k_{TFMS}, for the reactions in the presence of other anions in the rate law k_{obsd} = (k_{TFMS} + k_xK[X])(1 + K[X])⁻¹. ^c Obtained kinetically. ^d This value is to be compared with the spectrophotometrically determined value of 40 ± 7 M⁻¹. ^e Determined spectrophotometrically.

approach that has the potential of being a sensitive probe of the nonadiabatic (or electronic) effects in simple outer-sphere electron-transfer reactions. In this paper we present the first strong evidence that electron-transfer reactions that are significantly nonadiabatic can have their rates increased by coupling to dissolved species with relatively small ionization energies.

It is possible to examine biomolecular quenching rates of electronically excited transition-metal complexes in kinetic regimes that are insensitive to Franck-Condon but relatively sensitive to purely electronic factors.^{18,19} The quenching rates of electronically excited Cr(phen or bpy)₃³⁺ by Co(III) complexes, reactions that are sensitive to electronic coupling between donor and acceptor,¹⁹ appear to be increased by donor-acceptor (Cr(III), X⁻) charge-transfer mixing with Co(NH₃)₆X²⁺ quenchers.^{19b} For quenching reactions dependent mostly on the electronic matrix element, the rate constant is given by²⁰

$$k_q = K_0\nu \quad \nu^{1/2} = V_0e^{-\alpha r} \quad (1)$$

where the dependence on charge-transfer interactions may be attributed to a three-center donor-acceptor (or "superexchange") mixing



These charge-transfer perturbations are conveniently regarded as effecting an increase in the mean donor-acceptor orbital radii, α^{-1} .^{22,23} If this interpretation is correct, then charge-transfer

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(20) Obtained by setting the Franck-Condon factor (or the density of states parameter) equal to 1. The insensitivity of these reactions to Franck-Condon parameters has been discussed elsewhere.¹⁹ K₀ is an outer-sphere association constant; for Co(NH₃)₆³⁺, $\alpha = 5.5 \text{ nm}^{-1}$, $(V_0)^2 \approx 3 \times 10^{12} \text{ s}^{-1}$.

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(22) For a charge-transfer perturbation, the induced dipole moment along the line of centers between nuclei is $\mu_z = \alpha_z F_z = e\delta r_z$, where the polarizability is²³

$$\alpha_z = \delta\mu_z/\delta F \approx eC/\Delta E_{CT}$$

and F is the effective field strength. Thus, the effective orbital radius along this axis may be represented

$$\alpha^{-1} = \alpha_0^{-1} + \delta r_z = \alpha_0^{-1} + \frac{1}{e} \left(\frac{\delta\mu_z}{\delta F} \right) F_z^0(\alpha_0) + \dots$$

or

$$\alpha^{-1} = \alpha_0^{-1} + \sum_i \frac{C_i}{\Delta E_{CT,i}} F^0(\alpha_0) + \dots$$

For weak interactions

$$\alpha \approx \alpha_0 - \alpha_0^2 F^0(\alpha_0) \sum \frac{C_i}{\Delta E_{CT,i}}$$

(23) Mulliken, R. S.; Person, W. B. "Molecular Complexes"; Wiley-Interscience: New York, 1969.

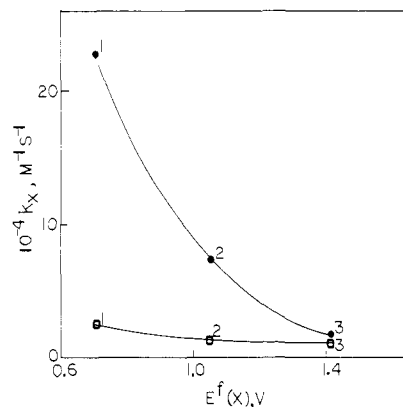


Figure 1. Variations in the bimolecular rate constants for Co(sep)²⁺ (●) and Ru(NH₃)₆²⁺ (○) reductions of [Co(phen)₃³⁺, X⁻] ion pairs with the X + e⁻ = X⁻ potential, E^f(X) for X⁻ = ascorbate (1), NO₂⁻ (2), and I⁻ (3). Values of E^f taken from: (a) Creutz, C. *Inorg. Chem.* **1981**, *20*, 4449. (b) Latimer, W. M. "Oxidation Potentials"; Prentice Hall: Englewood Cliffs, NJ, 1952. (c) Woodruff, W. H.; Margerum, D. W. *Inorg. Chem.* **1973**, *12*, 962. All reactions at 25 °C and ionic strength maintained at 0.10 M with LiCF₃SO₃.

perturbations must also play a significant role in mediating donor-acceptor interactions in electron-transfer reactions. Such effects could become very important in determining electron-transfer rates when the donor and acceptor centers are separated by appreciable distances as appears to occur in some metalloprotein systems.²⁴

We have selected the Co(sep)²⁺ reduction of Co(phen)₃³⁺ as a convenient test system because Co(III)-Co(II) reactions very commonly seem to have significant nonadiabatic components ($\nu \ll k_B T/\hbar$)^{8c,10c,15,16} and because the rates are conveniently measurable. We have investigated the perturbations on this rate caused by different [Co(phen)₃³⁺, X⁻] ion pairs since the charge-transfer properties of ion pairs are thoroughly documented and well understood.²⁴⁻²⁷ We have used the Ru(NH₃)₆²⁺/Co(phen)₃³⁺ reaction as a reference system since the Ru(III)-Ru(II) couples appear to be relatively adiabatic.¹⁰ Thus, the rate of this reference reaction should be less susceptible to perturbation by charge-transfer mixing of donor and acceptor wave functions.

Our observations are summarized in Table I and in Figure 1. We find that the rate of the Co(sep)²⁺/Co(phen)₃³⁺ reaction is very sensitive to the nature of the [Co(phen)₃³⁺, X⁻] species while the Ru(NH₃)₆²⁺/Co(phen)₃³⁺ reaction rate is almost independent of the nature of the ion pair. Furthermore, the magnitude of the effect increases inversely with the energy of the perturbing ion-pair charge-transfer state. It is significant that the effect of these perturbations is to increase the ratio k_x(Co)/k_x(Ru) from the value of 0.5 found in the TFMS media to 9 in ascorbate media, thus approaching the value expected for purely adiabatic reactions, k_x(Co)/k_x(Ru) = 45.²⁹⁻³¹ While other factors such as hydrogen

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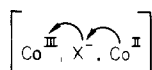
(26) Endicott, J. F.; Ferraudi, G. J.; Barber, J. R. *J. Phys. Chem.* **1975**, *79*, 630.

(27) It is to be noted that Sutin and co-workers²⁸ have reported some remarkable anion effects in electron-transfer reactions of polypyridyl complexes. These effects were complicated by the coordination of the anions to the labile partner and are not to be regarded as similar to the weak perturbations of anions in the second coordination sphere which we have investigated. Furthermore, the effects reported by these previous workers were characterized by high-order terms in [X⁻] appearing in the rate law. Interpretation of such effects is complicated by unknown association constants, changes in potentials of M^{III}X/M^{II}X couples compared to the M(III)-M(II) couples, etc. Finally, we note that the effects found by Sutin and co-workers were orders of magnitude more important for NCS⁻ than Cl⁻, whereas we find that when the anions are confined to outer coordination spheres, the effects of NCS⁻ and Cl⁻ (both very small) are comparable, as one would expect from the relatively large potentials for the X⁻ → X + e⁻ couples.

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bonding may play a role in promoting electron transfer in these systems, these effects seem to be relatively small.³²

We propose that the mechanism for the perturbation of nonadiabatic electron-transfer rates by charge-transfer interactions can be described as a super-exchange interaction

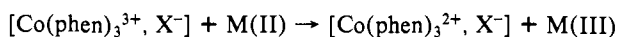


and that the perturbation is weighted as the sum of the inverse of the vertical transitions to the ion-pair charge-transfer state $^*[\text{Co}^{\text{II}}(\text{phen})_3, \text{X}]$ and the ionized reductant $^*[\text{Co}(\text{sep})^{3+}, \text{e}^-(\text{aq})]$. The effect of the perturbation is to increase donor-acceptor overlap between the reactants (here $\text{Co}(\text{phen})_3^{3+}$ and $\text{Co}(\text{sep})^{2+}$) in the collision complex. The preferred geometrical arrangement for these outer-sphere interactions is by no means clear. We suspect that several arrangements contribute and that the net perturbation can conveniently be regarded as a correction to the spherical-wave approximation on which (1) is based.²²

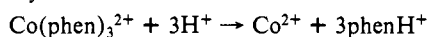
We deliberately selected a weak but simple and well-defined charge-transfer interaction for this study. The effect we have found may be useful as a probe of nonadiabaticity in electron-transfer reactions. Contingent on the values of α , straightforward application of (1) implies that nearly all electron-transfer reactions are significantly nonadiabatic. That many reactions seem adiabatic suggests that a large number of effects contribute to the electronic matrix element; most likely among these are the large orbital radii of heavy metals (i.e., leading to small values of α), the collective effect of a large number of high-energy charge-transfer perturbations (e.g., involving H_2O , TFMS^- , ClO_4^- , etc.), and exchange coupling of electronically degenerate systems.

The complexes $\text{Co}(\text{phen})_3(\text{ClO}_4)_3$,³³ $\text{Co}(\text{sep})\text{Cl}_3$,³⁴ and $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ were prepared and purified according to standard procedures; purity was established by electronic absorption spectra and elemental analysis. Solutions containing $\text{Co}(\text{sep})^{2+}$ or $\text{Ru}(\text{NH}_3)_6^{2+}$ were prepared from the trivalent salts by reduction with Zn.

The kinetics of the reactions



were monitored at 305 nm since a following reaction ($t_{1/2} \sim 5$ s), tentatively identified as



complicated infinite time measurements at other wavelengths. Pseudo-first-order conditions were used with $[\text{M}(\text{II})] > [\text{Co}(\text{phen})_3^{3+}]$. Ionic strength was maintained at 0.10 M with LiCl-

F_3SO_3 . The slow reaction of ascorbate with $\text{Co}(\text{phen})_3^{3+}$ was not a complicating feature since this counterion was kept with the reductant until the electron-transfer reaction was initiated by stopped flow mixing.

Registry No. $\text{Co}(\text{sep})^{2+}$, 63218-22-4; $\text{Ru}(\text{NH}_3)_6^{2+}$, 19052-44-9; $\text{Co}(\text{phen})_3^{3+}$, 18581-79-8.

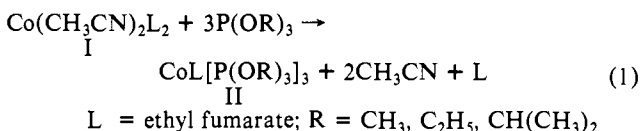
Trialkyl Phosphite Complexes of Cobalt

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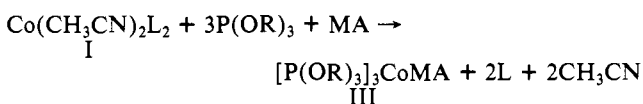
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Hydrogenation, carbonylation, and oligo- and polymerization reactions over cobalt(0) complexes are of current interest. Carrying on our investigations²⁻⁵ on the reactivity of mononuclear d^9 metal complexes, we have studied the partial or total ligand displacement of bis(ethyl fumarate)bis(acetonitrile)cobalt(0) (I). This paper deals with the preparation of the paramagnetic complexes tris(trialkyl phosphite)(fumarate)cobalt(0) (II) and tris(trialkyl phosphite)(maleic anhydride)cobalt(0) (III). Complexes II were prepared according to



All operations were run in N₂ or Ar atmosphere. The reaction was carried out by addition of a slight excess (10%) of phosphite to a solution of I in degassed toluene. Ligand exchange took place immediately and was accompanied by a change from red to greenish yellow. Vacuum distillation of solvent and excess phosphite left a dark solid residue which was extracted with degassed hexane and filtered. The filtrate was cooled at -78 °C and gave a good yield of II in the form of yellow plates.

When the above reaction was run in the presence of 1 equiv of maleic anhydride (MA) a further ligand substitution led to III, as follows:



In case of IIIa, R = CH₃ the product separated almost quantitatively when the reaction mixture cooled. Recrystallization from toluene gave a crop of pure compound (mp 134-135 °C) as dark red prismatic crystals suitable for X-ray studies. Microanalytical data and cryoscopic determinations of the molecular weight in benzene are consistent with the above mentioned mononuclear nature of the molecules. Considerable NMR line-broadening shows that the compounds are paramagnetic. The EPR spectrum of the powdered sample of IIIa (at 298 K) shows a broad signal centered at $g_{\text{iso}} \approx 2.10$ due to the d^9 system with $s = 1/2$.

Since only rather few examples of mononuclear d^9 complexes of cobalt have been prepared⁵⁻¹⁰ and in view of the paucity of

(29) Based on the Marcus square-root relation.⁴ Thus, for $k_{\text{ab}} = (k_{\text{aa}}k_{\text{bb}}K_{\text{ab}}/f_{\text{ab}})^{1/2}$ and $k_{\text{cb}} = (k_{\text{cc}}k_{\text{bb}}K_{\text{cb}}/f_{\text{cb}})^{1/2}$, $k_{\text{ab}}/k_{\text{cb}} \approx (k_{\text{aa}}K_{\text{ab}}/k_{\text{cc}})^{1/2}$. We have used $k_{\text{exch}}[\text{Co}(\text{sep})^{3+,2+}] = 5 \text{ M}^{-1} \text{ s}^{-1}$,³⁰ $k_{\text{exch}}[\text{Ru}(\text{NH}_3)_6^{3+,2+}] = 3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$,³¹ and $K_{\text{aa}} = 1.2 \times 10^6$. Note that if the $\text{Co}(\text{sep})^{3+,2+}$ is nonadiabatic, one expects $k_{\text{x}}(\text{Co})/k_{\text{x}}(\text{Ru}) > 45$.

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(32) Note that NO₂ and ascorbate are basic and the protons on $\text{Co}(\text{sep})^{3+}$ may be relatively acidic. We do find a 4.5-fold rate enhancement for the $\text{Co}(\text{phen})_3^{3+}/\text{Co}(\text{sep})^{2+}$ reaction in acetate medium (but no effect for the $\text{Ru}(\text{NH}_3)_6^{2+}$ reductions) as compared to the rate in a NaTFMS medium at the same pH (viz., $1 \times 10^{-5} \text{ M H}^+$). This effect may originate in a hydrogen-bonding interaction. Such an interaction with the ground-state species necessarily results in a shift in the M(III)-M(II) potential, and 25-40 mV shifts to more negative potentials are observed for the $\text{Co}(\text{sep})^{3+,2+}$ couple, but not for $\text{Ru}(\text{NH}_3)_6^{3+,2+}$, in nitrite, ascorbate, and acetate media (the largest shift is for acetate) compared to TFMS. We have not corrected for these apparent hydrogen-bonding effects because their kinetic significance is unknown (hydrogen bonding to the 3+ ion, as manifested in E' , should tend to increase the "solvent" reorganizational barrier) and because the effects seem relatively small. That the charge-transfer effects dominate the rate patterns we have reported is substantiated by predictable responses in $k_{\text{x}}[\text{Co}(\text{sep})^{2+}]/k_{\text{x}}[\text{Ru}(\text{NH}_3)_6^{2+}]$ when E' for the $\text{Co}(\text{PP})_3^{3+,2+}$ couple is altered by using substituted polypyridyls (PP = 5-nitro-1,10-phenanthroline, 1,10-phenanthroline, or 3,4,7,8-tetramethyl-1,10-phenanthroline) and $\text{Co}(\text{phen})_2(\text{chn})^{3+}$ (chn = cyclohexanediamine) oxidants (work in progress).

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