

Communications

Assessment of Nonadiabaticity in Outer-Sphere Electron-Transfer Reactions

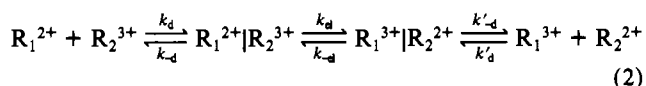
Sir:

In recent years, Balzani and co-workers have promoted an approach designed to disentangle nuclear and electronic factors in electron-transfer reactions of ground and of electronically excited states.¹⁻⁴ On the basis of this approach, they have reported values of κ_{11} and ΔG_{11}^* in eq 1 for the self-exchange reactions

$$k_{11} = (k_d/k_{-d})\kappa_{11}(k_b T/h) \exp(-\Delta G_{11}^*/RT) \quad (1)$$

of several redox couples. Definitions in eq 1: k_{11} , second-order rate constant for self-exchange reaction; k_d and k_{-d} , rate constants for formation and for dissociation, respectively, of the outer-sphere complex formed between the two oxidation states; κ_{11} and ΔG_{11}^* , electronic and nuclear factors, respectively, for internal electron transfer within the outer-sphere complex. The reported^{1,3} values of κ_{11} and ΔG_{11}^* , when introduced in eq 1, yield values of k_{11} that differ from the measured rate constants by several orders of magnitude.⁵ Since the authors failed to point out^{1,3} these large discrepancies,⁵ they did not offer any explanation. Evidently, this is a highly unsatisfactory situation since a very important and useful result of electron-transfer theory is that the rate constants for cross-reactions can be calculated, in principle, from the measured reduction potentials and self-exchange rate constants of the individual couples, and whenever discrepancies occur and are noted, some insight into the details of the mechanisms of the reactions under consideration are revealed.^{6,7} It is the purpose of this communication to show that Balzani's approach¹⁻³ cannot be reconciled with the measured self-exchange parameters of the redox couples and to point out several other problems with the approach. Moreover, we present an alternate treatment that makes use of the measured properties of the individual couples and of Marcus' cross relationship modified⁸ to take into account nonadiabaticity.

Balzani's Approach to the Assessment of Nonadiabaticity. Application of the steady state approximation to the sequence of elementary steps in eq 2 yields eq 3,⁹ where k is the second-order



$$k = k_d / \left(1 + \frac{k_{-d}}{k_{el}} + \frac{k_{-d}}{k'_{-d}} \frac{k_{-el}}{k_{el}} \right) \quad (3)$$

rate constant for the cross-reaction between R_1^{2+} and R_2^{3+} . $k_{-d} \sim k'_{-d}$ and $RT \ln(k_{-el}/k_{el}) = \Delta G_{el}^\circ$, the standard free energy change for the internal electron-transfer reaction of $R_1^{2+}|R_2^{3+}$. The dependence of k_{el} upon ΔG_{el}° and $\Delta G^*(0)$, the intrinsic barrier, is assumed^{1,3} to be governed by the empirical relation in eq 4. Moreover, $\Delta G^*(0)$ and κ_{12} are assumed to obey eq 6 and $\Delta G_{12}^* =$

$$\Delta G_{el}^\circ + \frac{\Delta G^*(0)}{\ln 2} \ln [1 + \exp(-\Delta G_{el}^\circ(\ln 2)/\Delta G^*(0))] \quad (4)$$

$$k_{el} = \kappa_{12}(k_b T/h) \exp(-\Delta G_{12}^*/RT) \quad (5)$$

7, respectively. Introduction of eq 4, 5, and 7 into eq 3 yields

$$\Delta G^*(0) = (\Delta G_{11}^* + \Delta G_{22}^*)/2 \quad (6)$$

$$\kappa_{12} = (\kappa_{11}\kappa_{22})^{1/2} \quad (7)$$

eq 8. A homogeneous series of cross-reactions is defined as one

$$k = k_d / \left\{ 1 + \frac{k_{-d}h}{k_b T(\kappa_{11}\kappa_{22})^{1/2}} \exp \left(\Delta G_{el}^\circ + \frac{\Delta G^*(0)}{\ln 2} \ln [1 + \exp(-\Delta G_{el}^\circ(\ln 2)/\Delta G^*(0))] \right) / RT + \exp(\Delta G_{el}^\circ/RT) \right\} \quad (8)$$

for which k_d , k_{-d} , $\Delta G^*(0)$, and κ_{12} are constant, and a homogeneous series of reactants have constant values of ΔG_{22}^* , and κ_{22} as well. Then, the rate constants for the cross-reactions of a given redox couple (couple 1) with a homogeneous series of reactants (couple 2) of known (and equal) values of ΔG_{22}^* and κ_{22} are fitted to eq 8 by taking k_d and k_{-d} as constant parameters (with values estimated¹⁰ from empirical equations) and ΔG_{11}^* and κ_{11} as floating parameters.¹⁰

The Hexaquoiron(III)-Hexaquoiron(II) Couple. Since the most extensive set of rate constants pertains to the reactions of $Fe^{3+/2+}$ with $ML_3^{3+/2+}$ ($M = Ru, Os$; $L = bpy, phen$), we focus our comments on this system.

The first criticism pertains to the insensitivity of the fits of the experimental points to eq 8 with respect to the value of κ_{11} , at least

- (1) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Indelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.
- (2) Balzani, V.; Scandola, F. In "Energy Resources by Photochemistry and Catalysis"; Grätzel, M., Ed.; Academic Press: New York, 1983; Chapter 1, p 1. Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
- (3) Sandrini, D.; Gandolfi, M. T.; Maestri, M.; Bolletta, F.; Balzani, V. *Inorg. Chem.* **1984**, *23*, 3017.
- (4) Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1979**, *101*, 6140. Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.
- (5) Values of k_{11} (in $M^{-1} s^{-1}$) calculated from reported^{1,3} values of κ_{11} and ΔG_{11}^* and the corresponding experimental values: $Fe^{3+/2+}$, 2.4×10^{-4} and 4.5; $Co(NH_3)_6^{3+/2+}$ (and $Co(NH_3)_5OH_2^{3+/2+}$), 3.2×10^{-6} and $\sim 1 \times 10^{-6}$; $Co(phen)_3^{3+/2+}$ (and $Co(bpy)_3^{3+/2+}$), 3.9×10^{-2} and 42; $Co(en)_3^{3+/2+}$, 4.4×10^{-3} and 7.7×10^{-5} .
- (6) Hupp, J. T.; Weaver, M. J. *Inorg. Chem.* **1983**, *22*, 2557.
- (7) MacCartney, D. H.; Sutin, N. *Inorg. Chem.* **1983**, *22*, 3530.
- (8) Sutin, N. "Inorganic Reactions and Methods"; Zuckerman, J. J., Ed.; Springer-Verlag: West Berlin; in press.

(9) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(10) The fits in ref 1 and 3 appear to have been done graphically.⁴

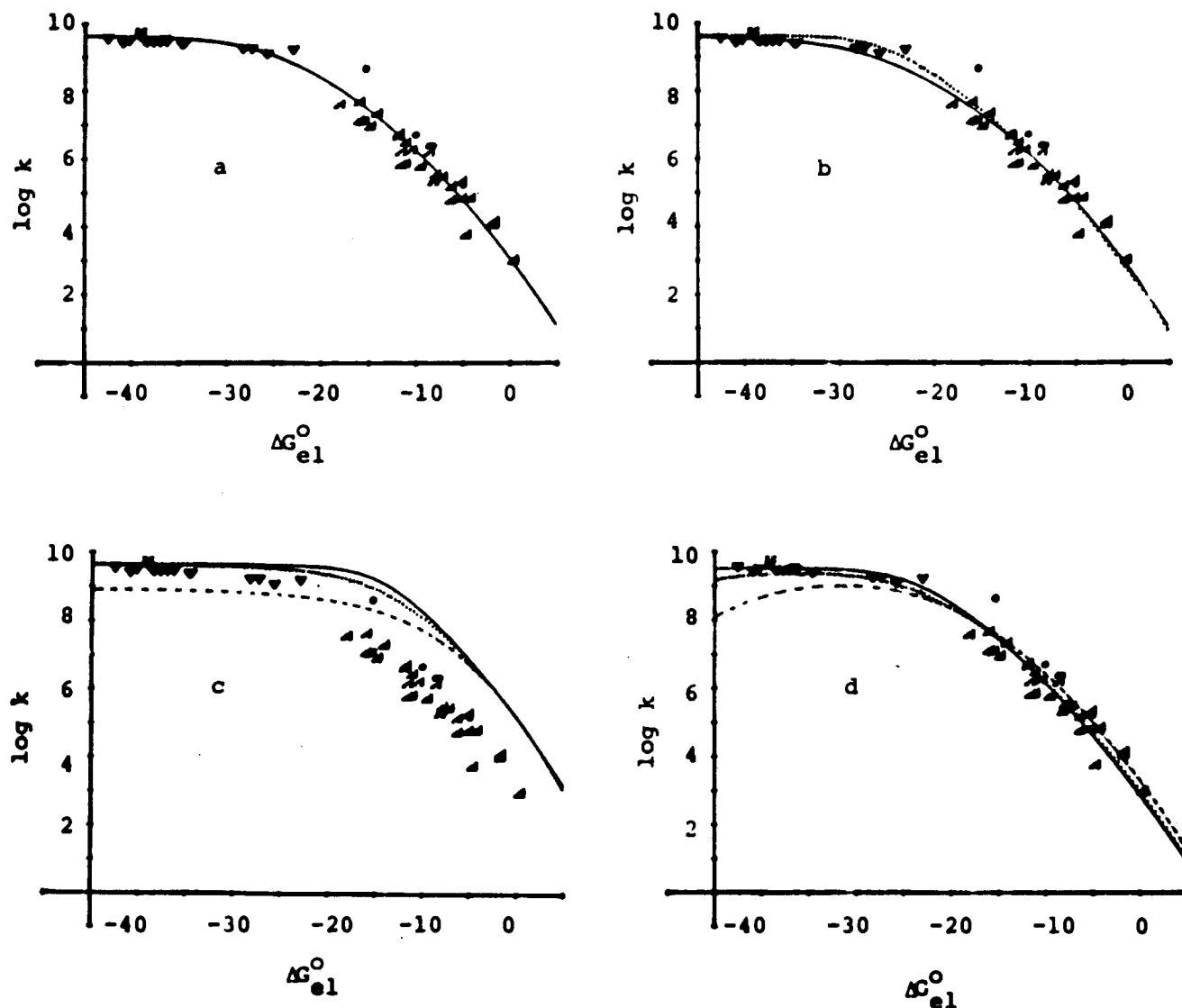


Figure 1. Plots of $\log k$ vs. ΔG_{e1}° for redox reactions of the $\text{Fe}^{3+/2+}$ couple: (a) solid line, calculated¹ from eq 8 with $k_d = 4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{-d} = 2.8 \times 10^9 \text{ s}^{-1}$, $\Delta G_{11}^{\circ} = 17.4 \text{ kcal/mol}$, $\kappa_{11} = 2.5 \times 10^{-3}$, $\Delta G_{22}^{\circ} = 6.0 \text{ kcal/mol}$, and $\kappa_{22} = 1$; (b) dashed line, calculated from same equation and same parameters as in part a except $\Delta G_{11}^{\circ} = 15.7 \text{ kcal/mol}$ and $\kappa_{11} = 1.4 \times 10^{-4}$; solid line, same as dashed line except $\Delta G_{11}^{\circ} = 21.4 \text{ kcal/mol}$ and $\kappa_{11} = 1$; (c) solid line, same as in part a except $\Delta G_{11}^{\circ} = 15.2 \text{ kcal/mol}$ and $\kappa_{11} = 1$; dashed line, same as in part a except $\Delta G_{11}^{\circ} = 9.7 \text{ kcal/mol}$ and $\kappa_{11} = 1 \times 10^{-4}$; dotted line, same as in part a except $\Delta G_{11}^{\circ} = 4.3 \text{ kcal/mol}$ and $\kappa_{11} = 1 \times 10^{-8}$; (d) solid line, calculated from eq 11 and parameters given in text; dotted line, same as solid line except $\Delta G_{11}^{\circ} = 12.4 \text{ kcal/mol}$ and $\kappa_{11} = 1 \times 10^{-2}$; dashed line, same as solid line except $\Delta G_{11}^{\circ} = 9.7 \text{ kcal/mol}$ and $\kappa_{11} = 1 \times 10^{-4}$. Symbols: \blacktriangledown , reactions of Fe^{3+} with Cr(II), Ru(II), and Os(II) polypyridine complexes; \blacktriangle , reactions of Fe^{2+} with Fe(III), Ru(III), Os(III), and Cr(III) polypyridine complexes; \bullet , reactions of Fe^{3+} with Ru(II) ammine complexes.

in the mildly nonadiabatic regime ($\kappa_{12} > 10^{-3}$). The homogenized^{1,11} rate constants for the $\text{Fe}^{3+/2+}\text{-ML}_3^{3+/2+}$ system are plotted vs. ΔG_{e1}° in Figure 1a, together with the curve calculated from eq 6 and 8 and the reported¹ values of the necessary parameters. Note that κ_{11} was fixed at 2.5×10^{-3} (cf. below) and ΔG_{11}° was adjusted for a best fit.¹ It will be seen that indeed a reasonably good fit was obtained.¹ However, an equally good fit is obtained (Figure 1b, dashed line) with $\Delta G_{11}^{\circ} = 15.7 \text{ kcal/mol}$ and $\kappa_{11} = 1.4 \times 10^{-4}$, the values derived from a nonlinear least-squares fit of $\log k$ to eq 8 keeping all the parameters constant except ΔG_{11}° and κ_{11} . Similarly, a good fit is obtained (Figure 1b, solid line) by fixing κ_{11} at 1 and floating only ΔG_{11}° .¹²

Next we show that Balzani's choice of $\kappa_{11} = 2.5 \times 10^{-3}$ for the self-exchange reaction of the $\text{Fe}^{3+/2+}$ couple is based on a misinterpretation of a reported¹³ electronic factor. The measured¹³

entropies of activation for the $\text{Ru}(\text{NH}_3)_5\text{L}^{2+}\text{-Fe}^{3+}$ reactions (L = nicotinamide or isonicotinamide) were found to be ~ 6 eu more negative than calculated from eq 9^{14,15} under the assumption that

$$\Delta S_{12}^{\ddagger} = 0.5(\Delta S_{11}^{\ddagger} + \Delta S_{22}^{\ddagger} + \Delta S_{12}^{\circ}) + R \ln (\kappa_{12}/(\kappa_{11}\kappa_{22}))^{1/2} \quad (9)$$

the last term in eq 9 is zero. From the entropy defect, Taube et al. inferred that, if the self-reactions are adiabatic, the cross-reactions are nonadiabatic with $\kappa_{12} \sim 0.05$.¹³ Balzani and co-workers¹ utilized the latter value, $\kappa_{22} = 1$, and eq 7 to calculate $\kappa_{11} = 2.5 \times 10^{-3}$ for the $\text{Fe}^{3+/2+}$ self-exchange. However, it is evident that if eq 7 were obeyed, there would be no entropy defect. All that can be inferred by comparing measured and calculated entropy of activation is that the cross-reaction is more nonadiabatic than predicted on the basis of eq 7, and therefore it is inappropriate

(11) For a series of homogeneous reagents, the observed rate constants are corrected ("homogenized") for any differences in the charges and sizes of the reagents and for ionic strength.¹

(12) In general the third term in the denominator of eq 8 is negligible, and for highly exoergic reactions the second term reduces to $k_{-d}h/k_bT \cdot (\kappa_{11}\kappa_{22})^{1/2}$. With $k_{-d} \sim 2 \times 10^9 \text{ s}^{-1}$ and $\kappa_{22} = 1$, the contribution of this term is 20% for $\kappa_{11} = 3 \times 10^{-6}$.

(13) Brown, G. M.; Krentzien, H. J.; Abe, M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 3374.

(14) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213.

(15) This equation includes the nonadiabaticity of exchange and cross-reactions⁸ but neglects the α^2 factor, which is ~ 0.01 for the reactions under consideration.

to utilize the latter equation to calculate the electronic factor for the $\text{Fe}^{3+/2+}$ self-exchange.

Finally we comment on the discrepancy between the rate constant for self-exchange of the $\text{Fe}^{3+/2+}$ couple calculated from eq 1 ($2.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ by taking¹⁶ $k_d/k_{-d} = 0.09 \text{ M}^{-1}$ and introducing the reported^{1,17} values of κ_{11} and ΔG_{11}^\ddagger) and the experimental¹⁸ value $4.5 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and ionic strength 0.55 M . We regard any treatment of cross-reactions that is incompatible with the independently measured self-exchange rate constants¹⁹ and does not explain the discrepancy as suspect. Moreover, if the measured rate constant for the self-exchange reaction of the $\text{Fe}^{3+/2+}$ couple is introduced in eq 8, totally unacceptable fits are obtained (Figure 1c) regardless of how the measured value of k_{11} is apportioned between κ_{11} and ΔG_{11}^\ddagger .

Similar criticisms can be raised with the treatment of the $\text{Co}(\text{bpy})_3^{3+/2+}$, $\text{Co}(\text{phen})_3^{3+/2+}$, $\text{Co}(\text{en})_3^{3+/2+}$, and $\text{Co}(\text{NH}_3)_6^{3+/2+}$ reactions,³ except that the situation is even more unsatisfactory because there are few available reactions with homogeneous reagents. In this context, it is important to point out that the homogenization procedure utilized for nonhomogeneous reagents (e.g., they have ΔG_{22}^\ddagger and/or κ_{22} values different from those for the homogeneous series) requires a knowledge of either ΔG_{11}^\ddagger or κ_{11} for the couple under consideration.²⁰ Then, the other (unknown) parameter is obtained from eq 6 and 8. The homogenized rate constant is then calculated from eq 6 and 8 by utilization of the known and obtained parameters for couple 1 and the ΔG_{22}^\ddagger and κ_{22} values appropriate to the homogeneous series of reagents. Finally, all rate constants are fitted to eq 6 and 8 in order to extract values of ΔG_{11}^\ddagger and of κ_{11} . There are several objections. First, any experimental approach that yields ΔG_{11}^\ddagger or κ_{11} must certainly yield a value of k_{11} as well, and therefore both parameters would be known to begin with. Second, the homogenized rate constants for nonhomogeneous reagents (which are calculated by utilizing the known ΔG_{11}^\ddagger and κ_{11}) are treated¹ (in conjunction with the rate constants for the homogeneous reagents) to obtain ΔG_{11}^\ddagger and κ_{11} . But since the latter are "built in" in some of the constants to be treated, we have the elements of a circular reasoning. Finally, it is noteworthy that the homogenized rate constants for the nonhomogeneous reagents lie systematically above (see circles in Figure 1) the values for the homogeneous reagents. As will be seen below, this is probably a manifestation of the breakdown of eq 7.

The Marcus-Sutin Approach Corrected for Nonadiabaticity.

It is possible to reconcile the measured self-exchange rate constants for the $\text{Fe}^{3+/2+}$ couples and for the homogeneous reagents with

the rate constants for the cross-reactions by allowing for nonadiabaticity but without requiring that eq 7 be obeyed. Since there is evidence for the inverted region,²¹ we prefer to use the Marcus relationship (eq 10). Introduction of eq 5 and 10 into eq 3 yields

$$\Delta G_{12}^\ddagger = 0.5(\Delta G^\ddagger(0) + \Delta G_{\text{el}}^\circ) + (\Delta G_{\text{el}}^\circ)^2/16\Delta G^\ddagger(0) \quad (10)$$

eq 11. The rate constants for the reactions of the $\text{Fe}^{3+/2+}$ with

$$k = k_d \left\{ 1 + \frac{k_{-d}h}{k_b T \kappa_{12}} \exp[0.5(\Delta G^\ddagger(0) + \Delta G_{\text{el}}^\circ) + (\Delta G_{\text{el}}^\circ)^2/16\Delta G^\ddagger(0)]/RT + \exp(\Delta G_{\text{el}}^\circ/RT) \right\} \quad (11)$$

the series of homogeneous reagents were fitted (nonlinear least-squares) to eq 11 by taking $k_d = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (the average of the values of k at high exoergonicity), $k_{-d} = 2.2 \times 10^9 \text{ s}^{-1}$, $\Delta G_{11}^\ddagger = 15.2 \text{ kcal/mol}$ (calculated from eq 1 with $k_{11} = 4.5 \text{ M}^{-1} \text{ s}^{-1}$, $\kappa_{11} = 1$, and $k_d/k_{-d} = 0.09 \text{ M}^{-1}$), $\Delta G_{22}^\ddagger = 6 \text{ kcal/mol}$ and $\kappa_{22} = 1$ and by floating κ_{12} (resulting best-fit value 5.2×10^{-3}). It will be seen (Figure 1d, solid line) that an entirely satisfactory fit is obtained.²² This fit is fairly sensitive to the choice of κ_{11} .²³ Thus, considerably poorer fits are obtained with $\kappa_{11} = 1 \times 10^{-2}$ (corresponding value of $\Delta G_{11}^\ddagger = 12.4 \text{ kcal/mol}$) (dotted line) or with $\kappa_{11} = 1 \times 10^{-4}$ (corresponding value of $\Delta G_{11}^\ddagger = 9.7 \text{ kcal/mol}$) (dashed line). Our proposed interpretation stands in strong contrast with that of Balzani. In our interpretation, the self-exchange of the $\text{Fe}^{3+/2+}$ is taken to be adiabatic and the cross-reactions are nonadiabatic, whereas in Balzani's interpretation the $\text{Fe}^{3+/2+}$ self-exchange is taken to be nonadiabatic and the cross-reactions, because eq 7 is postulated¹ to be obeyed, turn out to be nonadiabatic. However, eq 7 has not been tested in systems where κ_{11} , κ_{22} , and κ_{12} are independently known, and its validity is open to question. For instance, it is possible for a cross-reaction to be nonadiabatic while one or both of the corresponding self-exchange reactions are adiabatic or vice versa.^{24,25} Moreover, for some reactions of Fe^{2+} with tris(polypyridine) complexes, it has been suggested⁷ that the electronic coupling for the exchange reactions is larger than that for the cross-reactions. In fact, the coupling between metal centers—and hence the value of the electronic factor—is a sensitive function of the distance between the metal centers, the extent of overlap between donor and acceptor orbitals, and perhaps the exoergonicity of the reaction; therefore, it is doubtful that eq 7 has general applicability. Turning to the Marcus-Sutin approach, for the homogeneous reagents under consideration, an approximately common value of κ_{12} in eq 11 is possible, but with nonhomogeneous reagents, values of κ_{12} are likely to exhibit substantial variations. Therefore, any treatment that requires a constant κ_{12} for a wide variety of reagents is unlikely to have any broad applicability.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE 8203887. A.H. is grateful

- (16) This is the value at 0.55 M ionic strength calculated from the Fuoss-Eigen equation. See, for example: Miralles, A. J.; Armstrong, R. E.; Haim, A. *J. Am. Chem. Soc.* **1977**, *99*, 1416.
- (17) Regardless of which pairs of values of κ_{11} and ΔG_{11}^\ddagger are utilized in eq 1, the calculated values are smaller than the experimental values. Thus, with the least-squares values $\kappa_{11} = 1.4 \times 10^{-4}$ and $\Delta G_{11}^\ddagger = 15.7 \text{ kcal/mol}$, $k_{11} = 2.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. With $\kappa_{11} = 1$ and $\Delta G_{11}^\ddagger = 21.4 \text{ kcal/mol}$ (solid curve in Figure 1b), $k_{11} = 1.1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$.
- (18) Silverman, J.; Dodson, R. W. *J. Phys. Chem.* **1952**, *56*, 846.
- (19) On the basis of theoretical considerations, it has been suggested that the measured rate constant for self-exchange of the $\text{Fe}^{3+/2+}$ couple includes contributions of interpenetration of the inner hydration shells to distances smaller than the 0.70-nm distance of closest approach: Tembe, B. L.; Friedman, H. L.; Newton, M. D. *J. Chem. Phys.* **1982**, *76*, 1490. Under these circumstances, the experimental value of the self-exchange rate constant would be inappropriate for making comparisons of genuine outer-sphere cross-reactions where the iron contact radius is 0.35 nm , and a smaller, "effective" outer-sphere rate constant would be applicable. The hypothesis of interpenetration of the inner-coordination shells in the self-exchange reaction but not in cross-reactions serves to rationalize the observation that cross-reactions of the $\text{Fe}^{3+/2+}$ couple are more nonadiabatic than the component self-exchange reactions. However, note that the discrepancy between experimental and fitted values applies also to $\text{Co}(\text{bpy})_3^{3+/2+}$, $\text{Co}(\text{phen})_3^{3+/2+}$, and $\text{Co}(\text{en})_3^{3+/2+}$, where interpenetration of the inner-coordination shells is precluded.
- (20) In the first paper,¹ the authors indicate that the homogenization of reactions of the $\text{Eu}^{3+/2+}$ couple could not be carried out because independent values of κ_{11} and ΔG_{11}^\ddagger were not known. In the second paper,³ homogenization of reactions of the $\text{Co}(\text{NH}_3)_6^{3+/2+}$, $\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+/2+}$, $\text{Co}(\text{en})_3^{3+/2+}$, $\text{Co}(\text{bpy})_3^{3+/2+}$, and $\text{Co}(\text{phen})_3^{3+/2+}$ couples were performed, but it is not apparent to us where the necessary values of κ_{11} or ΔG_{11}^\ddagger were obtained.

- (21) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.
- (22) Hupp and Weaver⁶ have presented an interesting treatment of cross-reactions of the $\text{Fe}^{3+/2+}$ couple. Under the assumption that the cross-reactions obey the adiabatic Marcus relationship but that the effective outer-sphere rate constant for self-exchange is $7.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (rather than the experimental value $4.5 \text{ M}^{-1} \text{ s}^{-1}$), they have obtained a satisfactory fit between experimental and calculated rate constants for a wide variety of cross-reactions involving $\text{Fe}^{3+/2+}$. Since the "effective" outer-sphere rate constant was considerably smaller than the measured value, they made the suggestion that the latter represents an inner-sphere, water-bridged pathway. However, such pathways are very unlikely, if not precluded (Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264) and the experimental value of the self-exchange rate constant is taken to represent the outer-sphere pathway.
- (23) However, the resulting value of κ_{12} should not be taken literally. The rate constants were measured at high sulfate ion concentrations and may contain contributions of sulfate-dependent pathways.
- (24) Przystas, T. J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, *95*, 5545.
- (25) Endicott, J. F.; Ramasami, T.; Gaswick, D. G.; Tarnilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301.

to Dr. N. Sutin for several helpful discussions.

Department of Chemistry
State University of New York
Stony Brook, New York 11794

Urs Führoz
Albert Haim*

Received February 11, 1985

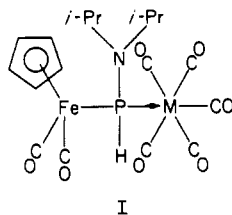
Synthesis of Heterobimetallic Complexes from Metal Carbonyl Complexes of Bis(diisopropylamino)phosphine

Sir:

Recently we reported¹ the facile and selective cleavage of one diisopropylamino group from the bis(diisopropylamino)phosphine metal carbonyl complexes $(i\text{-Pr}_2\text{N})_2\text{PHM}(\text{CO})_n$ ($i\text{-Pr}$ = isopropyl; $n = 5$, $M = \text{Cr}$, Mo , and W ; $n = 4$, $M = \text{Fe}$) with hydrogen halides HX ($X = \text{Cl}$ and Br) to give the corresponding metal carbonyl complexes $i\text{-Pr}_2\text{NP}(\text{H})\text{XM}(\text{CO})_n$. We have now found that reactions of these latter complexes with the strongly nucleophilic² metal carbonyl anion $\text{CpFe}(\text{CO})_2^-$ provide a route to novel heterobimetallic complexes containing a bridging $i\text{-Pr}_2\text{NPH}$ phosphido group having potentially reactive P-H and P-N bonds. The complexes initially formed in such reactions in at least three cases undergo facile single decarbonylation reactions with formation of a heteronuclear metal-metal bond. These complexes therefore provide a direct indication of the effects of metal-metal bond formation on the properties of phosphido complexes. Related heterobimetallic diphenylphosphido chemistry, involving however totally different preparative methods, was reported in 1971 by Yasufuku and Yamazaki.³

A tetrahydrofuran solution of $\text{NaFe}(\text{CO})_2\text{Cp}$ freed from excess sodium amalgam⁴ was treated at -78°C with a stoichiometric amount of $i\text{-Pr}_2\text{NP}(\text{H})\text{XM}(\text{CO})_5$ ($M = \text{Cr}$, $X = \text{Br}$; $M = \text{Mo}$ and W , $X = \text{Cl}$). After the mixture was stirred overnight at room temperature, the solvent was removed in vacuum. The residue was extracted with pentane. Filtration, concentration, and cooling the pentane extracts gave orange-brown crystals of the corresponding $\text{CpFe}(\text{CO})_2\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)\text{M}(\text{CO})_5$ derivative (Table I).

These complexes appear to have structures I ($M = \text{Cr}$, Mo , W) containing an intact $\text{CpFe}(\text{CO})_2$ unit and no heteronuclear metal-metal bond. Their infrared spectra in the $\nu(\text{CO})$ region



I

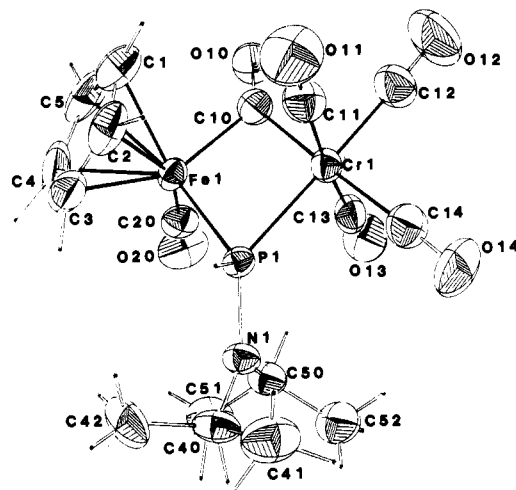
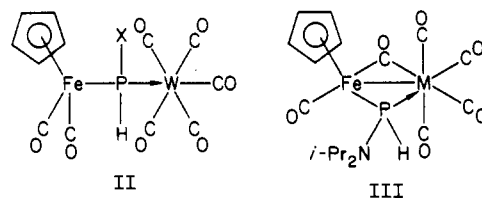


Figure 1. ORTEP diagram of the complex $\text{CpFeCr}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$ (III, $M = \text{Cr}$).

(Table I) exhibit no bridging carbonyl frequencies, and among the terminal carbonyl frequencies, two (e.g., those at 1970 and 1920 in $\text{CpFe}(\text{CO})_2\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)\text{Cr}(\text{CO})_5$) can be assigned to the $\text{CpFe}(\text{CO})_2$ unit, with the pattern of the remaining $\nu(\text{CO})$ frequencies corresponding to that expected for the $\text{M}(\text{CO})_5$ group. A property of $\text{CpFe}(\text{CO})_2\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)\text{W}(\text{CO})_5$ (I, $M = \text{W}$) of chemical interest is the cleavage of its remaining diisopropylamino group by hydrogen halides HX ($X = \text{Cl}$ and Br) in hexane solution to give the corresponding brown crystalline derivatives $\text{CpFe}(\text{CO})_2\text{PHXW}(\text{CO})_5$ (II, $X = \text{Cl}$ and Br).



II

III

The most interesting chemical property of the complexes $\text{CpFe}(\text{CO})_2\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)\text{M}(\text{CO})_5$ ($M = \text{Cr}$ and W) is their facile photochemical decarbonylation to give the corresponding complexes $\text{CpFeM}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$, shown by X-ray crystallography to have structures III ($M = \text{Cr}$ and W) containing a heteronuclear metal-metal bond. Thus a red-orange pentane solution of $\text{CpFe}(\text{CO})_2\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)\text{M}(\text{CO})_5$ becomes deep brown after only 5 min of ultraviolet irradiation. Evaporation of solvent from the filtered pentane solution after 10 min of irradiation followed by recrystallization from hexane gave black $\text{CpFeCr}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$. The structure III ($M = \text{Cr}$) of this complex was suggested by the observation of a bridging $\nu(\text{CO})$ frequency at 1811 cm^{-1} (Table I) in addition to several terminal $\nu(\text{CO})$ frequencies. This unusual structure was subsequently confirmed by X-ray diffraction. Our initial infrared spectra of the tungsten analogue $\text{CpFeW}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$ failed to exhibit its bridging $\nu(\text{CO})$ frequency. We therefore also determined the structure of $\text{CpFeW}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$ by X-ray diffraction. After this structure determination indicated that $\text{CpFeW}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$ had structure III ($M = \text{W}$) completely analogous to $\text{CpFeCr}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$, we reran the infrared spectrum in much more concentrated solution and found the expected bridging $\nu(\text{CO})$ frequency around 1800 cm^{-1} , which was much weaker than that of its chromium analogue.

The structures of $\text{CpFeM}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$ ($M = \text{Cr}$ and W) indicate that the iron is bonded to a terminal carbonyl group and pentahapto bonded to a cyclopentadienyl ring and that the other metal M is bonded to four terminal carbonyl groups. The iron and M atoms are within bonding distances ($\text{Fe-Cr} = 2.733(2)\text{ \AA}$ in $\text{CpFeCr}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$ and $\text{Fe-W} = 2.827(4)\text{ \AA}$ in $\text{CpFeW}(\text{CO})_6\text{P}(\text{H})(N\text{-}i\text{-Pr}_2)$). These metal-metal bonds are bridged by a carbonyl group ($\text{Fe-C} = 2.023(9)$, $\text{Cr-C} = 2.023$

- King, R. B.; Fu, W.-K. *J. Organomet. Chem.* **1984**, 272, C33.
- Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, 88, 5121.
- Yasufuku, K.; Yamazaki, H. *J. Organomet. Chem.* **1971**, 28, 415.
- King, R. B. *Acc. Chem. Res.* **1970**, 3, 417.
- The compounds $\text{FeMC}_{17}\text{H}_{20}\text{O}_6\text{NP}$ ($M = \text{Cr}$ and W) are isomorphous, forming monoclinic crystals of space group $P2_1/c$ with $Z = 4$. For $M = \text{Cr}$: $a = 14.362(5)\text{ \AA}$, $b = 7.733(2)\text{ \AA}$, $c = 19.244(8)\text{ \AA}$, $\beta = 104.00(3)^\circ$, $V = 2073.8(12)\text{ \AA}^3$, $D_{\text{calcd}} = 1.515\text{ g/cm}^3$. For $M = \text{W}$: $a = 14.491(5)\text{ \AA}$, $b = 7.808(2)\text{ \AA}$, $c = 19.456(8)\text{ \AA}$, $\beta = 103.17(3)^\circ$, $V = 2143.6(12)\text{ \AA}^3$, $D_{\text{calcd}} = 1.874\text{ g/cm}^3$. Data (5734 points for $M = \text{Cr}$ and 5929 points for $M = \text{W}$) were collected at room temperature by using molybdenum $K\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$), a variable scan rate, a θ - 2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° below $K\alpha_2$ to a maximum 2θ value of 116° . Data were corrected for Lorentz, polarization, and background effects. After removal of redundant data and space group forbidden data, 2414 ($M = \text{Cr}$) and 2271 ($M = \text{W}$) reflections were considered observed [$I > 3.0\sigma(I)$]. The final agreement factors, R , after successive least-squares/different Fourier cycles were 5.3% for $M = \text{Cr}$ and 6.8% for $M = \text{W}$.