gaps are achieved in nearly planar transoid geometries. A detailed interpretation of the azulene effect would then involve eq 6-8, where brackets designate exciplexes

$$^{s}p + Az \stackrel{ks}{\longleftarrow} ^{s}[pAz]$$
 (6)

$${}^{\mathfrak{s}}[\mathsf{p}\mathsf{A}\mathsf{z}] \stackrel{k_{7}}{\rightleftharpoons} {}^{\mathfrak{s}}[\mathsf{t}\mathsf{A}\mathsf{z}] \tag{7}$$

$${}^{3}[tAz] \xrightarrow{\wedge 3} t + {}^{3}Az \qquad (8)$$

or encounter complexes.¹³ Accordingly, k'_{sz} in eq 3 is replaced by the expression in eq 9, which reduces to

$$k'_{az} = \frac{k_{b}K_{7}(k_{8}/k_{-6})}{(k_{8}K_{7}/k_{-6}) + k_{8}/k_{-7} + 1}$$
(9)

eq 10 assuming that k_6 , k_{-6} , and k_8 are diffusion con-

$$k'_{az} = k_{dif} K_7 / (1 + K_7)$$
(10)

trolled and that equilibration step 7 is faster than diffusional separation of the donor-acceptor pair. This mechanism accounts for the dependence of $k'_{az}\tau$ values on solvent viscosity,⁶ and, using $k_{dif} = 10^{10} M^{-1} \sec^{-1}$, gives $K_7 \simeq 0.04$ in benzene at 30°.

The deactivation of stilbene triplets by oxygen to either ground state isomer suggests that the 22 kcal/mol energy gap required in eq 2, if ${}^{1}\Delta_{g}$ oxygen is produced, is achieved with nearly unit efficiency by torsional displacement toward either transoid or cisoid geometries. The larger energy gaps required for excitation transfer to azulene and other quenchers are apparently achieved only by torsional displacement toward transoid geometries.

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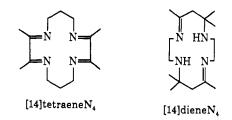
(13) For a related case see R. A. Caldwell, J. Amer. Chem. Soc., 92, 3229 (1970). (14) Fellow of the Alfred P. Sloan Foundation, 1971-1973.

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Structural Evidence for Variations in the Franck-Condon Barrier to Electron Transfer between Low-Spin Cobalt(II) and Cobalt(III)¹

Sir:

We recently reported² the discovery of a 0.5 Å cobaltaxial ligand distortion in low spin $Co([14]dieneN_4)$ - $(OH_2)_2^{2+}$, and we called attention to the fact that this distortion is of sufficient magnitude to account for the very small self-exchange rate constant of the Co([14]dieneN₄)(OH₂)₂³⁺-Co([14]dieneN₄)(OH₂)₂²⁺ couple $(k_{\text{exchange}} = 2 \times 10^{-7} M^{-1} \text{ sec}^{-1} \text{ at } 70^{\circ}).^{3.4}$ In their related kinetic study, Rillema, et al.,4 found the selfexchange rate for the $Co([14]tetraeneN_4)(OH_2)_2^{3+}$ $Co([14]tetraeneN_4)(OH_2)_2^{2+}$ couple to be at least 10⁶ larger than the comparable rate for the closely related couple with [14]dieneN4 equatorial ligands, and these authors cited some limited spectroscopic evidence for stronger association of axial ligands in Co¹¹([14]tetraeneN₄)X₂ complexes than in Co¹¹([14]dieneN₄)X₂ complexes. Since both these cobalt(II) complexes are low spin,⁵ the two couples provide a unique opportunity to investigate directly the correlation of inner ligand reorganizational barriers with the magnitudes of self-exchange rates for electron transfer reactions.⁶



We are now able to report structural results for [Co-([14]tetraeneN₄)(OH₂)₂] (ClO₄)₂ and [Co([14]tetraeneN₄)- $(NH_3)_2$]Br₃ and can compare the reorganizational barrier based on these results to that inferred previously for the $Co([14]dieneN_4)(OH_2)_2^{2+}$ couple. For the tetraene couple, the cobalt(II)-OH₂ bond distance is found to be 0.3 Å longer than the cobalt(III)-NH₃ distance. In both tetraene compounds all equatorial cobalt-N distances are equivalent indicating that the distortion is confined to the axial direction. Using Stranks' method,7.8 and appropriate estimates of force constants,⁸ we estimate an inner-sphere reorganizational energy of 7 ± 1 kcal/mol, significantly less than the similar barrier of 20 ± 1 kcal/mol estimated for the diene couple.² A difference of 14 kcal/mol is easily sufficient to account for the $>10^{6}$ -fold difference in selfexchange rates between the two couples. It has been noted⁹ that the neglect of zero point and thermal vibrational energies leads to a slight overestimate of the reorganizational energy barrier when the above procedure is used. However, the correction should be comparable in both the diene and tetraene couples and thus does not significantly affect the value of the difference.

Several conclusions can now be drawn. First, the unusually slow cobalt(II)-cobalt(III) self-exchange for the diene couple results from an unusually large difference in bond lengths between the oxidized and reduced complexes. Second, the contributions of inner-sphere reorganizational barriers to the observed chemical re-

(5) Determined at 35° in 1 *M* NaCl solutions, $\mu_{eff} = 1.82$ BM for ([14]tetraeneN₄)Co(II) and $\mu_{eff} = 1.86$ BM for ([14]dieneN₄)Co(II).

(6) For pertinent reviews see (a) R. G. Linck, MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Inorg. Chem., 9 (1), 303 1971; (b) A. G. Sykes, Advan. Inorg. Chem. Radiochem., 10, 153 (1967); (c) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution," Academic Press, New York, N. Y., 1970; (d) N. Sutin, "Inorganic Biochemistry," Vol. 2, G. L. Eichhorn, Ed., Elsevier, New York, N. Y., 1973, Chapter 19, 2, G. L. Element, Ed., Elsevier, New Fork, N. F., 1975, Chapter 19, p 611; (e) R. A. Marcus, Annu. Rev. Phys. Chem., 15, 155 (1964); (f) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1965. (7) D. R. Stranks, Discuss. Faraday Soc., 29, 116 (1960). (8) For $r^{\pm} = (k_{II}r_{II} + k_{III}r_{II})/(k_{II} + k_{III})$, in which k_{II} and k_{III}

are force constants for the cobalt(II)-OH2 and cobalt(III)-OH2 stretching vibrations, respectively. In the actual calculation we use $k_{\rm II} \simeq 0.7 \times 10^{\rm s} \, \rm dyn \, cm^{-1}$ and $k_{\rm III} \simeq 1.7 \times 10^{\rm s} \, \rm dyn \, cm^{-1}$ which are values for the respective cobalt-NH₃ vibrations and find $r^{\pm} = 2.05 \, \rm \AA$. The total energy may then be derived from $E_{\text{total}} = k_{\text{II}}(r_{\text{II}} - r^{\ddagger})^2 + k_{\text{III}}$ $(r_{\rm III} - r^{\pm})^2$

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reac-tions," Wiley, 2nd ed, 1967, p 458.

⁽¹⁾ Partial support of this research by the Public Health Service (Grant AM 14341) and the National Science Foundation (Grant GP-15070) is gratefully acknowledged.

⁽²⁾ M. D. Glick, J. M. Kuszaj, and J. F. Endicott, J. Amer. Chem. Soc., 95, 5097 (1973).
(3) Abbreviations: [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,-

¹¹⁻tetraazacyclotetradeca-4,11-diene; [14]tetra
eneN_4 = 2,3,9,10-tetra-methyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetra
ene plus other abbreviations from ref 8 and 9.

^{(4) (}a) D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire. J. Chem. Soc., Chem. Commun., 495 (1972); (b) manuscript in preparation.

activity can be correlated to a surprisingly high degree to axial distances. Third, structural data can provide meaningful insights into kinetic mechanisms by way of constrained model systems.

It is now necessary to summarize the detailed stereochemistry about the cobalt ions in the four closely related compounds. All of the molecules have crystallographically required $\overline{1}$ symmetry. In the dienes the equatorial Co-N bond distances are 1.977 (17) and 1.926 (16) A with the shorter distance corresponding to the imine Co-N and the longer to the amine Co-N; there is no significant difference between the two diene complexes. In the tetraene systems, the four equatorial nitrogens are all imines and show an average Co-N distance of 1.903 (20) Å with no systematic difference between the two oxidation states. Thus, in addition to equalization of the Co-N equatorial distances in the tetraene relative to the diene, there is some indication of an overall tightening. This may result from a relaxation of the framework due to four equivalent bonds.

The axial bond distances are 2.482(5) and 1.954(6) Å for the +2 and +3 dienes and 2.289 (13) and 1.972 (15) Å in the +2 and +3 tetraenes, respectively. The long bonds in the low spin +2 systems result from the unpaired electron in the antibonding d_{z^2} orbital. The dramatic difference in axial bond lengths between the cobalt(II) diene and cobalt(II) tetraene may have its origin in either steric or electronic effects. Although the nonplanar diene complexes might be thought to undergo more steric interactions (especially geminal methylwater) than the tetraenes, this argument is somewhat less compelling if we note that the planar low spin cobalt(II) porphyrin, Co(3-pic)2(OEP), shows a similar long axial Co-N distance (2.386 Å).¹⁰ Scheidt has also reported a 2.436 Å Co-N distance in Pip₂CoTPP.¹¹ Moreover, comparison of torsion angles in cobalt diene systems with those in other metallodiene complexes provides no evidence of strain. The possibility of electronic effects resulting from interaction with the highly symmetric tetraene ring can only be tested with detailed molecular orbital calculations.

Intensity data for both the Co(II) and Co(III) complexes of ([14]tetraeneN₄) were collected on a Syntex P2₁ diffractometer using Mo K α radiation to a 2θ of 45° . The Co^{II} complex crystallizes in $P2_1/a$ with cell parameters a = 11.58(1) Å, b = 14.542(9) Å, c = 6.939(5) Å, and $\beta = 94.64 (7)^{\circ}$; the Co^{III} complex crystallizes in $P2_1/c$ with cell parameters a = 17.829(3)Å, b = 9.656(1)Å, c = 18.220 (3) Å, and β = 133.11 (1)°. The Co(II) structure was solved by Patterson-Fourier techniques and refined by full-matrix least-squares procedures with isotropic thermal parameters for the macrocyclic atoms and anisotropic parameters for the remaining atoms. The perchlorate counterion showed considerable rotational disorder. The Co(III) solution was achieved by a combination of probability and Fourier techniques and refined by full-matrix least-squares procedures with all thermal motion treated anisotropically. In both structures the possibility of five-coordinate disorder models were considered and convincingly rejected. Final discrepancy factors were 0.076 for 507 data and

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(11) W. R. Scheidt, J. Amer. Chem. Soc., 96, 84 (1974): Pip₂Co-TPP = bis(piperidine)- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphinatocobalt(II). 0.067 for 1595 data for the Co^{II} and Co^{III} compounds, respectively.

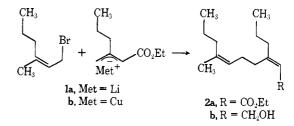
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Regioselectivity in the Alkylation of Lithium and Copper Ester Dienolates. An Allylic Transposition Associated with γ -Alkylation of Copper Dienolates

Sir:

Although dienolate anions, derived from α,β -unsaturated carbonyl compounds, undergo certain condensation reactions (Reformatsky,¹ Darzens,² and Aldol^{3,4}) selectively at the γ position, alkylation and protonation take place at the α position with high selectivity.^{5,6} Nevertheless, we were attracted to a γ alkylation approach to the synthesis of the novel codling moth alcohol, **2b**,⁷ because of its inherent simplicity.



In a model study, we found that the lithium dienolate 1a, formed by treatment of ethyl (*E*)-3-methyl-2-hexenoate (3)^{7b} with lithium diisopropylamide in THF, underwent alkylation with allyl bromide nearly exclusively at the α position, producing the isomeric esters 4a and 5a in a 95:5 ratio.⁸ The copper dienolate (1b)⁹ (from 3 by reaction with trityllithium and then cuprous iodide), however, gave substantially greater

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