molecular energy transfer occurs in these molecules, since (1) light emission occurs from the diphenylanthracene and acridone portions of the molecules, and (2) compounds III and IV are more efficient in light production than the parent compounds V and VI. Naphthalic hydrazide (V) itself chemiluminesces with low efficiency at 355 mμ in the aqueous system and at the same wavelength, but very weakly in DMSO. Compound III, on the other hand, shows strong emission at 425 and 440 mμ, the fluorescence wavelengths of diphenylanthracene, with only a weak emission at 355 mμ. A similar wavelength match was found in the DMSO system and also in the comparison of compound IV with N-methylacridone (Table I).

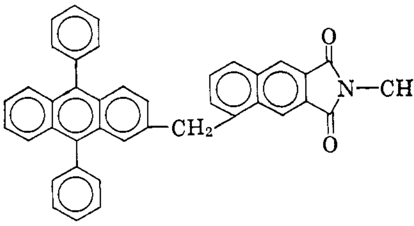
Table I. Comparison of Chemiluminescence and Fluorescence Wavelengths

	Wavelength maxima, mμ[a]	
	Aqueous system	90% dimethyl sulfoxide
A. Compound III		
Chemiluminescence of III	355,[b] 425, 440 (sh)	425, 440 (sh)
Fluorescence of total reaction products	355, 425, 440 (sh)	425, 440 (sh)
Fluorescence of 9,10-diphenylanthracene	425, 440 (sh)[c]	425, 440 (sh)
Fluorescence of disodium 2,3-naphthalenedicarboxylate	358	355[d]
B. Compound IV		
Chemiluminescence of IV	430, 450 (sh)	440
Fluorescence of total reaction products	430, 450 (sh)	440
Fluorescence of N-methylacridone	430, 450 (sh)[c]	440

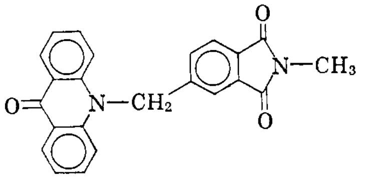
[a] Concentrations $<10^{-4}$ M; error ±3 mμ. [b] About 5% intensity of 425 mμ emission. [c] Dissolved initially in a small amount of ethanol to effect solution. [d] Extremely weak.

Concerning the quantum efficiencies, 4-methylphthalic hydrazide (VI) does not emit light in the aqueous system and naphthalic hydrazide is inefficient. Furthermore, a mixture of VI and N-methylacridone (10^{-4} M) does not yield light in the aqueous system, and a mixture of V and diphenylanthracene (10^{-4} M) yields no more light than a 10^{-4} M solution of V itself. Thus the intermolecular transfer of energy between the separate components is far less efficient than the intramolecular transfer in compounds III and IV at the concentrations used. In the water system the relative efficiencies of compounds VI, V, IV, and III in light production (relative to luminol at 100) are 0, 5, 8, and 26, respectively. Further improvements in the quantum yield should result from separate modifications at the energy production, transfer, and emission stages.

Syntheses.[5] N-Methyl-2,3-naphthalenedicarboimide was chloromethylated with bis(chloromethyl) ether and chlorosulfonic acid to give N-methyl-5-chloromethyl-2,3-naphthalenedicarboimide, mp 225–227° (the substitution pattern was determined by nmr spectroscopy). This material was allowed to react with 9,10-diphenylanthracene at 160° (with zinc in nitrobenzene) to give N-methyl-5-(9,10-diphenyl-2-anthracylmethylene)-2,3-naphthalenedicarboimide (VII), mp 259–261°.[6] Reaction of this imide with 95% hydrazine then gave hydrazide III, mp 252–256°. For the synthesis of compound IV, N,4-dimethylphthalimide was treated with NBS (or Br_2) and light to give the 4-bromomethyl compound, mp 129–131°. A condensation with the anion of acridone, prepared with NaH, gave 4-(9-acridonyl-10-methylene)-N-methylphthalimide (VIII), mp 291–293°. This imide was converted to hydrazide IV (mp 290° dec) with hydrazine.



VII



VIII

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[5] All compounds gave satisfactory analyses and spectral data.

[6] Friedel–Craft reactions of diphenylanthracene occur at the 2 position (R. G. Douris, *Compt. Rend.*, **229**, 224 (1949)).

The Effect of Nonbridging Ligands on the Rate of Electron-Transfer Reactions

Sir:

The effect of nonbridging ligands on the rate of electron-transfer reactions has been the subject of several recent investigations.[1-5] The results of these experiments have been interpreted on the basis of a model originally proposed by Orgel[6] and developed by Haim and co-workers.[1] According to this model, a variation in the nonbridging ligands leads to two effects that change the rate of electron transfer to a Co(III) or Cr(III) complex: the relative stabilization of the d_{z^2} orbital, and the ease with which the ligand *trans* to the bridge can be stretched. Benson and Haim proposed[1] that the ligand field strength of the variable ligand and the ease of aquation of the complex, respectively, could be used as a measure of these two

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[1] P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965), and references therein.

[2] R. D. Cannon and J. E. Earley, *ibid.*, **87**, 5264 (1965); **88**, 1872 (1966).

[3] A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

[4] D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966).

[5] There are numerous earlier papers that have found rate laws containing an anion path that is reasonably attributed to a nonbridging ligand effect, but the lability of the systems makes the interpretation of these results ambiguous.

[6] L. E. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p 289.

Table I. The Reduction of *cis*-$[Co(en)_2ClX]^{2+}$ by Fe^{2+} (25°, $\Sigma[ClO_4^-] = 1.0\ M$)

X	[Co(III)] $\times 10^3$, *M*	[Fe(II)], *M*	$[H^+]$, *M*	No. of expts	$k \times 10^4$, $M^{-1}\ sec^{-1}$	pK^a	λ_{max}, A	ϵ
NH_3					0.18[b]	9.26	5230[b]	70.5[b]
3,5-$(CH_3)_2$py	1.66–2.44	0.110–0.192	0.628–0.791	3	4.62 ± 0.23	6.15	5250	79.5
3-(CH_3)py	1.99–3.52	0.055–0.192	0.628–0.893	4	5.80 ± 0.38	5.66	5230	83.0
py	2.50–3.18	0.110–0.165	0.444–0.793	5	7.88 ± 0.14	5.17	5230	80.6
3-Clpy	1.65–2.18	0.081–0.196	0.652–0.827	6	20.1 ± 0.05	2.84	5200	77.3

[a] A. Albert, "Physical Methods in Heterocyclic Chemistry," Vol. 1, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, p 1. [b] Reference 1.

effects. Considering the nature of the d_{z^2} orbital (in octahedral complexes it is capable of only σ bonding), we felt that a better measure of the relative stabilization of this orbital would be the σ-bonding strength of the variable ligand.[7] We report here a test of the hypothesis that within a series of complexes chosen to minimize variation of other effects (steric, $\Delta F°$) the change in rate of reduction is proportional to the σ-bonding ability of the variable nonbridging ligand.

Haim and co-workers have studied several reductions of *cis* and *trans* Co(III) complexes by Fe(II);[1] although ideally the ligand field strengths of their ligands can be broken down into a σ and π contribution,[8] and corrections can be made for variation in steric factors and changes in $\Delta F°$, there are not at present sufficient data to allow this to be done with any rigor. We therefore chose to study reactions in which an independent measure of the σ bonding strength of the nonbridging ligand was available and in which neglect of other factors could be justified. These criteria were met by studying the rate of reduction of $Co(en)_2ClX^{2+}$, where X is changed from ammonia[1] to pyridine or substituted pyridine derivatives. The acidity of the conjugate acid of X can then be taken as a measure of the σ-bonding ability of the ligand X. The test would be most rigorous if the reduction of the *trans* isomers were studied, but synthesis of these compounds for X = pyridine has not been successful. Therefore, we report the results of the reduction of the corresponding *cis* isomers.[9]

The pyridine and methyl-substituted pyridine complexes were prepared by the literature procedure[10] from *trans*-$[Co(en)_2Cl_2]Cl$.[11] $[Co(en)_2(Clpy)Cl](ClO_4)_2$ was prepared by treatment of *trans*-$[Co(en)_2ClN_3]ClO_4$[12] with $NOClO_4$[13] in triethyl phosphate followed by addition of Clpy and gentle heating (about 40°) for 10 hr.[14] All complexes were recrystallized from perchlorate ion solution. Analysis of the compounds indicated pure products. The complexes were assigned the *cis* configuration on the basis of the value of the extinction coefficients of their ligand-field absorption bands[15] (Table I). The rate of the reduction was followed with a Zeiss Model PM QII spectrophotometer equipped with a thermostated cell compartment. All solutions were degassed with oxygen-free nitrogen; reactions were carried out in absorption cells fitted with serum caps, and syringe techniques were used to transfer Fe(II) solutions. All kinetic results were consistent with the rate law

$$\text{rate} = k[\text{Co(III)}][\text{Fe(II)}]$$

and no dependency on the acidity of the solutions was found. The results of the kinetic experiments are given in Table I.

In order to test the applicability of the model of Benson and Haim, we need to establish two criteria:[16] (1) the ligand field strength of ammonia and pyridine are the same; (2) the rates of aquation of the corresponding complexes, *cis*-$[Co(en)_2ClX]^{2+}$, do not differ significantly. Although the available data are limited, they indicate that the ligand field strength of pyridine is equal to that of NH_3.[17] Further, in those studies that have used substituted pyridines as ligands, there seems to be no trend of ligand field strength with the acidity of the conjugate acid of the ligand[18] (there is σ–π compensation). The data available on the rate of aquation are at different temperatures and thus not strictly comparable. However, with reasonable values of activation parameters, the two rate constants are found to be very similar.[19a,b] All evidence thus points to the expectation that the model proposed by Benson and Haim should yield comparable rate constants for the reduction of the NH_3 and pyridine complexes. In fact, they differ by a factor of about 45; indeed, the rate of reduction of the corresponding aquo complex is slower than that of the pyridino complex by a factor

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(7) In addition, the data of M. Green, K. Schug, and H. Taube (*Inorg. Chem.*, 4, 1184 (1965)) indicate that in the reduction of $Co(en)_2NH_3X^{n+}$ by Cr(II) there is no preferential stretching of the *trans* ligand.

(8) D. S. McClure, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 498.

(9) In these *cis* isomers, the octahedral wave functions $d_{x^2-y^2}$ and d_{z^2} are no longer eigenfunctions of the system; they mix under the influence of the lowering of symmetry. Nevertheless both mixed wave functions are changed in energy by a change in the σ component of the ligand field of X. In the *trans* isomers, the energy of only one orbital (d_{z^2}) is changed; therefore, although both *cis* and *trans* isomers will test the theory, the differences in rate constants would be expected to be larger in the case of the *trans* isomers.

(10) J. C. Bailar, Jr., and L. B. Clapp, *J. Am. Chem. Soc.*, 67, 171 (1945).

(11) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

(12) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

(13) G. Brauer, "Handbuch der Preparativen Chemie," F. Enke Verlag, Stuttgart, 1954, p 253.

(14) See R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966), for the general procedure.

(15) R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956); T. Yasui and Y. Shimura, *Bull. Chem. Soc. Japan*, **36**, 1286 (1963); S. C. Chan and F. Leh, *J. Chem. Soc., Sect. A*, 760 (1966).

(16) Benson and Haim assumed that the reduction of the complexes was by the inner-sphere mechanism. Although we follow this assumption, it is not necessary for the application of either their theory or ours; the same requirements for relative orbital energy pertain in the outer-sphere mechanism. For further support of the inner-sphere mechanism, see A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 5343 (1966).

(17) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965); C. K. Jørgenson, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, pp 111, 295; S. A. Johnson and F. Basolo, *Inorg. Chem.*, 1, 925 (1962).

(18) A. B. P. Lever, S. M. Nelson, and T. M. Shepherd, *ibid.*, **4**, 810 (1965); S. M. Nelson and T. M. Shepherd, *ibid.*, **4**, 813 (1965).

(19) (a) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, 78, 709 (1956); (b) F. Basolo, J. G. Bergmann, R. E. Meeker, and R. G. Pearson, *ibid.*, **78**, 2676 (1956); (c) S. C. Chan, *J. Chem. Soc.*, 5137 (1963).

of 2, although the ligand field strength of water is certainly less than that of pyridine, and the rate of aquation[19c] of the aquo complex is equal to or faster than that of the pyridino complex.

The hypothesis we put forth above is supported by the data. Ammonia and the series of substituted pyridines have roughly the same ligand field strength,[18] although that of Clpy may be slightly lower. However, the value of the σ bonding strength of the ligands, as measured by the acidity of the conjugate acids,[20] decreases along the series $NH_3 > 3,5\text{-}(CH_3)_2py > 3\text{-}(CH_3)py > py > 3\text{-}Clpy$. These data indicate that the rate constant increases in direct response to the lower σ-bonding power of the variable nonbridging ligand.

The factors that influence the change in rate constant as nonbridging ligands are varied are numerous; it is clear that our hypothesis is not sufficient to account for all of the effects,[21] but we believe that there are many systems where the determining factor will be the σ-bonding strength of the nonbridging ligands. We are currently expanding the scope of these studies to include other cases in order to test more rigorously the hypothesis.

Acknowledgments. We wish to thank the Academic Senate of the University of California, San Diego, and the National Institutes of Health (Grant GM 14830) for financial support; and Professor J. Watson for helpful discussions. C. B. wishes to acknowledge financial support from Consejo de Desarrollo Cientifico y Humanistico de la Universidad Central, Caracas, Venezuela.

(20) That the σ bonding strength of the ligand is proportional to the p*K* of the corresponding conjugate acid of the ligand can be supported. There are some electronic configurations that can yield values of the relative σ bonding strength of ligands by McClure's treatment. One of these involves high-spin complexes of Fe(II). Data taken from a study of the spectra of such complexes indicate a roughly linear correlation between the relative σ bonding power of the substituted pyridine and the acidity of its conjugate acid: D. M. L. Goodgame, M. Goodgame, M. A. Hitchman, and M. J. Weeks, *Inorg. Chem.*, **5**, 635 (1966).

(21) The rate of reduction of *cis*-$Co(en)_2H_2OCl^{2+}$ compared to *cis* $Co(en)_2pyCl^{2+}$ is a special case. By using the p*K* as a measure of σ-bonding strength, we predict that the aquo complex should be reduced about 100 times faster than the pyridino complex. However, it is not to be expected that the p*K*–σ bonding correlation will hold for such different species.

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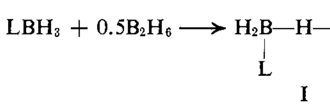
Further Studies and Comments on $B_2H_6 \cdot NR_3$

Sir:

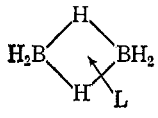
Recently[1] we discussed the properties of singly hydrogen-bridged boranes (I), prepared through reactions of amine boranes with diborane



$$LBH_3 + 0.5B_2H_6 \longrightarrow \underset{\displaystyle L}{H_2B}\text{—H—}BH_3$$

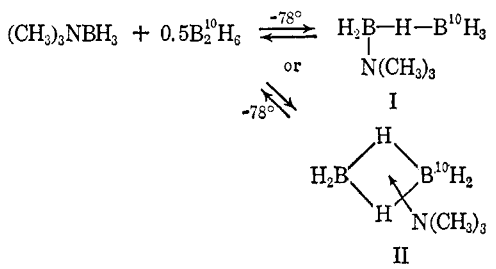
I

where L is an amine base. Eastham[2] has reinterpreted our nmr data,[1] concluding that the material we studied was effectively an intact diborane molecule with the ligand symmetrically attached through a π bond between an nonbonding orbital of diborane and the lone pair of the amine to give II.[3] Experimental work described below is consistent with structure I. Furthermore, this new information plus available thermodynamic data militate strongly against the structure proposed by Eastham.[2]



II

For the systems we have studied,[1] structure II would have to be formed through a reaction in which *a σ boron–nitrogen bond is broken.* In a tracer study, we added $B^{10}{}_2H_6$ to $(CH_3)_3NBH_3$ which contained a normal distribution of boron isotopes. In principle, this gave rise to one of the two structures in eq 1.



(1)

This reaction is reversible; diborane added to the amine borane can be quantitatively pumped away and recovered. Results presented in Table I below clearly show that there is essentially no enrichment of boron-11 in the recovered diborane. This result is consistent with structure I and refutes the presence of structure II. For structure II, the symmetrical attachment of the amine to diborane requires that a statistical distribution of boron isotopes be present in the recovered diborane.

Table I. Mass Spectra of Recovered Diborane

	Relative intensities			
			Diborane Recovered	
e/m	B_2H_6[a]	$B^{10}{}_2H_6$[a]	A[b]	B[c]
20	...	2.5	2.0	2.6
21	...	6.4	5.2	6.7
22	2.6	68.7	62.3	68.5
23	32.9	29.4	35.1	41.4
24	88.2	49.0	50.5	54.8
25	52.6	100	100	100
26	100	7.4	19.0	15.9
27	100	2.5	9.7	2.0
28	...	...	...	...

[a] Relative intensities observed from samples used in this study. [b] In A, $B^{10}{}_2H_6$ was added to $(CH_3)_3NBH_3$ in CH_2Cl_2, and the system was continuously stirred for 48 hr at −78° before recovery of diborane. [c] In B, $B^{10}{}_2H_6$ was added to $(CH_3)_3NBH_3$ in glyme, and the system was continuously stirred for 10 hr at −78° before recovery of diborane.

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(1) S. G. Shore and C. L. Hall, *J. Am. Chem. Soc.*, **88**, 5346 (1966).

(2) J. F. Eastham, *ibid.*, **89**, 2237 (1967).

(3) Structure II is considered to be analogous to that suggested for butyllithium dimer coordinated to ether;[2] Z. K. Cheema, G. W. Gibson, and J. F. Eastham, *ibid.*, **85**, 3517 (1963). However, since the coordinate bond between lithium and ether is an ordinary σ bond, we believe that it should not be cited as an analog of structure II, which involves an unusual type of coordinate π bond.