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Electron Transfer. 48. Redox Bridges Featuring Broken Conjugation. Variation in the Insulating Fragment[1]

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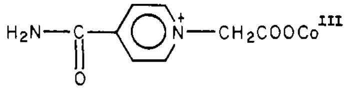
Specific rates of reduction, using Cr^{2+}, Eu^{2+}, and V^{2+}, of a series of (carboxylato)cobalt(III) complexes, each with an activated pyridine ring insulated from the $COOCo^{III}$ group by a saturated or partially saturated fragment, are compared. In several instances Cr(II) and Eu(II) rates exceed those for a number of Co(III) oxidants in which the pyridine nitrogen is directly conjugated with the carboxyl group. The most marked accelerations are observed for complexes of the type $Inic^{+}CCOOCo^{III}$, with rates falling off as the chain between functions is lengthened. Rates do not appear to be sensitive to the precise makeup of this chain, only to the number of atoms comprising it. The present results are consistent with intervention of a homoallylic type intermediate of type VIII, proposed earlier, if it is assumed that the observed accelerations reflect delocalization of the migrating electron and that transmission of spin density between functions operates through bonds comprising the intervening chain, as well through the space separating the reducing center from the π-electron region of the ring. The attenuation of acceleration resulting from chain elaboration is less dramatic for Eu^{2+} than for Cr^{2+}, suggesting a greater through-space interaction for the lanthanide center, a difference which may reflect differences in the symmetry character of the donor orbitals. Rate enhancements observed with Cr(II) and Eu(II) do not extend to V(II), presumably because the latter center is too weak a reductant to partake significantly in charge transfer to the pyridine ring.

Early studies on the mechanism of electron transfer between metal centers demonstrated that incorporation of an olefinic[3] or aromatic[4] function into a ligand serving as a redox bridge could significantly accelerate reduction of a bound oxidizing center. For a considerable period thereafter, it was generally believed that such rate enhancement could occur only if the unsaturated fragment lay in conjugation with the donor group coordinated to the oxidizing ion.[5,6] In 1979, however, we described several $(NH_3)_5Co^{III}$ complexes in which conjugation between a ligated carboxyl and a pyridine ring activated by a γ-C(=O)NH function was interrupted by a saturated unit; certain of these complexes were nevertheless reduced by Cr^{2+} and Eu^{2+} more rapidly than a number of related complexes in which conjugation is unbroken.[7]

In the present work we have examined further examples of such "insulated" bifunctional complexes, being interested, in particular, in how the ease of electron transfer depends upon the length and nature of the insulating fragment. Although additional rate enhancements have been found, none is as striking as that observed for the prototype oxidant of this type[7] (complex I), which features a $COOCo^{III}$ function separated, by a CH_2 group, from an activated pyridine ring in which the hetero nitrogen bears a positive charge.



I

Experimental Section

Inorganic Materials. Lithium perchlorate,[8] aquopentaamminecobalt(III) perchlorate,[4] and solutions of $Cr(ClO_4)_2$,[4] $Eu(ClO_4)_2$,[9] and $V(ClO_4)_2$[10] were prepared as described.

Organic Ligands. Isonicotinate esters of α- and β-hydroxy acids were prepared by a procedure analogous to that of Irikura and coworkers,[11] in which aqueous solutions sodium isonicotinate and the sodium salt of the appropriate chloro- or bromo-substituted aliphatic acid were mixed, brought to pH 8, and then kept at 85 °C for 5 h. The mixture was then cooled, the desired carboxyalkyl isonicotinate precipitated by addition of HCl, and the product recrystallized from dilute aqueous $HClO_4$.

N-(2-Carboxybenzyl)isonicotinamide, the ligand from which complex V was derived, was prepared by a method patterned after that of Hajdu and Sigman.[12a]

Cobalt Complexes. (Carboxylato)pentaamminecobalt(III) perchlorates were prepared from the aquopentaammine perchlorate as described.[4] Small quantities of the aquo complex were removed by passage through Bio-Rad Bio-Gel P-2 resin, eluting with water, and then concentrating by rotary evaporation.[7] In each case, λ_{max} was at 502 nm, showing that the products obtained featured cobalt(III) bound to carboxyl, rather than to a ring nitrogen (which would shift λ_{max} to 475 nm)[9] or to an amide function (λ_{max} at 505–525 nm).[12b] Analyses of new complexes appear in Table I.

Rate Measurements. Rates were estimated from measurements of absorbance changes on the Beckman Model 5260 recording spectrophotometer as described.[4,5a] Measurements were made at 502 nm. Reactions were first order each in Co(III) and reductant but were generally carried out under pseudo-first-order conditions with at least a tenfold excess of reductant. Reductant concentrations fell in the range 0.001–0.01 M, whereas $(Co^{III})_0$ was between 1×10^{-4} and 1×10^{-3} M. Most reductions were run in 1.0 M $HClO_4$, but a few were carried out at lower acidities with ionic strength adjusted to near unity with $LiClO_4$. In those instances where rates were measured at more than one acidity, no significant variation of specific rate with $[H^+]$ was noted. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life values within a single run agreed to within 6%, and average values did not differ significantly from those obtained by least-squares treatment of logarithmic plots of absorbance differences against reaction times. Specific rates obtained from replicate runs (generally three runs for each set of conditions) checked to better than 10%. A number of reductions by Eu^{2+} and V^{2+} yielded, instead of the usual logarithmic curves, decay curves that were much more nearly linear, indicating autocatalysis of the type reported in previous studies.[7,9,13] In such

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(2) On leave from Vivekananda College, Mylapore, Madras, India.

(3) (a) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955); (b) D. K. Sebera and H. Taube, *ibid.*, **83**, 1785 (1961).

(4) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(5) See, for example: (a) E. S. Gould, *J. Am. Chem. Soc.*, **88**, 2983 (1966); (b) P. K. Thamburaj, M. K. Loar, and E. A. Gould, *Inorg. Chem.*, **16**, 1946 (1977).

(6) However, E. S. Gould, N. A. Johnson, and R. B. Morland, *Inorg. Chem.*, **15**, 1929 (1976), have reported instances of rapid electron transfer through poorly conjugated (noncarboxyl) systems.

(7) C. A. Radlowski and E. S. Gould, *Inorg. Chem.*, **18**, 1289 (1979).

(8) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 5661 (1971).

(9) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972).

(10) (a) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 3769 (1969); (b) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

(11) T. Irikura, S. Sato, K. Kasuga, Y. Abe, and T. Tamada, Japanese Patent 2707 (1967); *Chem. Abstr.*, **67**, 90691*m* (1967).

(12) (a) J. Hajdu and D. S. Sigman, *Biochemistry*, **16**, 2481 (1977); (b) E. S. Gould, *J. Am. Chem. Soc.*, **90**, 1740 (1968).

(13) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2369 (1974).

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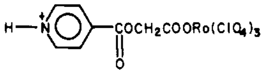
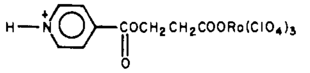
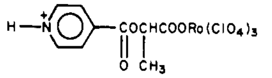
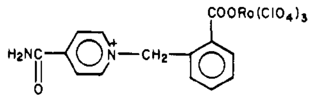
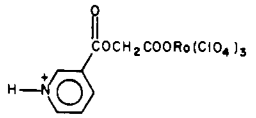
Table I. Analyses of (Carboxylato)pentaamminecobalt(III) Perchlorates

complex	% C		% H		% Co	
	calcd	found	calcd	found	calcd	found[a]
 (II)[b]	15.3	14.9	3.50	3.66	9.4	9.3
 (III)	16.9	16.6	3.76	3.98	9.2	9.5
 (IV)	16.9	16.7	3.76	4.05	9.2	9.4
 (V)	24.0	24.7	3.86	4.02	8.4	8.0
 (VI)	15.3	16.0	3.50	3.24	9.4	9.6

[a] Reference 4. [b] Ro = "roseo" = $(NH_3)_5Co^{III}$.

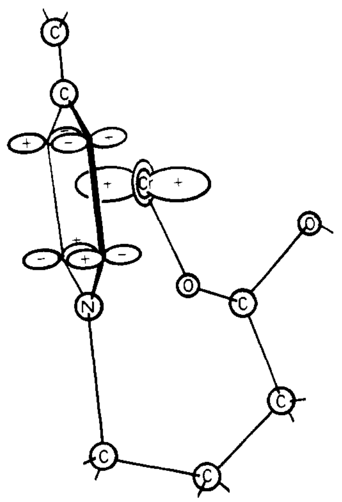


Figure 1. Proposed homoallylic type activated complex for the Cr^{2+} (or Eu^{2+}) reduction of carboxyl-bound cobalt(III) accelerated by an activated pyridine ring which is separated from $COOCo^{III}$ by a saturated fragment. The reducing electron from Cr^{2+} is taken as arising from the e_g orbital shown. Note the mismatch of orbital symmetry between this orbital and the $4B_2$ orbital of the pyridine ring, the lobes of which are labeled. The f_{z^3} orbital, from which the reducing electron in the Eu^{2+} reaction arises, is similar in shape to the e_g orbital, but its wave function changes sign on passage through the plane bisecting the ring at N and C_γ (see text).

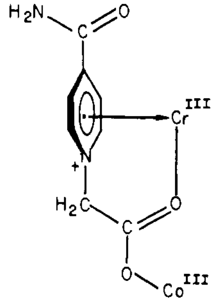
cases the autocatalytic component was suppressed by addition of excess Eu^{3+} or V^{3+} as described,[7] and decay curves derived from the uncatalyzed reaction were obtained. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Reaction profiles of several of the more rapid reductions during the first few milliseconds after mixing were examined in the stop-flow spectrophotometer in order to detect the appearance and decay of short-lived reaction intermediates. No evidence for such species was obtained.

Results and Discussion

Specific rates for the reduction by chromium(II) (k_{Cr}), europium(II) (k_{Eu}), and vanadium(II) (k_V) of the (carboxylato)cobalt(III) complexes in this study are listed in Table II. Several values obtained in previous work are also included for comparison. Ligands in the present series feature a pyridine ring activated by a C(=O)O or a C(=O)N function in the γ position. Such activation is essential for the rate enhancements, whether slight or sizable, observed here for the Cr(II) and Eu(II) reductions, for when such a function is shifted to the β position or removed from the ring, specific rates drop to, or fall below, the ranges characterizing reductions of simple aliphatic or aromatic $COOCo(NH_3)_5$ species, i.e., 0.1–0.3 $M^{-1}\ s^{-1}$ for Cr(II)[3b,4] and 0.5–1.5 $M^{-1}\ s^{-1}$ for Eu(II).[13] Rates for V(II) reductions appear to lie within the "normal" range.[5b,14] As in an earlier related study,[7] the activated pyridine rings are separated from the $COOCo^{III}$ groups by saturated fragments.

A case has been presented[7] that reductions of the type treated here utilize a transition state in which the reducing center is bound to the $COOCo^{III}$ function and that the activated ring, although necessary for the perceived rate enhancements, does not itself undergo reduction prior to participation of $COOCo^{III}$. This view is supported by characterization of the primary products ($COOCr^{III}$ derivatives) from the most rapid Cr(II) reductions, as well as by the observed rates of the Eu(II) reductions, which are found to be much greater than those for one-electron reductions of similarly activated rings in the absence of ligated Co(III).[15] An intermediate of type VIII has been proposed in order to accommodate evidence as to the point of attack (by the reductant) with the striking accelerations observed in the reductions of complex I.



VIII

If the less dramatically accelerated reductions of complexes of the "insulated" ligands in the present study are taken to

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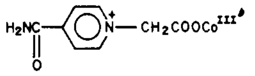
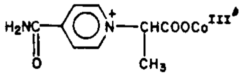
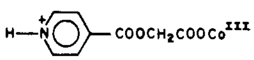
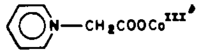
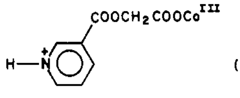
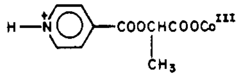
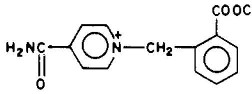
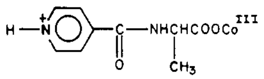
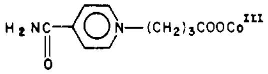
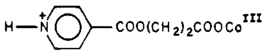
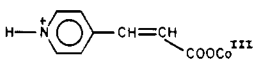
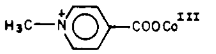
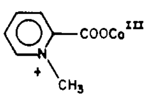
(14) See, for example: (a) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973); (b) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971); (c) J. C. Thomas, J. W. Reed, and E. S. Gould, *ibid.*, **14**, 1696 (1975).

(15) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *J. Am. Chem. Soc.*, **99**, 1073 (1977).

Table II. Specific Rates for Chromium(II), Europium(II), and Vanadium(II) Reductions of (Carboxylato)pentaamminecobalt(III) Complexes Derived from Ligands in Which Conjugation is Broken[a]

oxidant	k_{Cr}	k_{Eu}	k_V
 (I)	6.6×10^2	$1.6 \times 10^{2\,c}$	
	5.5×10^2	96^c	1.6
 (II)	4.2, 4.2^d	62^c	1.18^c
	0.034	0.82	
 (VI)	0.126	1.17	0.74
 (IV)	3.0	32^c	1.65
 (V)	2.2, 2.1^d	11	0.87^c
 (VII)	13.1^b	2.4^b	
	1.9^b		
 (III)	1.89	22^c	1.73^c
	2.2^e		1.08^e
	1.4^f	2.4^c	0.82
	0.087^f		

[a] Specific rates in $M^{-1}\ s^{-1}$ at 25 °C. Reactions were carried out in 1.0 M $HClO_4$ unless otherwise indicated. See Experimental Section for details. [b] Reference 7. [c] Autocatalytic reactions. Tabulated specific rates, referring to the uncatalyzed path, were obtained through suppression of autocatalysis by addition of 0.03–0.04 M Eu^{3+} or 0.004–0.07 M V^{3+} (see ref 7). [d] Reaction medium was 0.10 M $HClO_4$ + 0.90 M $LiClO_4$. [e] Reference 5b. [f] Reference 4; $\mu = 3.0$.

proceed through analogous "homoallylic" intermediates, comparisons of the various k_{Cr} and k_{Eu} values in Table II become of interest in connection with the following question: "To what extent is the interaction between the pyridine ring and the $COOM^{III}$ group in such intermediates transmitted through the series of bonds comprising the side chain rather than directly through space?" Similar questions have been considered in relation to a wide variety of species having interacting groups which are neither bonded to each other directly nor connected by unbroken conjugation. Although definitive answers are sometimes elusive, it is thought likely that through-space interactions predominate in certain structures featuring carbonium ion centers and C=C bonds,[16] carbon-centered radicals and C=C bonds,[17] sulfur-centered radicals and remote thia linkages,[18] $S—Ru^{III}$ and $S—Ru^{II}$ centers,[19] $py—Fe^{II}$ and $py—Co^{III}$ centers,[20] and pyridyl radicals and remote pyridinium groups.[21] Predominant through-bond interactions are less usual, but there is evidence for their operation in some bicyclic structures having both a nitrogen-centered radical and a C=O group.[22] Moreover, our kinetic data indicate that the latter mode of transmission is of importance in a number of the systems at hand.

Scale models have been constructed, not only for the suggested intermediate VIII but also for analogous species which would presumably intervene in reduction of oxidants II–V. In each case, some contact between Cr^{III} (or Eu^{III}) and the π-electron region of the pyridine ring is possible. However, with intermediate VIII, in which only a single CH_2 group separates the ring from the carboxyl, the fit is tight and requires that Cr^{III} approach the ring obliquely, that the CH_2COOCr^{III} unit lose its flexibility and that there be considerable restraint of motion of the water molecules in the first coordination sphere of Cr^{III}. As additional atoms are interposed between the two centers, contact between functions is facilitated and entropy requirements become progressively less severe.

Nevertheless, within the series at hand, reductions by Cr^{2+} and Eu^{2+} are found to be most rapid for $Inic^+CH_2COOCo^{III}$ (I) and $Inic^+CHMeCOOCo^{III}$,[7] with rate enhancing action becoming attenuated as the chain between functions is lengthened to three members (complexes II, IV, and V) and further to four (complex III). The implication is, then, that interaction between the activated ring and the carboxyl-bound metal center is necessary for the accelerations noted, that this acceleration reflects delocalization of the unpaired electron which ultimately migrates to Co(III), but that transmission of spin density between functions operates, in substantial part, through the intervening chain. Interestingly, the makeup of this chain appears to be less important than the number of atoms comprising it. Thus, k_{Cr} values are comparable for oxidant II, in which the "insulating chain" is C(=O)OC, for oxidant V, in which it is CC=C (including a portion of an aromatic ring), and for complex VII, in which it is C(=O)NC.

The trend in Eu(II) rates, although in the same direction as that for Cr(II) rates, is less pronounced, i.e., k_{Eu} is seen to fall off much less sharply with elongation of the chain than does k_{Cr}. The difference in selectivity is that expected if through-space interaction (which, in contrast to through-bond interaction, is relatively insensitive to the length of the insulating fragment) were to contribute more prominently to spin delocalization in the transition states for Eu^{2+} reductions than is the case for Cr^{2+} reductions. As indicated in Figure 1, the transition state leading to the proposed intermediate features a mismatch of orbital symmetry between the e_g orbitals of octahedrally coordinated Cr(II) (one of which furnishes the migrating electron) and the lowest unoccupied ($4B_2$) orbital associated with the pyridine ring.[23,24] This mismatch is a consequence of the retention of sign of the wave function of the metal orbital on passage through the plane bisecting the

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(16) See, for example: P. R. Story and B. C. Clark, Jr., in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1972, Chapter 23.

(17) J. W. Wilt in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, pp 466–480.

(18) W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976).

(19) C. A. Stein and H. Taube, *J. Am. Chem. Soc.*, **100**, 1635 (1978).

(20) J.-J. Jwo, P. L. Gaus, and A. Haim, *J. Am. Chem. Soc.*, **101**, 6189 (1979).

(21) M. Itoh and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 1843 (1968).

(22) S. F. Nelson, C. R. Kessel, L. A. Grezzo, and D. J. Steffik, *J. Am. Chem. Soc.*, **102**, 5482 (1980).

(23) The two low-lying unoccupied molecular orbitals in pyridine, $7A_1$ and $4B_2$, have different symmetry characters but nearly the same energies (they are degenerate in benzene). In the unsubstituted base, $7A_1$ is assigned slightly the lower energy, reflecting the greater electronegativity of the hetero atom.[24] In the present systems, which feature a strongly electron-withdrawing group attached to the carbon opposite the nitrogen, from which electron density is further drained by N-protonation or N-alkylation, a reversal of levels is expected.

(24) See, for example: (a) J. D. Petke, J. L. Whitten, and J. A. Ryan, *J. Chem. Phys.*, **48**, 953 (1968); (b) D. L. Harris and M. D. Bertolucci, "Symmetry and Spectroscopy", Oxford, New York, 1978, p 379; (c) W. J. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, 1973, p 263.

ring at N and C_γ and is presumed not to extend to the 4f orbital involved in electron transfer from Eu^{2+},[25,26] for the latter undergoes a sign inversion on passage through the same plane. On this basis, through-space interaction between the ring and metal center may be taken to assume a more significant role in the Eu(II) reactions, and the different attenuation patterns noted for the two reductants may thus be linked (albeit tentatively) to differences in the symmetry character of the donor orbitals.

Specific rates for reduction by V^{2+} (k_V values) do not appear to be enhanced by the ligands used in this study. This lack of response cannot be reasonably attributed to the limit on inner-sphere rates imposed by sluggish substitution at the V(II) center,[10,27] for a number of carboxylato derivatives of $(NH_3)_5Co^{III}$ have been found to exhibit k_V values several times those noted here.[14a,28] Instead, we suspect that the formal potential of V^{2+} ($E° = -0.242$ V)[29] is not sufficiently negative to allow a significant degree of charge transfer to the pyridine ring, a condition presumably necessary for intervention of the proposed homoallylic intermediate.[30,31]

Registry No. II, 77482-19-0; III, 77482-22-5; IV, 77482-25-8; V, 77482-27-0; VI, 77482-30-5; pentaammine[4-carboxy-1-methylpyridiniumato(1−)-*O*]cobalt(3+) triperchlorate, 77482-31-6; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3.

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(25) It is assumed here that the ligand environments about both Eu(II) and Eu(III) in our systems are approximately octahedral. The 4f orbital taken to be active in the electron transfer process is the antisymmetric f_{z^3} orbital.[26]

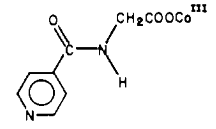
(26) See, for example: (a) H. G. Friedman, G. R. Choppin, and D. G. Feuerbacher, *J. Chem. Educ.*, **41**, 354 (1964); (b) M. K. Loar, M. A. Sens, G. W. Loar, and E. S. Gould, *Inorg. Chem.*, **17**, 330 (1978).

(27) N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1968).

(28) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968).

(29) (a) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **16**, 2516 (1977); (b) G. Jones and J. H. Colvin, *J. Am. Chem. Soc.*, **66**, 1573 (1944).

(30) A reviewer has directed our attention to the very low k_{Eu} value for complex VII (Table II), the only oxidant in this series with an amide function in the side chain. We suspect that this reflects the circumstance that this complex, like a large number of known N-alkylated amides,[31] exists preferentially as the trans conformer



XI

in which interaction between the pyridine ring and the carboxyl-bound reducing center is ruled out. Such a conformational preference would be expected to erode the proposed homoallylic route.

(31) See, for example, M. B. Robin, F. A. Bovey, and B. Basch, in "The Chemistry of the Amides", J. Zabicky, Ed., Wiley-Interscience, New York, 1970, p 1934.

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Symmetrical Cleavage and Some New Derivatives of Pyrazabole[1]

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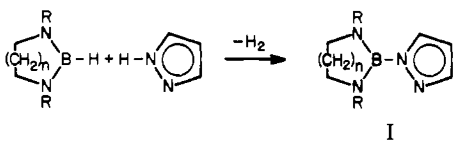
The B_2N_4 ring of pyrazabole as well as C-substituted pyrazaboles is symmetrically cleaved when boron-bonded hydrogen is replaced by strongly electron-donating amino substituents; monomeric pyrazol-1-ylboranes containing trigonal boron are obtained. However, hydrogen replacement by amino ligands of weak donor ability does not affect the pyrazabole structure. Similarly, boron-bonded organylthio groups lead to pyrazaboles in all cases.

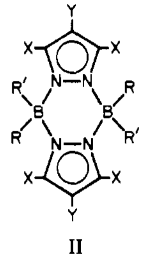
Although a wide number of boron derivatives of pyrazole are known,[2] the first examples of monomeric pyrazol-1-ylboranes containing trigonal borons have only recently been prepared[3,4] by the condensation of 1,3-dimethyl-1,3,2-diazaboracycloalkanes with pyrazole according to the equation



I

$R = CH_3; n = 2, 3$

It was concluded that strong π interaction of the nitrogen atoms of the aliphatic diamine moiety in I, possibly enhanced by the virtual planarity of the BN_2C_n heterocycle,[5] results in electronic saturation of the boron and thus prevents the dimerization of I to form "pyrazabole" structures of type II, containing a B_2N_4 heterocycle.



II

On this basis it should be possible to symmetrically cleave the pyrazabole skeleton of II, R = R′ = H, by appropriate hydrogen displacement at the exocyclic boron sites. In order to test this hypothesis and to develop a second route for the preparation of monomeric pyrazol-1-ylboranes, we have investigated the reaction of pyrazabole (II, R = R′ = X = Y = H) and C-substituted derivatives thereof with selected amines. In further documentation of the dependence of the monomeric structure of pyrazol-1-ylboranes on the electronic

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(1) Boron-Nitrogen Compounds. 90. For part 89 of this series see ref 4.

(2) "Gmelin Handbuch der Anorganischen Chemie"; Springer-Verlag: West Berlin, 1975; Vol. 23, Supplement Boron Compounds 5, pp 1-18.

(3) Niedenzu, K.; Weber, W. *J. Organomet. Chem.* **1980**, *195*, 25.

(4) Weber, W.; Niedenzu, K. *J. Organomet. Chem.* **1981**, *205*, 147.

(5) Niedenzu, K.; Miller, C. D. *Top. Curr. Chem.* **1970**, *15*, 191.

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