(9) (a) F. Scandola, C. Bartocci, and M. A. Scandola, *J. Phys. Chem.*, **78**, 572 (1974); (b) *J. Amer. Chem. Soc.*, **95**, 7898 (1973); (c) F. Scandola, private communication.

(10) The author is grateful to Professor V. Balzani for his recognition of this important point.

(11) This extrapolated value of E_{th} corresponds to about the origin of the low-energy ligand field absorption band of this complex, as noted previously by Scandola, *et al.*[9a] Irradiation of the ligand field band gives wavelength-independent yields of linkage isomerization and redox. The ratio of photoredox and photoisomerization is wavelength independent for this complex,[6,9] and at 254 nm $\phi(Co^{2+}) \simeq 0.5$.

(12) Note that (2) must be decomposed into two steps,

$$Co^{III}(NH_3)_5X \xrightarrow{\Delta H^{\ddagger}} \{Co^{III}(NH_3)_5, X^-\} \xrightarrow{\Delta H_{IP}^{\circ\prime}} \{Co^{II}(NH_3)_5, \cdot X\}$$

so that $\Delta H_c^\circ \simeq \Delta H^{\ddagger} + \Delta H_{IP}^{\circ\prime}$.

(13) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968); **67**, 853 (1963).

(14) See also discussion by N. Sutin, "Inorganic Biochemistry," Vol. 2, G. Eichhorn, Ed., American Elsevier, New York, N. Y., 1973, p 611.

(15) N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

(16) The quantities in (3) are as follows: λ_o, Marcus' outer-sphere reorganizational parameter; a_1 and a_2, radii of the reactants; r, distance of separation of the reactant centers in the transition state; D_{op}, square of the index of refraction of the medium; D_s, dielectric constant of the medium; e, charge on the electron.

(17) (a) M. D. Glick, J. M. Kuszaj, and J. F. Endicott, *J. Amer. Chem. Soc.*, **95**, 5097 (1973); (b) M. D. Glick, W. G. Schmonsees, and J. F. Endicott, *ibid.*, **96**, 5661 (1974).

(18) An alternative procedure would treat the CTTM transition as an intervalence transition and use the absorption maximum and bandwidth to estimate the reorganizational barriers[15] for (4) and (5); however this approach leads to relatively high energies for the thermally equilibrated CTTM states (E_0) and to activation barriers which seem inappropriately large (by about 15 kK/mol). The energy parameters so deduced could be interpreted as characteristics of the initial Franck–Condon state but are probably appreciably in error due to the large free energy changes associated with (5) and to a failure of the assumption of weak interaction between reactant centers. On the other hand Hush's equation $E^* = (E_{op})^2/4(E_{op} - E_0)$, with energy quantities estimated in the text, leads to barriers to ^{1}CT dissociation which vary from ~2 kK (for $E_0 = 20$ kK) to ~9 kK (for $E_0 = 22$ kK). The values of $\lambda/4$ obtained in the text lie within this range.

(19) The bulk dielectric relaxation time of water can be estimated to be in the range of 10^{-11}–10^{-12} sec, *e.g.*, using eq 7 in K. Fueki, D.-F Feng, and L. Kevan, *J. Phys. Chem.*, **78**, 393 (1974).

(20) In this estimate the following numerical values have been used in (3): $a_1 = 2.4$ Å (Co^{II}), $a_2 = 1.14$ Å (Br),[19] and $r = (1.4 + a_2)$ Å; the last value substitutes the covalent radius of Br for that of O in the transition state of the $Co(N_4)(OH_2)_2^{3+}$–$Co(N_4)(OH_2)_2^{2+}$ self-exchange reaction (see ref 16a). In obtaining $\lambda_i/4$, the inner-sphere reorganizational barrier estimated in ref 16a has been reduced by a factor of 2, assuming the major barrier is in compression of the Co^{II}–N bond and half of the resulting value (for a hypothetical self-exchange reaction) was used.

(21) See J. E. Huheey, "Inorganic Chemistry," Harper and Row, New York, N. Y., 1972, p 184.

(22) Actually (6) may underestimate k_4 for very exoergic recombinations: see (a) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970); (b) R. D. Van Duyne and S. F. Fischer, submitted for publication (private communication from Professor Fischer); (c) S. F. Fischer, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. INOR 20.

(23) The quantum yield actually is a complex function of several rate constants, k_9 the rate constant for electronic relaxation $^1CT \rightarrow {}^1A_1$ and k_D the rate constant for separation of radical-pair fragments: $\phi(Co^{2+}) = [k_4/(k_9 + k_4)][k_D/(k_5 + k_D)]$. For $k_d \approx 5 \times 10^{10}$ sec^{-1}, and $k_4 > 10^8$ sec^{-1}, estimates in the text lead to $\phi(Co^{2+}) \leq 7 \times 10^{-4}$, hence the statement that the estimated value of k_4 is too small. However, the value for k_4 is extremely sensitive to the energy difference of the equilibrated ^{1}CT state and ΔH_c°; if this energy difference had been taken to be 0 kK/mol rather than −4 kK/mol, $k_4 \approx 10^{10}$ sec^{-1} and $\phi(Co^{2+}) \leq 0.7$. Since the present estimates of ΔH_c°, E_{th}, and E'_{th} are each uncertain to about 2 kK/mol, it is unrealistic to expect information now available to permit accurate evaluation of quantum yields. The possibility that quantum yields may be used with this model to estimate more precise energy differences of species along the photoreaction coordinate will be considered elsewhere. The purpose of the present report is to provide a semiquantitative account of the contrasts in photochemical behavior noted in the introductory part of this paper.

(24) A frequently cited alternative is that k_5 is very large, consistent with present estimate, and that the photoproducts are formed from a secondary or solvent separated radical pair.[5,6] The possibility of observing a limiting yield for such alternatives is dependent on the lability of the solvent.[7,8]

(25) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970, Chapter 5, p 142.

(26) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952.

(27) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **12**, 962 (1973).

(28) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(29) This inferred value of $\Delta H^{\ddagger}$ is in excellent agreement with an activation energy of about 13 kK for aquation of $Co(NH_3)_5NO_2^{2+}$ estimated for a square-pyramidal transition state using the model proposed by S. T. Spees, Jr., J. R. Perumareddi, and A. W. Adamson, *J. Amer. Chem. Soc.*, **90**, 6626 (1968).

(30) See ref 21, p 127.

(31) F. A. Cotton and W. T. Edwards, *Acta Crystallogr., Sect. B.*, **24**, 474 (1968).

(32) U. Thewalt and R. E. Marsh, *Inorg. Chem.*, **9**, 1604 (1970).

(33) D. R. Stranks, *Discuss. Faraday Soc.*, **29**, 116 (1960).

(34) K. Nakamoto, "Infrared Spectra of Coordination Compounds," Wiley, New York, N. Y., 1965.

(35) In this calculation it has been assumed that the $Co(NH_3)_5NO_2^{2+}$ and $Co(NH_3)_5ONO^{2+}$ ground-state energies differ by about 4 kK/mol, based on the correlation of crystal field strengths and redox potentials.[36,37] Note that steric factors accounting for the nonspherical shape of NO_2 would probably reduce both k_5' and k_5'' in magnitude.

(36) P. A. Rock, *Inorg. Chem.*, **7**, 837 (1968).

(37) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).

(38) P. Debye, "Polar Molecules," Dover Publications, New York, N. Y., 1929, p 81.

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Received June 13, 1974

Migration of Ether Ligands in Etherates of Triborane

AIC404261

Sir:

While the ^{11}B nmr spectra of most of the Lewis base adducts of B_3H_7 are known to show the presence of *two* kinds of boron,[1–3] those of ether adducts were reported to consist of a single multiplet peak.[2,4] In an earlier work, however, somewhat unsymmetrical ^1H hyperfine structure in the ^{11}B resonance peak of B_3H_7·THF was pointed out.[1a] This dissymmetry of the peak could be due to an overlap of two different resonance peaks.

It was thought important to confirm the experimental facts with the aid of better instrumentation available now, because the observation of only one resonance peak in the B_3H_7 etherates has led one to speculate[2] that the ether molecule migrates in the adduct molecule or that a rapid base exchange is taking place, whereas the presence of two peaks would not necessitate such a speculation.

The sample of B_3H_7·THF was prepared by the method described earlier.[5] Approximately 1 *M* solutions of the compound in tetrahydrofuran, methylene chloride, and benzene were prepared in 10-mm o.d. nmr sample tubes. The sample of $B_3H_7 \cdot O(C_2H_5)_2$ was prepared by treating a diethyl ether solution of NaB_3H_8 with a stoichiometric amount of anhydrous HCl in a 10-mm o.d. nmr sample tube at −80°.[6] The concentration was about 1 *M* and a precipitate of NaCl was retained in the sample tube. The sample of NaB_3H_8 was prepared by the reaction of $NaBH_4$ with B_4H_{10} in diethyl ether.[7] The ^{11}B nmr spectra were recorded on a Varian XL-100 spectrometer operating at 32.1 MHz, temperature of the probe being at 20°.

The spectra of B_3H_7·THF and $B_3H_7 \cdot O(C_2H_5)_2$ are shown in Figures 1 and 2, respectively. Contrary to the two previous descriptions[2,4] that were based on the spectra obtained with lower frequency spectrometers (10–19.3 MHz), the resonance peaks, Figures 1a and 2a, are both unsymmetrical. The spectrum of B_3H_7·THF, Figure 1a, is compatible with that presented earlier.[1] The proton-decoupled spectra, Figures 1b and 2b, show two peaks separated clearly. The high-field peaks, which are attributed to the boron atoms attached to

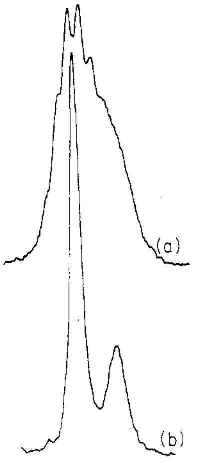

Figure 1. ^{11}B nmr spectra of $B_3H_7 \cdot THF$ in methylene chloride at 20°: (a) normal spectrum; (b) ^1H spin-decoupled spectrum.

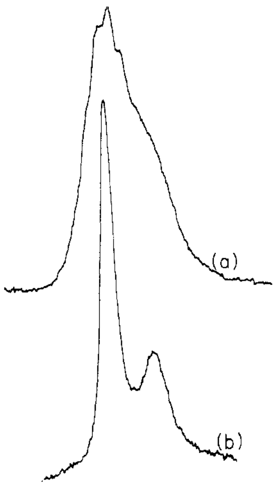

Figure 2. ^{11}B nmr spectra of $B_3H_7 \cdot O(C_2H_5)_2$ in diethyl ether at 20°: (a) normal spectrum; (b) ^1H spin-decoupled spectrum.

Table I

Compd	Solvent	Chem shift,[a] ppm (J_{BH}, Hz) B_2, B_3	B_1
$B_3H_7 \cdot THF$	THF	8.4 (39)	12.8
$B_3H_7 \cdot THF$	CH_2Cl_2	8.5 (40)	12.7
$B_3H_7 \cdot THF$	Benzene	8.1 (39)	12.5
$B_3H_7 \cdot O(C_2H_5)_2$	$(C_2H_5)_2O$	6.9 (37)	11.3

[a] $BF_3 \cdot O(C_2H_5)_2$ as the reference. Precision: better than ±0.2 ppm for the shifts and ±2 Hz for J_{BH}.

ethers, are broader than the low-field peaks. The area ratios are measured to be 2.1:1.0 and 1.8:1.0, respectively. Thus, the spectra of B_3H_7 etherates consist of two resonance peaks like those of other Lewis base adducts of B_3H_7. There appears to be a slight solvent effect on the chemical shifts. Data are listed in Table I.

The result described above indicates that neither the migration of the ether molecule in the adduct molecule nor base exchange is likely to be taking place at a rate comparable to the nmr time scale under the conditions employed here. The spectra of $B_3H_7 \cdot THF$ and $B_3H_7 \cdot O(C_2H_5)_2$ are consistent with the structure analogous to that of $B_3H_7 \cdot NH_3$[8] with a rapid H tautomerism taking place to make two of the boron atoms equivalent.

Acknowledgment. The author gratefully acknowledges the support of the National Science Foundation through Grant No. GP-32079.

Registry No. $B_3H_7 \cdot THF$, 52842-96-3; $B_3H_7 \cdot O(C_2H_5)_2$, 52842-97-4; ^{11}B, 14798-13-1.

References and Notes

(1) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 130; (b) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969, p 58.
(2) M. A. Ring, E. F. Witucki, and R. C. Greenough, *Inorg. Chem.*, **6**, 395 (1967).
(3) E. R. Lory and D. M. Ritter, *Inorg. Chem.*, **10**, 939, (1971); R. T. Paine and R. W. Parry, *ibid.*, **11**, 268, (1972).
(4) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **81**, 4496, (1959).
(5) L. J. Edwards, W. V. Ford, and M. D. Ford, *Proc. Int. Congr. Pure Appl. Chem.*, **16**, 475 (1958).
(6) G. Kodama and R. W. Parry, *Proc. Int. Congr. Pure Appl. Chem.*, **16**, 483 (1958); G. Kodama and R. W. Parry, *J. Amer. Chem. Soc.*, **82**, 6250 (1960).
(7) W. V. Hough and L. J. Edwards, *Advan. Chem. Ser.*, No. **32**, 190 (1961).
(8) C. E. Nordman and C. Reimann, *J. Amer. Chem. Soc.*, **81**, 3538 (1959).

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Received July 1, 1974

Misinterpretation of Isosbestic Points: Ambident Properties of Imidazole

AIC404416

Sir:

In a recent paper Tovrog and Drago[1] suggested that imidazole behaves as an ambident ligand toward transition metals, binding through both its imine and amine nitrogens, and that this observation has potentially very significant implications. Evidence cited for this hypothesis is the lack of isosbestic points in the visible spectrum as a function of ligand concentration and anomalous isotropic shift data in the imidazole pmr spectra.

Tovrog and Drago assumed that the existence of isosbestic points requires that only two chromophoric species are present in solution. In fact 2 + *N* species may be present providing there are *N* relations between the concentrations of these species, and these relations are independent of the parameter being varied.

Thus in the systems studied by Tovrog and Drago they propose two equilibria

$$Co + L \overset{K_1}{\rightleftarrows} LCo$$

$$Co + L \overset{K_2}{\rightleftarrows} L^*Co$$

where L*Co indicates a mode of binding of L different from that in LCo. However, for any concentration of L, the ratio of $[L^*Co]/[LCo]$ is a constant (K_2/K_1) independent of L. The existence of this relationship between the two proposed complexes (independent of [L]) reduces the number of degrees of freedom from 2 (no isosbestic point expected) to 1 (isosbestic point expected).

Thus, if the only complication in the systems investigated by Tovrog and Drago were ambident coordination, isosbestic points would be expected. The lack of isosbestic points indicates some other complication is present.[2] While the ambident coordination suggested by Tovrog and Drago seems to us unlikely, imidazole is ambident in the sense that it has a basic nitrogen and an acidic hydrogen.[6]

Another interesting system where isosbestic points have been