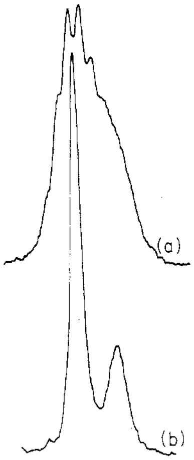

Figure 1. ^{11}B nmr spectra of B_3H_7·THF in methylene chloride at 20°: (a) normal spectrum; (b) ^1H spin-decoupled spectrum.

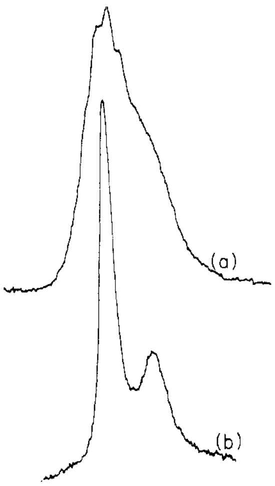

Figure 2. ^{11}B nmr spectra of $B_3H_7·O(C_2H_5)_2$ in diethyl ether at 20°: (a) normal spectrum; (b) ^1H spin-decoupled spectrum.

Table I

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

[a] $BF_3·O(C_2H_5)_2$ 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·THF and $B_3H_7·O(C_2H_5)_2$ are consistent with the structure analogous to that of $B_3H_7·NH_3$[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·THF, 52842-96-3; $B_3H_7·O(C_2H_5)_2$, 52842-97-4; ^{11}B, 14798-13-1.

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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

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

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

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 invoked to imply two species involves studies of Tolman, *et al.*[7,8] Several equilibria may be involved including

$$\mathrm{RhClL_3 + C_2H_4 \rightleftarrows (C_2H_4)RhClL_2 + L}$$

$$\mathrm{RhClL_3 \rightleftarrows RhClL_2 + L}$$

$$\mathrm{2RhClL_3 \rightleftarrows [RhClL_2]_2 + 2L}$$

where L = (*p*-tol)$_3$P.

In this example, the interpretations of the authors are well supported by other evidence. The presence or lack of isosbestic points in this system as a function of [C_2H_4] does not, however, in itself constitute either proof or evidence for the number of species in solution. Isosbestic points are not obtained in the absence of excess L because both L and C_2H_4 necessarily vary. In the presence of excess L (so L remains effectively constant) isosbestic points will be obtained regardless of whether two, three, or four of the above are present.

In kinetic studies, where the parameter varied is time, isosbestic points are obtained in cases where several different reactant and product species are present providing the equilibration of the species is rapid relative to the rate of the reaction. For example, the redox reaction

$$\mathrm{(M^{II}L_6 \rightleftarrows M^{II}L_5 \rightleftarrows M^{II}L_4) \rightarrow (M^{III}L_6 \rightleftarrows M^{III}L_5 \rightleftarrows M^{III}L_4)}$$

will give isosbestic points as a function of time at constant [L], but the position of the isosbestic points will not necessarily be the same for various concentrations of L.

The significance of the presence or absence of isosbestic points has been previously considered for several other examples.[9,10]

Registry No. Imidazole, 288-32-4.

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(2) The referees suggest that a 2:1 complex could be present in the Co(saloph) system. While possible, such a proposal seems somewhat unlikely in view of the lack of a 2:1 complex with pyridine and the observed differences between pyridines and imidazoles in analogous cobalt–porphyrin systems.[3,4] Other possible complications which may account for the anomalous visible spectra or nmr shift data, or both, include experimental difficulties, oxidation of the cobalt complex, aggregation of the Co(saloph) complex (the square-planar complex has an anomalous esr spectrum[5]), or a hydrogen-bonding interaction of the acidic hydrogen of imidazole. (Of interest is the fact that, for the cases where Tovrog and Drago indicated binding of imidazole through only the imine nitrogen, all of the imidazole protons show isotropic shifts while in those cases where ambident coordination is invoked, only the acidic hydrogen resonance shows a significant shift. Shifts with the analogous 1-methylimidazole, where an acidic hydrogen is absent, are reported to be small.)

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Received June 5, 1974