

basicities by nearly compensating solvation effects.^{2a,6} The relatively small reduction factors of about 15% for the aqueous solvent which are shown in Table I are expected on the grounds that hydration of the free bases and their conjugate acids by hydrogen bonding somewhat reduces the apparent extents of proton transfer in aqueous solution as compared to the "complete" proton transfer of the gaseous reaction.^{4,7}

The 2.0 kcal decrease in $-\Delta H_s^\circ(\text{BH}^+)$ shown by the 4-CH₃ substituent in pyridinium ion indicates that distant polar substituents exert relatively large effects upon the solvation of this cation. In fact, larger substituent effects, e.g., for 4-CN or NO₂, might lead to a violation of the structural categorization of $-\Delta H_s^\circ(\text{BH}^+)$ values (in the pyridine as well as in other series). In any case, it is clear that the effects of 4-substituents on $-\Delta H_s^\circ(\text{BH}^+)$ for the pyridinium series may be a leading term in the previously reported⁴ approximately 300% attenuation factor in base strengths between the gas phase and aqueous solution.

The results of Table I show also that the standard free energy charge, $\delta_R \Delta G_1^\circ(w)$, is somewhat superior to the standard enthalpy change, $\delta_R \Delta H_1^\circ(w)$, as an estimator of the intrinsic base strengths associated with the unsaturation effects behavior in aqueous solution. Several explanations for this type of result have been advanced.⁹

Acknowledgment. We are pleased to acknowledge the valuable assistance provided by Professor E. M. Arnett and Dr. J. F. Wolf in obtaining heats of solution of *c*-C₆H₁₂NH₂(l) and C₆H₅NH₂(l). We are also indebted to Professor D. H. Aue for communication of results prior to publication. Thanks are also due to Dr. W. G. Henderson for preliminary icr experiments with C₆H₅NH₂.

(6) E. M. Arnett and J. F. Wolf, *J. Amer. Chem. Soc.*, **95**, 978 (1973), have found dramatic evidence for this point of view from very large alkyl substituent effects on the heat of protonation of the relatively poorly solvated $\geq \text{PH}^+$ and $> \text{SH}^+$ cations in fluorosulfuric acid.

(7) P. Love, R. B. Cohen, and R. W. Taft, *ibid.*, **90**, 2455 (1968).

(8) D. H. Aue, H. M. Webb, and M. T. Bowers, private communication.

(9) (a) L. G. Hepler, *J. Amer. Chem. Soc.*, **85**, 3089 (1963); J. W. Larson and L. G. Hepler, *J. Org. Chem.*, **33**, 3961 (1968); (b) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, Chapter 12; (c) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 70-73; (d) cf. also P. D. Bolton, K. A. Fleming, and F. M. Hall, *J. Amer. Chem. Soc.*, **94**, 1033 (1972); (e) E. M. Arnett and D. R. McKelvey in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 6.

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Five-Coordinate Acetylene, Allene, and Olefin Complexes of Platinum(II) Containing Polypyrazolylborate Ligands

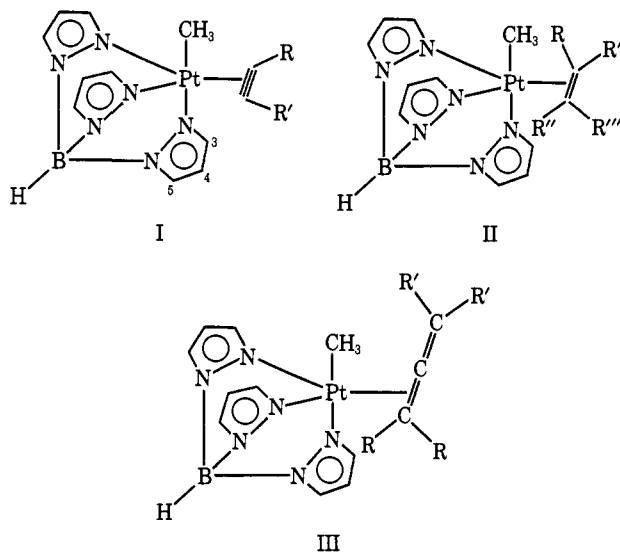
Sir:

Several years ago Trofimenko discovered the polypyrazolylborate ions¹ and prepared many complexes demonstrating the unusually strong coordinating ability

(1) S. Trofimenko, *J. Amer. Chem. Soc.*, **88**, 1842 (1966).

of this class of ligand.^{2,3} As a ligand, the polypyrazolylborate ion is analogous to the cyclopentadienyl ion in the sense that each can be regarded as a tridentate, six-electron donor group, although the polypyrazolylborate metal complexes are generally much more stable. For example, the complex⁴ [HB(pz)₃]Cu(CO) is very air and heat stable while the analogous cyclopentadienyl complex⁵ (C₅H₅)Cu(CO) is very reactive.

Therefore it appeared to us that a tridentate polypyrazolylborate ligand might well stabilize five-coordinate complexes of platinum(II). We have prepared the insoluble complex Pt(CH₃)[HB(pz)₃] which is probably polymeric with bridging pyrazolyl groups. The polymer is readily cleaved by a variety of acetylenes, olefins, and allenes to give the five-coordinate complexes I-III.



The acetylene complexes, I, with CF₃C≡CCF₃ and (CH₃)O₂CC≡CCO₂(CH₃) show the expected nmr patterns for the platinum methyl and acetylene groups. The protons on the 4 positions of the pyrazolyl rings are easily assigned since they appear as triplets due to coupling with the 3-H and 5-H protons of the ring. They appear as two distinct resonances in the ratio of 2:1, consistent with (a) two equatorial and one axial pyrazolyl rings and (b) stereochemical rigidity of the hydrotris(1-pyrazolyl)borate ligand. Coupling between ¹⁹⁵Pt (*I* = 1/2, 34% abundance) and the 4-H protons of both the equatorial and axial rings is observed thus confirming the tridentate nature of the polypyrazolylborate ion. The coupling constants *J*(Pt-H) are ≈ 10 and ≈ 3 Hz to the equatorial and axial 4-H protons which suggest that the group of highest trans influence⁶ (i.e., CH₃⁻) is trans to the axial pyrazolyl group. The nmr spectrum of I with the unsymmetrical acetylene C₆H₅C≡CCH₃ shows three resonances which may be assigned to the 4-H protons indicating that the acetylene is not rotating and is constrained within the trigonal

(2) S. Trofimenko, *Accounts Chem. Res.*, **4**, 17 (1971).

(3) S. Trofimenko, *Chem. Rev.*, **72**, 497 (1972).

(4) M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1124 (1972).

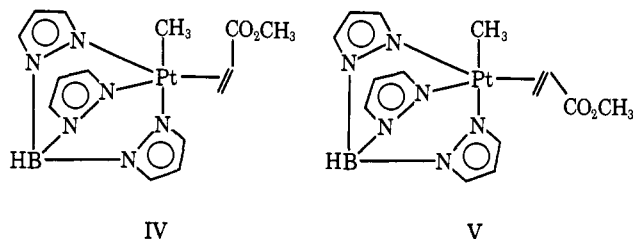
(5) F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 5114 (1970).

(6) For a review of the trans influence see T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, in press.

plane.^{7,8} A strong band observed in the infrared spectrum of each compound in the region 1800–1900 cm^{-1} is assigned to $\nu_{\text{C}\equiv\text{C}}$ and is indicative of considerable Pt $d\pi \rightarrow \text{C } p\pi^*$ (π back-bonding).

By selectively decoupling the equatorial and axial 4-H protons it is possible to assign resonances due to the 3-H and 5-H protons on the pyrazolyl rings. The 3-H protons show considerable coupling to platinum-195 (6–10 Hz) while the 5-H protons show a coupling constant of less than 1 Hz.

The olefin complexes, II, with maleic anhydride, dimethyl maleate, methacrylonitrile, crotonaldehyde, diethyl fumarate, *p*-benzoquinone, and methyl acrylate give the expected ^1H nmr patterns with a coupling constant between ^{195}Pt and the olefinic hydrogens of ~ 81 Hz. The nmr spectra are consistent with restricted rotation of the olefin and constraint within the trigonal plane. For the disubstituted ethylenes methacrylonitrile and crotonaldehyde, two geometrical isomers were observed in the ratio 1:1. However, the room temperature nmr spectrum of the methyl acrylate complex showed the presence of two isomers IV and V in



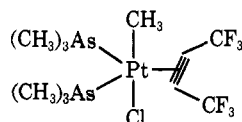
the ratio of 2:1. The high-temperature nmr spectra of IV and V exhibit two types of fluxionality. As the temperature is raised the resonances of the pyrazolyl rings coalesce to three peaks in the ratio of 1:1:1 (100°) which is consistent with rotation of the three rings⁹ about the C_{3v} axis of the ligand. At 150° the resonances due to IV and V converge as a result of rotation of the olefin, presumably about the Pt–olefin bond.¹⁰ On cooling the two isomers are again obtained in the same 2:1 ratio.

$\text{Pt}(\text{CH}_3)[\text{HB}(\text{pz})_3]$ also reacts with tetramethyl- and 3,3'-dimethylallene to give III. All five methyl resonances in the nmr spectrum of the $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}(\text{CH}_3)_2$ complex show coupling to ^{195}Pt with coupling constants of 2.5, 8.5, 52.5, 70.0, and 72.0 Hz. The nmr spectrum of the $(\text{CH}_3)_2\text{C}=\text{C}=\text{CH}_2$ complex is consistent with coordination of the allene through the $-\text{C}=\text{CH}_2$ double bond.

The polymer $\text{Pt}(\text{CH}_3)[\text{HB}(\text{pz})_3]$ is cleaved by carbon monoxide to give the five-coordinate complex $\text{Pt}(\text{CH}_3)[\text{HB}(\text{pz})_3](\text{CO})$. However, unlike the complexes de-

(7) If the acetylene were rotating or perpendicular to the trigonal plane the two equatorial pyrazolyl rings would be equivalent.

(8) A single-crystal X-ray structure of the analogous five-coordinate



complex shows that the acetylene is bonded in the trigonal plane; see B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Can. J. Chem.*, **50**, 2276 (1972).

(9) P. Meakin, S. Trofimenko, and J. P. Jesson, *J. Amer. Chem. Soc.*, **94**, 5677 (1972).

(10) B. F. G. Johnson and J. A. Segal, *J. Chem. Soc., Chem. Commun.*, 1312 (1972).

scribed above the carbonyl compound is stereochemically nonrigid at room temperature (*i.e.*, the ^1H nmr spectrum shows the equivalence of the 3-H, 4-H, and 5-H protons), and we believe the fluxionality is due to rotation of the pyrazolyl rings since ^{195}Pt coupling is observed to both the 3-H and 4-H protons of the pyrazolylborate rings. A “tumbling” or associative–dissociative exchange¹¹ would necessitate loss of ^{195}Pt coupling if intermolecular. The limiting low-temperature spectrum ($\sim -120^\circ$) shows the expected pattern for two equatorial and one axial pyrazolyl ring.

We are currently investigating the reactions of the coordinated ligands toward insertion of the platinum group into the $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ bonds^{12–14} as well as reactions of the coordinated allenes.¹⁵

- (11) S. Trofimenko, *J. Amer. Chem. Soc.*, **91**, 3183 (1969).
- (12) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **9**, 2670 (1970).
- (13) H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, **10**, 18 (1971).
- (14) T. G. Appleton, M. H. Chisholm, and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 8912 (1972).
- (15) D. W. Lichtenberg and A. Wojcicki, *J. Amer. Chem. Soc.*, **94**, 8271 (1972).

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Proton Magnetic Resonance Confirmation of Cis–Trans Isomerism in an Anionic σ Complex

Sir:

We wish to confirm and support the recent clarification of the problem of cis–trans isomerism in 1:2 *sym*-trinitrobenzene–sulfite σ complexes provided by Bernasconi and Bergstrom.¹ Although there have been many reports of 1:2 complexes like **1**, which should exhibit cis–trans isomerism,^{2–8} until this recent kinetic study¹ there was no strong evidence for such isomerism. The complex **1** ($\text{X} = \text{SO}_3^-$) is particularly puzzling, since its formation constant and pmr spectrum have been determined,⁸ and it has been isolated as a crystalline salt.⁹ The reported pmr spectrum⁸ is not in accord with Bernasconi and Bergstrom's recent results,¹ which predict that both cis and trans isomers **1a** and **1b** ($\text{X} = \text{SO}_3^-$) are of similar stability. Only two singlets were observed at τ 3.9 (2 H) and 1.4 (1 H) in a dilute solution of *sym*-trinitrobenzene (TNB) in 0.8 *M* sodium sulfite, where formation of the 1:2 complex is essentially complete.⁸ Although both H_a and H_b in **1a** and **1b** might have identical shifts, it is most unlikely that H_d and H_e would also have identical shifts. It is difficult to understand this discrepancy between the pmr and kinetic data.

As a clarification, we report here the 100-MHz pmr spectrum of a freshly prepared dilute solution of TNB in saturated sodium sulfite solution (D_2O). At high

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(2) M. R. Crampton and M. El Ghariani, *J. Chem. Soc. B*, **330** (1969).

(3) M. R. Crampton and V. Gold, *ibid.*, 893 (1966).

(4) K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967).

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(6) R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *ibid.*, **23**, 227 (1967).

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(8) M. R. Crampton, *ibid.*, 1341 (1967).

(9) R. A. Henry, *J. Org. Chem.*, **27**, 2637 (1962).