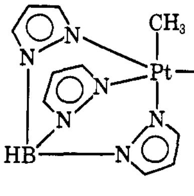
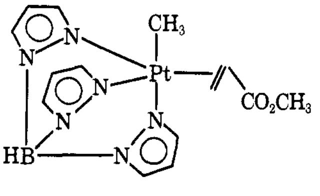
plane.[7,8] A strong band observed in the infrared spectrum of each compound in the region 1800–1900 cm^{-1} is assigned to $\nu_{(C\equiv C)}$ and is indicative of considerable Pt d$\pi \rightarrow$C pπ^* (π back-bonding).

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 ^{1}H nmr patterns with a coupling constant between ^{195}Pt and the olefinic hydrogens of $\sim$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 rings[9] 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.



IV



V

Pt(CH$_3$)[HB(pz)$_3$] also reacts with tetramethyl- and 3,3′-dimethylallene to give III. All five methyl resonances in the nmr spectrum of the (CH$_3$)$_2$C=C=C(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 (CH$_3$)$_2$C=C=CH$_2$ complex is consistent with coordination of the allene through the –C=CH$_2$ double bond.

The polymer Pt(CH$_3$)[HB(pz)$_3$] is cleaved by carbon monoxide to give the five-coordinate complex Pt(CH$_3$)[HB(pz)$_3$](CO). However, unlike the complexes described above the carbonyl compound is stereochemically nonrigid at room temperature (*i.e.*, the ^{1}H 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 exchange[11] would necessitate loss of ^{195}Pt coupling if intermolecular. The limiting low-temperature spectrum ($\sim -120°$) 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 C≡C and C=C bonds[12–14] as well as reactions of the coordinated allenes.[15]

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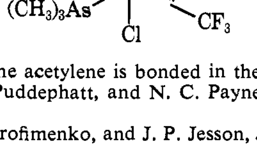
(7) If the acetylene were rotating or perpendicular to the trigonal plane the two equatorial pyrazolyl rings would be equivalent.

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



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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 study[1] there was no strong evidence for such isomerism. The complex **1** (X = 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 spectrum[8] is not in accord with Bernasconi and Bergstrom's recent results,[1] which predict that both cis and trans isomers **1a** and **1b** (X = 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$_c$ 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$_2$O). At high

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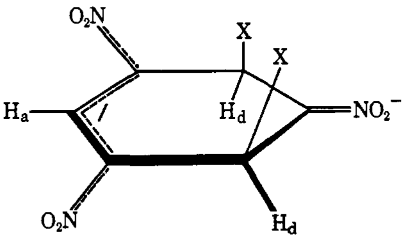
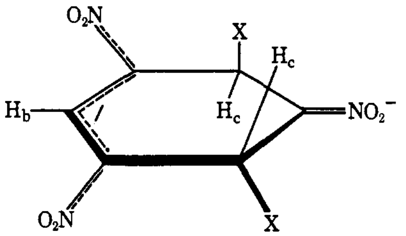


1a



1b

field, singlet resonances occur at τ 4.2 and 3.9 ppm (in a ratio of 45:55) for the sp^3 protons in the two isomers of **1** ($X = SO_3^-$). At low field, singlets for the corresponding nitronate protons occur at τ 1.6 and 1.5 (45:55). The τ 4.2 and 1.6 resonances integrate for 2 H and 1 H, respectively, as do the τ 3.9 and 1.5 absorptions. The shift difference between the nitronate protons in these isomers is much smaller than that of the corresponding sp^3 ring protons, as expected. The two sets of absorptions, one for each of the isomeric structures in a ratio of 45:55, are clearly in accord with the results of Bernasconi and Bergstrom.[1]

As we pointed out 2 years ago,[10] it is likely that *all* 1:2 σ-complex adducts can exist in isomeric cis and trans forms. Determination of equilibrium constants for such species by standard methods, *i.e.*, Benesi–Hildebrand or related procedures, must of course consider this fact, since the electronic spectral characteristics of these isomers are usually almost identical.

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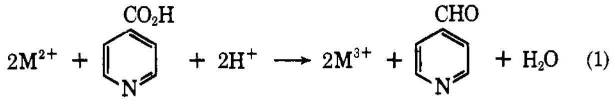
Reactions of Pyridinecarboxylic Acids with Eu^{2+}(aq), Cr^{2+}(aq), and V^{2+}(aq). Selective Reduction of the Carboxylic Group

Sir:

The few reactions of pyridinecarboxylates with aqueous metal ions of low valence hitherto known involve the pyridine ring.[1] Here we report on the selective reduction of the carboxylic group by Eu^{2+}(aq), Cr^{2+}(aq), and V^{2+}(aq).

Usually, the reduction of the carboxylic group requires vigorous conditions. It is interesting in this respect, that even in the polarographic reduction of pyridinecarboxylic acids there is no general agreement among the various authors,[2] as to whether the observed waves are due to catalytic discharge of hydrogen, to reduction of the —CH=N— bond, or to the reduction of the carboxylic group. In the systems reported here, however, reduction of the carboxylic group does take place readily under mild conditions, namely at room temperature, in aqueous solutions acidified with HCl or $HClO_4$, under an inert argon atmosphere.

The consumption of Eu^{2+}(aq) during its reaction with isonicotinic acid can be followed by adding excess Fe(III) and titrating the Fe(II) amperometrically with Ce(IV). The products of the reaction are Eu^{3+}(aq) and isonicotinaldehyde. The latter was isolated in the form of its oxalate complex,[3] as well as in the form of the complex with sulfur dioxide,[4] after precipitating with Na_2CO_3 and filtering out the europium ions. The nmr spectrum of the organic product after reoxidation by air was found to be identical with that of the isonicotinic acid. The yield in excess isonicotinic acid was determined by titrating the aldehyde with $KMnO_4$. The stoichiometry corresponds to the overall reaction



$$2M^{2+} + C_5H_4N\text{-}CO_2H + 2H^+ \longrightarrow 2M^{3+} + C_5H_4N\text{-}CHO + H_2O \qquad (1)$$

In a typical experiment for the determination of the stoichiometry the initial concentrations were $[Eu^{2+}]_0 = 0.2\ M$, $[\text{isonicotinic acid}]_0 = 0.6\ M$, and $[HCl] = 2\ M$.

Isonicotinaldehyde was also obtained using chromous and vanadous ions. It was isolated and identified as described above. Trivalent chromium was precipitated with alkali. During the neutralization a soluble red complex between Cr(III) and the excess isonicotinic acid is formed, which by further addition of alkali turns into an insoluble green complex. From a reaction mixture containing vanadous ion and an excess of isonicotinic acid, isonicotinaldehyde was also obtained, after precipitation of vanadium with alkali. The overall process with Cr^{2+}(aq) and V^{2+}(aq) is also described by reaction 1.

In solutions acidified with HCl or $HClO_4$, europous ion was found to give isonicotinaldehyde faster than chromous. The reaction with vanadous is overall slower. Typically, in a solution containing 1 M $HClO_4$, 0.07 M Eu^{2+}, and 0.11 M isonicotinic acid, the reaction was completed in about 1.5 hr. In similar solutions the reaction with Cr^{2+}(aq) takes several hours, whereas the reaction with V^{2+}(aq) is even slower. All three ions react faster at lower acidities. A detailed investigation[5] indicated that the reaction between chromous and isonicotinic acid proceeds in two time-resolved one-electron transfer steps through formation

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