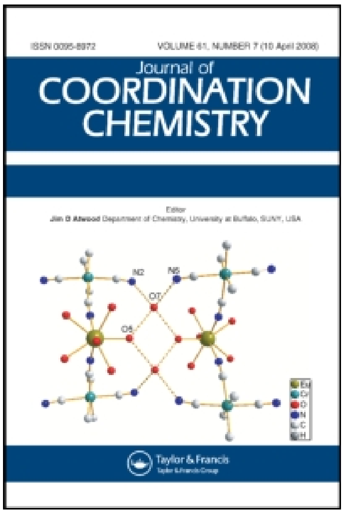

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Spiro Cations based on Bis-Bidentate Tetrakis(1-Pyrazolyl)Borate Ligand

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Spiro Cations based on Bis-Bidentate Tetrakis(1-Pyrazolyl)Borate Ligand

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S. TROFIMENKO

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Sir:

The ability and propensity of tetrakis(l-pyrazolyl)-borate ion, $B(pz)^-{}_4$, to act as a uninegative tridentate ligand of local C_{3v} symmetry have been well established.[1] We wish to report the first instance of this ligand acting in bis-bidentate fashion and forming novel types of spiro-cations[2] according to the following scheme:

$$\begin{tikzcd}
B(pz)_4^- + ML_2X \arrow[r] & {[(pz)_2B(pz)_2ML_2]} \arrow[r] \arrow[d, "M'L'_2X"] & {[L_2M(pz)_2B(pz)_2ML_2]^+} \\
 & {[L'_2M'(pz)_2B(pz)_2ML_2]^+} &
\end{tikzcd}$$

where M is a four-coordinate metal or metalloid, *X* is a leaving group such as chloride or tosylate and L is some kind of mono-dentate ligand, or $L_2 = \pi$-allyl.

The reaction of $B(pz)_4{}^-$ with two equivalents of π-allylpalladium chloride dimer (or its 2-substituted analog) gives the cationic species Ia, while with Et_2BOTSs the analogous cation Ib is produced. In each case a singly bridged, neutral intermediate such as $B(pz)^4$-π-allyl or 4, 4-bis(1-pyrazolyl)-pyrazabole is formed. These become the major products when the reactants are used in 1 : 1 ratio. This should make it possible, by a judicious choice of $B(pz)_4ML_2$ where $B(pz)_4$ is bidentate ,to synthesize species of the type L'_2M' $(pz)_2B(pz)_2ML_2$ where both, M, M′ and L, L′ may be different. For instance, the cation Ic which contains two dissimilar bridging groups has been synthesized by the reaction of $B(pz)_4Pd$-π-allyl with Et_2BOTs as well as by the reaction of 4,4-bis(1-pyrazolyl)pyrazabole with π-allylpalladium chloride dimer.

All these rapid reactions were carried out in DMF and the products were isolated by diluting the DMF solution with water, followed by the addition of aqueous NH_4PF_6 solution. The precipitated hexafluorophosphates are soluble in polar solvents and can be recrystallized from acetonitrile.

The nmr spectrum of Ib was compatible with either a static (planar $B(pz)_2B$ rings) or dynamic (rapidly inverting $B(pz)_2B$ rings) D_{2d} symmetry as it showed only one type of pyrazolyl group to be present. Molecular models indicate the unstrained structure to be puckered, although a structure involving two planar pyrazabole rings can be constructed with only a small distortion of the N—B bonds.

The nmr spectrum of cation Ia indicated stereochemical non-rigidity and well-defined limiting spectra could be obtained (Fig. 1). They could be matched by computer-simulated spectra on the basis of which values of $\Delta G = 15.5$ kcal and $E_A = 14.3$ kcal were obtained.[3]

The low temperature limiting spectrum is consistent with a structure containing two pairs of equivalent pyrazolyl groups (essentially C_2 symmetry) as indicated by molecular models. They show that unlike a $B(pz)_2B$ ring, a $B(pz)_2M$ ring cannot possibly be planar, but must be puckered in the boat form. This puckering has been established in $H_2B(3, 5\text{-}Me_2pz)_2Mo$ $(CO)_2$-π-allyl by a recent X-ray structure determination.[4] The process by

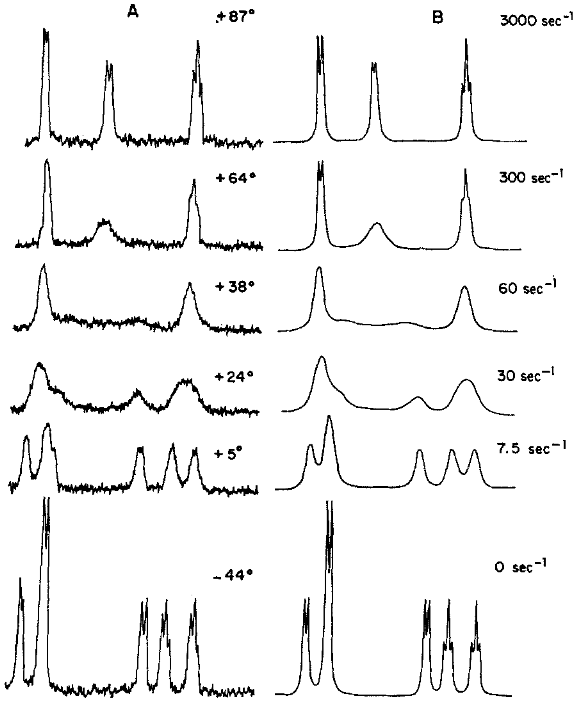


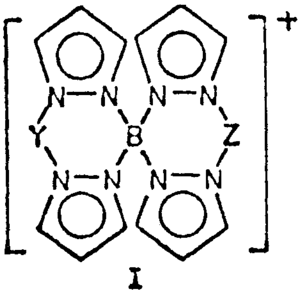
FIGURE 1. Temperature dependence of the nmr spectrum of Ia (A = recorded; B = computer-simulated) in the pyrazolyl region.

which the environments of all four pyrazolyl groups become averaged could involve either a rapid inversion of both $B(pz)_2Pd$ rings or a dissociation of the B—Pd bond (probably solvent-assisted) followed by displacement of one coordinated pyrazolyl group by the unattached one. At no time do the *syn* and *anti* protons of the π-allyl group become spectroscopically equivalent as is usually observed in the case of δ–M inter-conversions.

The room temperature spectrum of Ic was well-resolved showing two pairs of identical pyrazolyl groups (B-bridged and Pd-bridged) and was consistent with a static or dynamic C_{2v} symmetry for the cation.

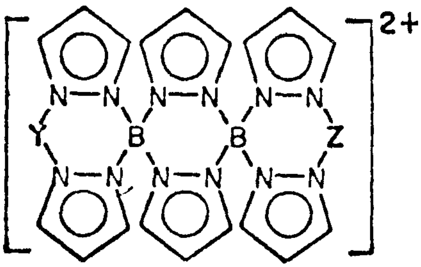
Actually, the spiro cations described here may be regarded as members, for $n = 1$, of a series generally defined by the structure III, Examples of $n = 0$ would be the previously reported pyrazaboles,[5] or metallocycles containing two 1,2-dihapto pyrazolide bridges.[6] Further members of this series have been prepared by the reaction of 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole with either π-allylpalladium chloride dimer or with Et_2BOTs. These cations were isolated as hexafluorophosphate salts and characterized by analytical data and nmr spectroscopy. The nmr spectra of both, IIa and IIb showed only two types of pyrazolyl groups present in 2 : 1 ratio and were thus compatible with static or dynamic D_{2h} symmetry.

The nmr spectra of both, IIa and IIb showed



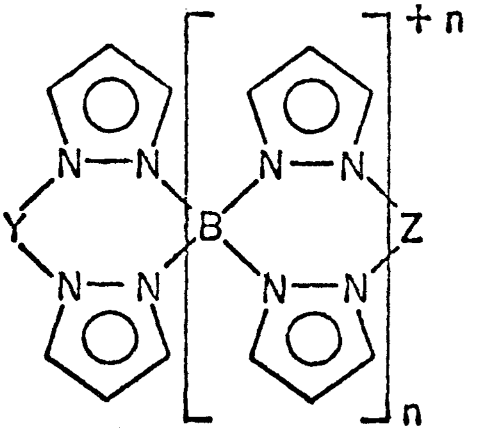
I

(*a.*) $Y = Z =$ Pd-π-CH_2CRCH_2
(*b.*) $Y = Z = BEt_2$
(*c.*) $Y = BEt_2$ $Z =$ Pd-π-CH_2CRCH_2



II

(*a.*) $Y = Z =$ Pd-π-CH_2CRCH_2
(*b.*) $Y = Z = BEt_2$



III

only two types of pyrazolyl groups present in 2 : 1 ratio and were thus compatible with static or dynamic D_{2h} symmetry.

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