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Preliminary communication

GROUP IB METAL CHEMISTRY

V. SOME FLUXIONAL COMPLEXES CONTAINING COPPER OR SILVER

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Summary

Fluxional poly(pyrazolyl)borate complexes of copper and silver, including the carbonyl $Cu(CO)B(pz)_4$, contain coordinated and free pyrazolyl groups, which interchange rapidly on the NMR time scale at room temperature; low temperature limiting spectra can be obtained for some copper complexes at —100°.

The preparation and some reactions of stable copper carbonyl complexes containing hydrotris(pyrazolyl)borate ligands have been described [1]. Extension to the tetrakis(pyrazolyl)borate series afforded $Cu(CO)B(pz)_4$ (I) (L = CO) (m.p. 150° (dec.); ν(CO) 2083 cm^{-1}), the proton NMR spectrum of which contains only three equal intensity resonances at τ 2.28, 2.34 and 3.84. It is not possible for all pyrazolyl groups in the $B(pz)_4$ ligand to coordinate to one metal atom, so that this observation taken in conjunction with the osmometric molecular weight found for a monomer, suggests that this complex is fluxional in solution.

This was confirmed by low temperature NMR studies of solutions of the carbonyl, and of a number of related complexes $CuLB(pz)_4$(I) (L = PR_3, AsR_3, etc.). A typical series of spectra, obtained for $Cu(PEt_3)B(pz)_4$, is illustrated in Fig. 1. The low temperature limiting spectrum contains six peaks, which can be divided into two sets of three signals, of relative intensities 3/1. The proposed tetrahedral coordination about copper in $Cu(L)HB(pz)_3$ has been confirmed by a single-crystal X-ray diffraction study of the carbonyl (L = CO) [2]. It is likely therefore that the signals of intensity 3 can be assigned to the protons of three coordinated pyrazolyl groups, with the others being resonances of a free pyrazolyl group.

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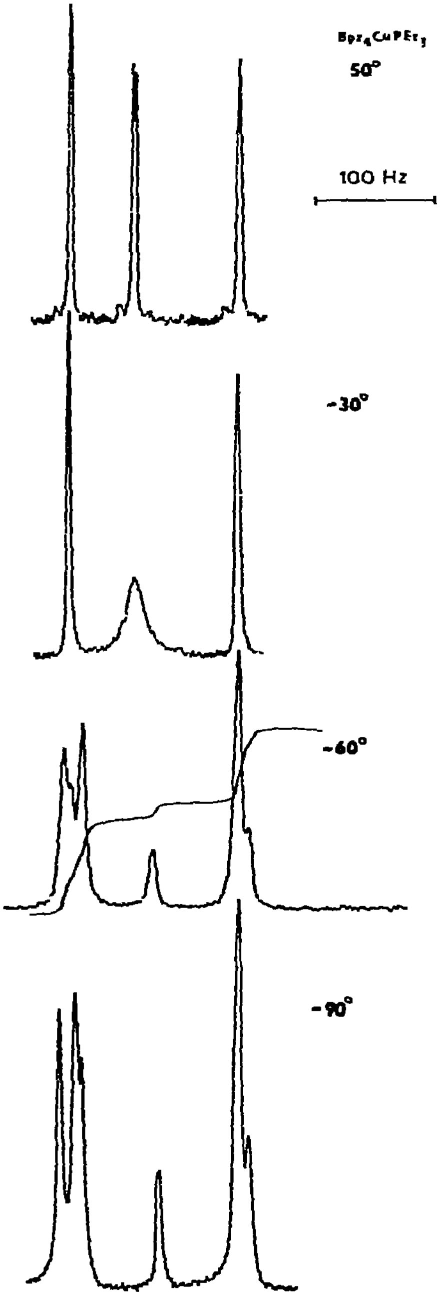
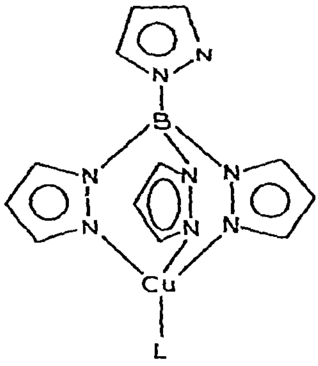


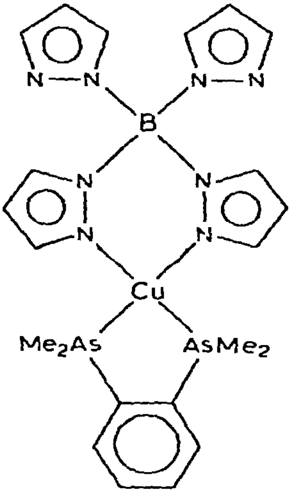
Fig. 1. Proton NMR spectra of Cu(PEt$_3$)B(pz)$_4$ at various temperatures.

At room temperature, all pyrazolyl groups interchange rapidly (on the NMR time scale), probably by a dissociative—associative mechanism, whereby random dissociation of one of the coordinated pyrazolyl groups is followed by association of one of the two groups which are now free in the three-coordinate intermediate.

Reactions of the various carbonyls with bidentate ligands produce com-



(I)



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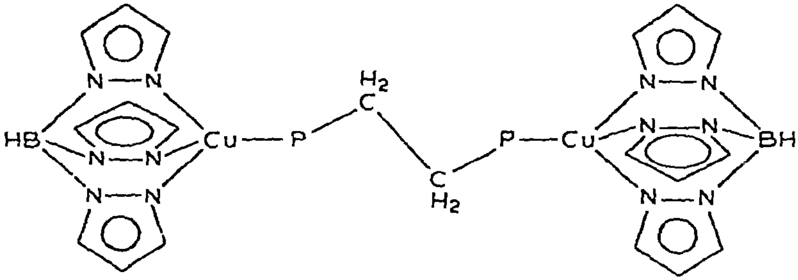

(II)

plexes of two types. If the ligand is sufficiently flexible to act either as an exobidentate or an endobidentate, such as 1,2-bis(diphenylphosphine)ethane (dppe), binuclear derivatives, such as $[CuHB(pz)_3]_2$(dppe) (II), are obtained, in which the former ligand configuration occurs. In contrast, more constrained donor molecules, such as 1,2-bis(dimethylarsino)benzene (diars), form simple chelate (endobidentate) complexes, such as $CuB(pz)_4$(diars) (III).

We find that where there are more than four potential donor sites in the ligands attached to the metal, complexes of type III exhibit fluxional behaviour. In these cases, the low temperature limiting spectra indicate that two or three pyrazolyl groups remain attached to the metal atom. For example, with $CuB(pz)_4$(diars) at the lowest temperatures, two sets of three peaks are obtained for the pyrazolyl proton resonances, with relative intensities 1/1, consistent with the instantaneous structure III. Also evident is a broadening of the aromatic resonances of the diars ligand, which probably results from a second dynamic process which can occur with a bidentate poly(pyrazolyl)borate ligand, the flipping of configurations of the $\overline{\mathrm{BNNCuNN}}$ ring.

We have extended these studies to the analogous silver(I) complexes, but have not yet been able to obtain the low temperature limiting spectra of these derivatives. Qualitative comparisons of related complexes, e.g. $MB(pz)_4[P(OMe)_3]$ (M = Cu or Ag), suggest that the dynamic processes are easier with silver than with copper, equivalent spectra being obtained at temperatures some 60° higher with the latter element.

To our knowledge, fluxional complexes of this type have not been described previously for these elements, although fluxional behaviour has been observed previously with several other poly(pyrazolyl)borate derivatives of transition metals [3, 4]. Similar behaviour has also been found for complexes of gold(III), such as $AuCl_2RB(pz)_3$ (R = H or pz) [5].

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