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Group IB Metal Chemistry. Part. IV. New Stereochemically Non-rigid Complexes Containing Gold

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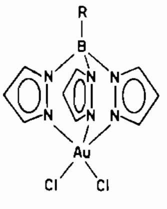
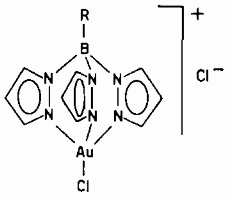
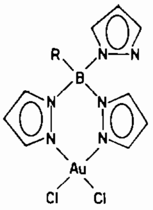
The reactions between gold(III) chloride (as $HAuCl_4 \cdot 3H_2O$) and the potassium salts of poly(pyrazolyl)borate anions, $KRB(pz)_3$ (R = H or pz; pz = pyrazolyl, $C_3H_3N_2$)[1,2] afford the bright yellow derivatives $AuCl_2RB(pz)_3$. Three structures for these complexes may be envisaged: the five-coordinate complex (I), a salt containing the four-coordinate cation (II), or a neutral four-coordinate complex containing a bidentate $RB(pz)_3$ group (III).



(I)



(II)



(III)

Structure (II) may be ruled out on the basis of conductivity measurements; chloride cannot be precipitated by silver(I) ion, and addition of large anions (BPh_4^-, PF_6^-) fails to give the corresponding salts.

At room temperature the proton n.m.r. spectrum of $AuCl_2HB(pz)_3$ contains only two broad signals, at τ 2.00 and 3.52, in the ratio 2:1. These resonances can be assigned to the 'outer' and 'inner' protons, respectively, of the pyrazolyl groups. On cooling the solution, the peaks broaden and eventually develop into a six-line pattern, which is fully resolved at –60 °C. Some of these spectra are illustrated in Fig. 1.

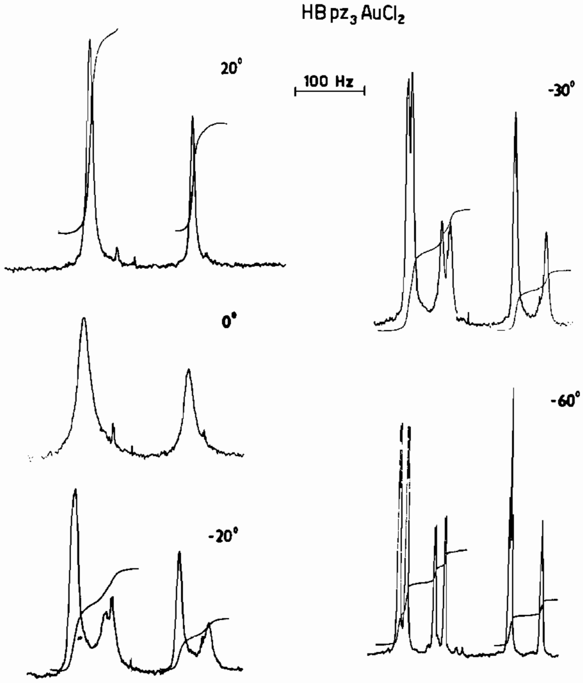


Fig. 1. Proton n.m.r. spectrum of $AuCl_2HB(pz)_3$ at various temperatures between 20 and –60 °C (in d_6-acetone).

Although the room temperature spectra support structure (I), the low temperature limiting spectrum shows conclusively that the complex has the square-planar structure (III). In this, two of the pyrazolyl groups are coordinated to the metal, while the third is free. At room temperatures, all pyrazolyl groups interchange by a process which is rapid on the n.m.r. timescale; random dissociation of one of the coordinated pyrazolyl groups followed by inversion and coordination of one of the free pyrazolyl group(s). This process may be related to those involved in exchange of free and coordinated pyrazolyl groups in copper and silver complexes such as $B(pz)_4MP(OMe)_3$, although in the present case it is notably slower. Trofimenko[4] has described similar rapid exchange of pyrazolyl groups in palladium and zinc derivatives.

Generally, gold(III) complexes are square planar,

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and it is not possible for three pyrazolyl groups of a poly(pyrazolyl)borate ligand to coordinate to one metal atom with this geometry. The exchange process may be facilitated, however, by some distortion towards trigonal bipyramideal geometry, which would allow the formation of a five-coordinate intermediate. Well characterised five-coordinate gold(III) complexes include $AuCl_3(LL)$ (LL = 2,2′-biquinolyl)[5].

We are unable to determine at this stage whether the dynamic process described above is accompanied by flipping of the $\overline{BNNAuNN}$ ring from one conformation to another, as found in other bidentate poly(pyrazolyl)borate complexes, such as $MoB(pz)_4(CO)_2(h^5\text{-}C_5H_5)$, and postulated for $CuB(pz)_4(diars)$.[3]

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