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Preliminary communication

RHODIUM COMPLEXES OF PYRAZOLE AND DERIVED LIGANDS: ANOTHER CASE OF METAL-SHUTTLING?

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Summary

Rhodium complexes containing poly(pyrazolyl)borate ligands are described, and the fluxional nature of some of them considered.

We have extended our studies [1] of complexes of the platinum metals with polypyrazolylborate ligands [2] to rhodium. We wish to report some preliminary results, including examples of boron—carbon bond cleavage, and a further example of tautomerism in a nitrogen-donor complex involving metal-shuttling between donor atoms.

Rhodium(III) chloride reacts readily with $KHB(Pz)_3$ to give an off-white solid, which with hexafluorophosphate affords $[Rh\{HB(Pz)_3\}_2]PF_6$ (Pz = pyrazolyl). It is likely that the cation is octahedral, and an analogy may be drawn with $[Rh(\pi\text{-}C_5H_5)_2]^+$[3].

With $[Rh(CO)_2Cl]_2$ and the tri- and tetra-pyrazolylborate anions however, insoluble materials are obtained, which give binuclear fragments in their mass spectra. These complexes have been characterised as $[Rh_2\{HB(Pz)_3\}_2(CO)_3]_n$ and $[Rh_2\{B(Pz)_4\}_2(CO)_3]_n$, respectively, probably with $n = 1$. However, their insolubility may suggest a polymeric nature. Others [4] have reported their reaction with iodine to afford the complexes $[RhL(CO)I_2]$.

The reaction between $[Rh(CO)_2Cl]_2$ and $KHB(Me_2Pz)_3$, on the other hand, afforded only $[Rh(Me_2Pz)(CO)_2]_2$ (I). This complex, and the unsubstituted pyrazole analogue (II), can be synthesised from $[RhCl(CO)_2]_2$ and the pyrazole in the presence of triethylamine:

$$[Rh(CO)_2Cl]_2 + PzH \rightarrow RhCl(CO)_2(PzH) \xrightarrow{-HCl} [Rh(CO)_2(Pz)]_2$$

The formation of the dimethylpyrazolyl complex from the boron ligand must

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proceed via B—C bond cleavage, a reaction which is becoming more common in polypyrazolylborate chemistry.

The ^1H NMR spectrum of the chloro complex (II) is unusual. Instead of the three resonances expected for a complex of the structure shown, two are found. The 3,5-dimethylpyrazole complex similarly exhibits only one methyl resonance instead of the two expected, together with a single signal for H(4). On cooling solutions of these complexes, changes in the ^1H NMR spectra occur, with limiting spectra showing the expected resonances consistent with the instantaneous structures.

Explanations of the fluxional process occurring with these compounds may involve a dissociative process, or an intramolecular exchange ("shuttling") of the hydrogen and the metal between the two nitrogen atoms.

(I) R = Me ; (II) R = H

At this stage we are not able to comment further on the mechanism. Similar phenomena have been reported recently by several authors [5] for some ruthenium—imidazole complexes.

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