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Preliminary communication

STRUCTURE AND REACTIVITY OF SOME RHODIUM(I) AND RHODIUM(III) POLY-1-PYRAZOLYLBORATE COMPLEXES

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Summary

Complexes of the general type $(RBPz_3)Rh(Alkene)_2$ have been shown to involve a fluxional h_2-polypyrazolylborate ligand. The alkene groups are readily displaced by phosphines, N_2 or CO but only the latter yields stable products.

The NMR spectrum of $(HBPz_3)Rh(C_2H_4)_2$ (Ia) (Pz = 1-pyrazolyl) consists of two sets of resonances assigned to eight equivalent ethylene protons and three equivalent pyrazole rings respectively [1]. The equivalence of the ethylene protons (ascribed to rapid rotation of the C_2H_4 groups) and of the three pyrazole rings led Trofimenko [1] to suggest that complex (Ia) contained a fluxional h_2-$HBPz_3$ ligand and was thus analogous to the 16-electron (Acac)Rh-$(C_2H_4)_2$ [1] rather than to the 18-electron $CpRh(C_2H_4)_2$ [2]. However, a similar NMR spectrum could be produced by an 18-electron structure involving a h_3-$(HBPz_3)$ ligand in which rotation about the C_3 axis of the ligand is rapid on the NMR time-scale [3]. This possibility has now been tested.

The new complexes (Ib), (IIa) and (IIb), (COD = 1,5-cyclooctadiene) were prepared in an analogous fashion to (Ia) [1] and the NMR spectra of each indicates a single pyrazole environment only. For complex (IIa) this indicates that olefin rotation per se plays no part in the averaging of pyrazole environments. The spectra of complexes (Ib) and (IIb) conclusively rule out the possibility of a rotating h_3-PBz_4 ligand since here the three-coordinated pyrazole groups and the single free group would be distinguishable. Trofimenko's proposed dynamic 16-electron h_2-structure [1] is therefore verified. Thus the stability of the new 16-electron h_2-complex (III) which we have also prepared was not unexpected. Complexes (Ia) and (IIa) form stable 1/1 complexes with $HgCl_2$, (IVa) and (IVb). These complexes are insoluble in all but strongly coordinating solvents in which dissociation is probable and therefore the NMR spectra, similar to (Ia) and (IIa), are not helpful in assigning the site of attachment of the $HgCl_2$ group.

$(RBPz_3)Rh(C_2H_4)_2$

(Ia, R = H;
Ib, R = Pz)

$(RBPz_3)Rh(COD)$

(IIa, R = H;
IIb, R = Pz)

$(H_2BPz_2)Rh(COD)$

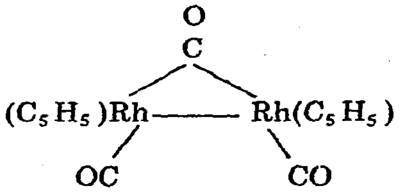
(III)

$(HBPz_3)RhL_2 \cdot HgCl_2$

(IVa, L = C_2H_4;
IVb, L_2 = COD)

$(RBPz_3)_2Rh_2(CO)_3$

(Va, R = H;
Vb, R = Pz)



(VI)

$(RBPz_3)Rh(CO)I_2$

(VIIa, R = H;
VIIb, R = Pz)

The 16-electron (Acac)Rh(C_2H_4)$_2$ is distinguished from 18-electron (C_5H_5)Rh(C_2H_4)$_2$ by a difference in the lability of the ethylene groups. The formal 16-electron configuration of the (Acac) complex facilitates rapid displacement of the alkene groups via 18-electron activated complexes [4]. In contrast the ethylene ligands in the 18-electron (C_5H_5)Rh(C_2H_4)$_2$ are displaced by nucleophiles only under vigorous conditions via a dissociative process. As expected, the alkene groups in complexes (Ia,b) and (IIa,b) were readily displaced by Ph_3P or $Ph_2PCH_2CH_2PPh_2$ but the products could not be obtained in a pure state. Displacement of C_2H_4 was also observed when dinitrogen was passed through a solution of (Ia) in CH_2Cl_2. The only isolable product was $[(HBPz_3)_2Rh]^+Cl^-$ and the presumed [4] intermediate N_2-complex could not be detected. Under similar conditions CO reacted readily with (Ia,b) and (IIa,b) to give the new highly insoluble pale yellow carbonyls (Va) and (Vb) respectively. These carbonyls can also be prepared by the reaction of the appropriate pyrazolylborate ligand with $[Rh(CO)_2Cl]_2$*.

Complexes (Va) and (Vb) are formally related to $Cp_2Rh_2(CO)_3$ which is known to have structure (VI) [6] but the new complexes may differ structurally from the C_5H_5 analogue. The extreme insolubility of the former suggests a polymeric structure in which $Rh_2(CO)_3$ units are bridged by *exo*-polydentate [7] polypyrazolylborate ligands. The observation of a single CO stretching frequency at 1845 (Va) or 1839 cm^{-1} (Vb) suggests that in contrast to the Cp analogue

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*This reaction has been independently studied by Bruce et al. [5].

the steric bulk of the pyrazolylborate structures forces all CO groups in the $Rh_2(CO)_3$ units to adopt a μ_2-configuration.

Complexes (Va) and (Vb) in CH_2Cl_2 suspension reacted with I_2 to give the deep red iodo-carbonyls (VIIa) and (VIIb) in low yield (ca. 10 - 20%). The NMR spectrum of complex (VIIb) shows that in solution at room temperature there are two distinct non-interconverting pyrazole environments in the ratio 3/1. Complexes (VIIa) and (VIIb) are thus h_3-polypyrazolylborate complexes, formal analogues of $(C_5H_5)Rh(CO)I_2$, and are among the very few true pyrazolylborate "half sandwiches" so far synthesised outside the Cr group [7]. The high ν(CO) value in complex (VIIa), 2090 cm^{-1} is consistent with a formal Rh^{III} structure.

Correct analytical data were obtained for all new complexes unless otherwise stated.

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