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Preliminary communication

New cationic rhodium(I) olefin complexes: the unusual conformation of the ethylene ligands in $[Rh(C_2H_4)_3(CH_3CN)_2]BF_4$

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The synthesis of cationic metal complexes containing olefins as ligands is a subject of increasing interest, and several synthetic methods have been claimed to be of general application[1–3]. Although some cationic carbonyl complexes with mono-olefins are known (*viz.* $Mn(CO)_5(C_2H_4)^{+}$,[4], $CpFe(CO)(C_2H_4)^{+}$ [5], $Re(CO)_4(C_2H_4)_2{}^{+}$ [6], $Rh(CO)(PMe_2Ph)_2(C_2H_4)_2{}^{+}$ [7], and related compounds), in most cases only diene complexes were obtained by the routes above.

We have now succeeded in obtaining a series of new cationic rhodium(I) mono-olefin complexes, using a chlororhodium complex containing mono-olefin ligands and a cuprous complex ion as electrophile. When solutions of $[Rh(C_2H_4)_2Cl]_2$ and $[Cu(CH_3CN)_4]BF_4$ ($[Rh] = [Cu] = 0.02\,M$) in CH_2Cl_2 saturated with ethylene were combined at room temperature, a white powder separated, and this was followed after several days by a very slow precipitation of large yellow needles in an almost quantitative yield. An apparatus providing slow diffusion of the two solutions was used for the reaction in order to facilitate the growing of crystals and the mechanical separation of the two products.

The stoichiometry of the reaction was shown by GLC to be: $\frac{1}{2}[Rh(C_2H_4)_2Cl]_2 + [Cu(CH_3CN)_4]^{+} + C_2H_4 \rightarrow [Rh(C_2H_4)_3(CH_3CN)_2]^{+} + CuCl + 2CH_3CN$. The crystalline product is stable in an ethylene atmosphere, but loses some (up to 1 mole) of the coordinated ethylene very slowly when ground in a mortar at room temperature under a stream of argon. It is possible that a tetracoordinated complex is formed under these conditions. The product dissolves with rapid decomposition in most polar solvents, and is slightly soluble in $CHCl_3$ and in THF. The analytical data are consistent with the formula $[Rh(C_2H_4)_3(CH_3CN)_2]BF_4$. The amount of ethylene in the complex was confirmed by mass spectral analysis after pyrolysis at 80°, 120° and 160°.

This is the first reported well-defined cationic complex with a mono-olefin as ligand, and with no other strong π-acceptor ligands, such as CO or phosphines. The IR data are consistent with a coordination complex of ethylene. The bands due to the coordinated ethylene are almost the same as in other complexes[8], except for the strong band at about 400 cm^{-1}, which is absent in the case of our complex. If the assignment of this band in other ethylene complexes, such as Zeise's salt, to the antisymmetric Me—C stretching[9] is correct, this suggests that rhodium-to-ethylene back-donation is not significant in this complex.

The X-ray structure has been investigated in these laboratories by the crystallographic group, full details will be given in a separate paper. The cation has a bipyramidal trigonal structure, the three ethylene C—C axes being, within experimental errors, coplanar with the trigonal plane, (unlike the structure found for other ethylene complexes with d^8 metal systems[10]). The two CH_3CN ligands occupy the apical positions (Fig. 1). The C—C distance in the ethylene ligands (1.34 Å) is practically identical with that in the free molecule. This unusual conformation is in accord with a σ-type complex, with a low degree of back-donation. Furthermore, this situation fullfils the steric requirements for a pentacoordinate complex.

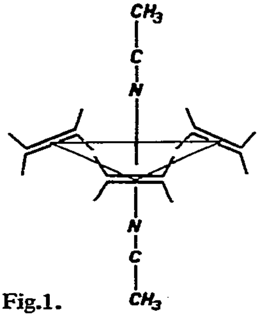

Fig.1.

Since the Rh—C and the Rh—N distances were found to be resp. 2.2 and 2.0 Å, it can be calculated that the distance from an ethylene C to an apical N would be much too short (*viz.* 2.4 Å) if the ethylene ligands were parallel to the trigonal axis, the actual distance being 2.9 Å.

Unfortunately, the NMR spectra cannot be regarded as significant, due to the low stability of the solutions. However, a broad signal at τ 7.4 observed in liq. SO_2 at −60° can probably be assigned to the coordinated ethylene.

On trying to extend the synthesis to other olefins, we found that the chloro ligand abstraction can be carried out from other olefin complexes (namely, bis-propylene, bis-cyclooctene chlororhodium(I) dimers) and $[Cu(CH_3CN)_4]BF_4$. In the case of the cyclooctene complex, we succeeded in obtaining yellow crystals by addition of petroleum ether to the filtered cold solution in the presence of C_8H_{14}. The analytical data are consistent with the formula $[Rh(C_8H_{14})(CH_3CN)_3]BF_4$; the NMR spectrum in CD_3OD confirms the ratio of $C_8H_{14}CH_3CN$ 1/3. On the other hand the reaction between $[Rh(C_8H_{14})_2Cl]_2$ and $[Cu(C_8H_{14})(CH_3CN)_2]BF_4$ (the latter prepared by recrystallisation of $[Cu(CH_3CN)_4]BF_4$ from boiling cyclooctene) gave a different complex, of composition $[Rh(C_8H_{14})_2(CH_3CN)_2]BF_4$. We shall describe the reactions of these complexes later.

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