A *cis*-Influence of π-Bonding Ligands in Two Rhodium( ) Complexes

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Summary The molecular geometries of tris(triphenylphosphine)rhodium(I) chloride and bistriphenylphosphine(tetrafluoroethylene)rhodium(I) chloride illustrate a *cis*-influence of perfluoroethylene relative to triphenylphosphine.

THE bond lengths in a number of planar platinum(II) complexes have been summarised and demonstrate the *trans*-influence of a number of ligands on the platinum–chlorine bond length; the *trans*-influence of a given ligand was shown to be related to its electronegativity and to the ligand–metal $p(\sigma)$ overlap integrals.[1] We have now completed structural analyses of the isoelectronic rhodium(I) complexes—tris(triphenylphosphine)rhodium(I) chloride and bistriphenylphosphine(perfluoroethylene)rhodium(I) chloride. The results (Figure) demonstrate an unexpectedly large *cis*-influence of the olefin ligand in contrast to the small *trans*-influence of ethylene, for example, in Zeise's salt[2] and a diolefin complex of platinum(II).[3]

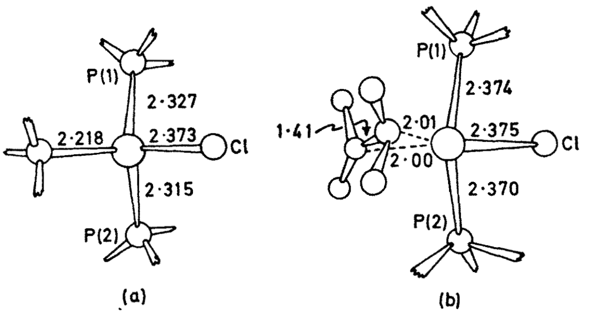

FIGURE. *Bond lengths* (Å) in (a) *tris(triphenylphosphine)rhodium(*I) *chloride and* (b) *bistriphenylphosphine(tetrafluoroethylene)rhodium*-(I) *chloride. E.s.d's in the bond lengths average* 0·008 Å (Rh–P *and* Rh–Cl), 0·02 Å (Rh–C) *and* 0·03 Å (C–C).

The co-ordination of the rhodium in both complexes is not planar, the distortion towards a tetrahedral arrangement of the ligands being particularly marked in tris(triphenylphosphine)rhodium chloride; the distortion serves to minimise intramolecular non-bonded interactions. The metal–chlorine bond length is essentially independent of the substitution of one phosphine ligand by tetrafluoroethylene and is also identical, within experimental error, with that in $(Ph_3P)_2(CS)RhCl$.[4] The two mutually *trans*-phosphine ligands are seen, however, to be very sensitive to the *cis*-olefin–phosphine substitution; the difference of 0·05 Å between the two mean bond lengths, [Rh–P(1), Rh–P(2)] of 2·37 $[(Ph_3P)_2C_2F_4RhCl]$ and 2·32 Å $[(Ph_3P)_3RhCl]$ is highly significant.

The essential invariance of the Rh–Cl bond length in these complexes rules out the possibility that the *cis*-influence stems from the modification of the metal *s*-orbital on ligand substitution. We note that substitution of triphenylphosphine by perfluoroethylene increases the bond lengths and, we assert, decreases the π-bond orders of the two *cis*-metal to phosphine bonds. The charge requirements (electroneutrality) of the metal are largely met in the tetrafluoroethylene complex by charge-transfer to the low-lying antibonding orbitals of this ligand, whereas in the tristriphenylphosphine complex, the mutually *trans* metal–phosphine bonds must, of necessity, have a considerable π-bond order.

The co-ordinated C_2F_4 ligand is, as expected, [1,5] non-planar. The four fluorine atoms form a plane with the carbon atoms displaced a mean distance of 0·44 Å from this plane towards the metal.

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