

Non-Primary Valence Interactions In Low Valent Transition Metal Complexes and Some Possible Implications for the Structure of Coordinatively Unsaturated Species

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Since the original suggestion¹ of a geometrical basis for facile intramolecular hydrogen transfer in transition metal-tertiary phosphine complexes, the scope of *ortho*metallation (intramolecular oxidative addition) reactions has broadened considerably. Although the *ortho*-hydrogens of tertiary phosphine ligands are often observed to be positioned close to vacant coordination sites (for example, axial positions in four coordinate species), there was little direct evidence on whether the metal-hydrogen interaction was effectively bonding or not. In two recent structural analyses, Cotton *et al.*^{2,3} have shown the bonding capacity of an aliphatic C-H bond: if the C-H bond be formally regarded as a two-electron donor, an effective 18-electron configuration is provided for the metal atom in the complexes $(Et_2Bpz_2)Mo(CO)_2(2-PhC_3H_4)$ and $(Et_2)(Bpz_2)(C_2H_2)(CO)_2Mo$ (Bpz is here the pyrazolylborate ligand). The formation of a three centre-two electron bond is reflected in a short metal-hydrogen 'non-bonded' distance of *ca.* 2.0 Å and Cotton *et al.* demonstrate³ that what we shall call a *non-primary valence interaction* with a carbon-hydrogen bond is competitive energetically with alternative metal-cyclic polyolefin bonding.

For the later transition metals, particularly those complexes based on d^8 and d^{10} metal ions, two structural analyses^{4,5} deserve comment in the context of non-primary valence interactions *formally* providing a rare gas configuration to the metal. The fourteen electron complexes $Pd[PPh(t-Bu)_2]_2$, $Pd[P(t-Bu)_3]_2$ and $Pd[P(cyclohexyl)]_3$ have been analysed crystallographically: two *ortho*-hydrogen atoms are positioned at *ca.* 2.7 Å from the metal and

are essentially co-planar with the palladium and phosphorus atoms in the di(*t*-butyl)phenylphosphine derivative. The palladium atom can be thought of, therefore, as achieving a formal eighteen electron configuration through a five centre-four electron bond (counting, rather artificially, each C-H bond as two-centre in this polycentre interaction). Support for an attractive polycentric interaction was claimed⁵ in the observed temperature variation of the ¹H nmr spectrum which shows two *ortho*-hydrogen signals at τ 0.93 and 2.48 at -60 °C and, accordingly, similarity between the structures in the solid state and in solution.

An analogous situation is obvious from our structural characterisations of tris(triphenylphosphine)-rhodium(I) chloride. This complex crystallizes in two distinct crystal modifications depending on the mode of synthesis. Red crystals⁶ are *ortho*-rhombohedral, space group $Pna2_1$ with $a = 32.98$, $b = 12.26$, $c = 10.99$ Å,

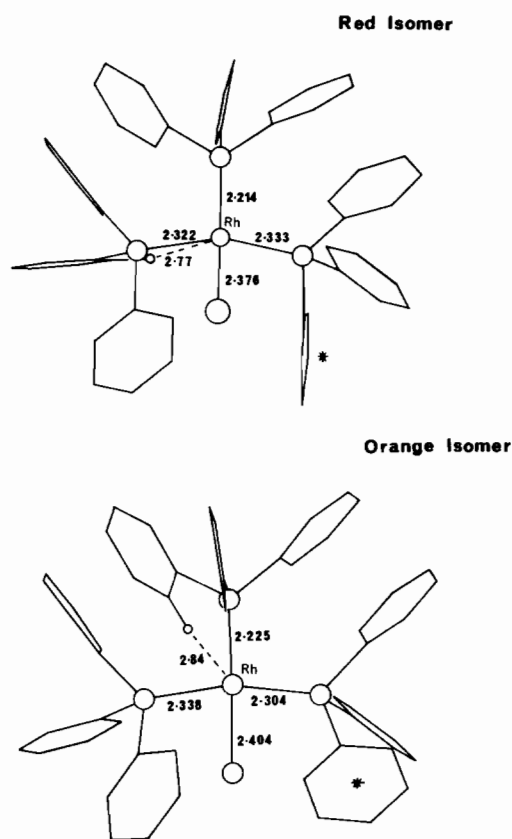


Fig. 1. Molecular structure of $RhCl(PPh_3)_3$.

$Z = 4$, $\rho_{\text{obs}} = 1.38 = \rho_{\text{calc}} \text{ g cm}^{-3}$. The orange allotrope belongs to the same space group but with a very different unit cell ($a = 19.47$, $b = 12.69$, $c = 18.20 \text{ \AA}$, $Z = 4$, $\rho_{\text{obs}} = 1.37 = \rho_{\text{calc}} \text{ g cm}^{-3}$). The red crystals were analysed in Sheffield and Edmonton with no significant differences in the results ($R \sim 0.04$ for 1500 reflexions; Mo $K\alpha$), while the orange isomer was analysed in Edmonton only ($R = 0.047$ for 1412 reflexions; Cu $K\alpha$, absorption correction). The stereochemistries of the two forms are illustrated in the Figure. The coordination spheres are seen to be very similar with the ligands providing a distorted planar stereochemistry⁶. Corresponding metal–ligand bond lengths are identical within experimental error, with the possible exception of the Rh–Cl bond which is positioned approximately *trans* to an *ortho*-hydrogen atom in the orange isomer. The very different intermolecular packing in the two crystals is reflected in different conformations of the phenyl groups in the complex but, with the exception of one (asterisked) ring, these can be seen to have similar ($\pm 30^\circ$) orientations with respect to the mean coordination plane. A quasi-eighteen valence electron configuration is provided in both isomers *but by different ortho-hydrogen atoms*; major changes in the intermolecular force field do not remove the separate non-primary valence interactions (in the red isomer, the next shortest rhodium–hydrogen distances are 2.94 and 3.17 \AA ; in the orange isomer, they are 2.94 and 2.97 \AA).

Three remarks seem appropriate. Firstly, we cannot take too literally the concept of a C–H bond being a two-electron donor. With Craig and Doggett⁷, we prefer the view that the rare gas rule reflects the situation when the metal *d*-electrons experience a potential from the ligands which, in symmetry and magnitude, closely approximates that experienced by the *d*-electrons in the adjacent rare gas atom. The non-primary valence interactions round off, as it were, the asymmetric potential in a two- and (planar) four-coordinate complex. They do not necessarily lead to considerable charge transfer to the metal through, say, the vacant $5p_z$ orbital of the rhodium ion for the modification of the potential could be

via a predominantly electrostatic interaction.

Secondly, there has been much discussion of the mechanism of catalysis of a number of reactions by $\text{RhCl}(\text{PPh}_3)_3$ particularly with regard to the role of the fourteen-electron species, $\text{RhCl}(\text{PPh}_3)_2$. Tolman *et al.*⁸ have suggested that it may be effectively a 16-electron system with an extra electron pair being denoted by an aromatic ring. We note that in $[(\text{Me}_2\text{Ph})\text{P}]_4\text{Mo}$ one tertiary phosphine coordinates through a phenyl ring, thereby creating an 18-electron configuration for the metal⁹, and a similar arrangement could be envisaged for the bis-phosphine rhodium chloride intermediate. An energetically more accessible, electronically saturated species is, however, the trigonal bipyramid arrangement with two *ortho*-hydrogen atoms occupying axial positions. They could relax easily in the formation of the dimeric species $[(\text{Ph}_3\text{P})_2\text{RhCl}]_2$ or an adduct, $(\text{Ph}_3\text{P})_2\text{-Rh}(\text{Cl})\text{L}$. This is an attractive, albeit speculative, reason for postulating intermediates with non-primary valence interactions contributing to the electronic requirements of the metal for they will be obviously separated from other catalytically active structures by low activation energies corresponding to, say, hindered rotation around phosphorus–carbon bonds. A careful, systematic survey of non-primary valence interactions in the solid state and of their persistence, or otherwise, in solution is needed.

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