Stereochemistries of and Bonding in Complexes of Third-row Transition-metal Halides with Tertiary Phosphines

By L. ASLANOV,† R. MASON,* A. G. WHEELER, and P. O. WHIMP

(*Department of Chemistry, University of Sheffield, Sheffield,* S3 7HF)

Summary Bond lengths in eight tertiary phosphine complexes of third-row transition-metal halides are summarised and discussed.

A SERIES of complexes ML_2Cl_4 and ML_3Cl_3, where L is a mono(tertiary phosphine) and M a number of third-row transition metals in their 4+ and 3+ oxidation states, has been synthesised and characterised by Chatt and his co-workers.[1] The complexes offer the opportunity of studying the dependence of M–L and M–Cl bond lengths on the effective charge and electronic configuration of the metal, the *trans*-influence of tertiary phosphine ligands on metal–chlorine bonds and of clarifying our views on the nature of transition metal–phosphorus bonds.

TABLE. *Bond lengths and their standard deviations* (Å) *in bis-tertiary phosphine- and tris-tertiary phosphine-complexes of metal halides*

M^{IV} complexes

Ion Bond	W^{IV}	Re^{IV}	Os^{IV}	Ir^{IV}	Pt^{IV}
M–Cl	2·339(3)	2·331(3)	2·319(3)	2·324(5)	2·332(5)
M–P	2·550(3)	2·505(3)	2·448(3)	2·392(5)	2·393(5)

M^{III} complexes

Ion Bond	Re^{III}	Os^{III}	Ir^{III}
M–Cl(*trans* to Cl)	2·353(6)	2·347(6)	2·361(6)
M–Cl(*trans* to P)	2·454(6)	2·439(6)	2·429(6)
M–P(*trans* to P)	2·458(6)	2·408(6)	2·363(6)
M–P(*trans* to Cl)	2·401(6)	2·350(5)	2·277(6)

The complexes $M(PMe_2Ph)_2Cl_4$ (M = W^{IV}, Re^{IV}, Os^{IV}, Ir^{IV}) and $Pt(PEt_3)_2Cl_4$ all crystallise in the monoclinic system, space group $P2_1/c$; $Z = 2$ so that the complexes have exact C_1 symmetry (*trans*-configuration). *X*-ray data have been collected by counter diffractometer methods and the analyses have provided rather accurate molecular parameters [a typical reliability index for *ca.* 1400 independent reflexions for each complex is 0·04; $\sigma(\rho) \approx 0{\cdot}12 e Å^{-3}$ and hydrogen atoms on the phenyl ring of the phosphine ligand have been located in stereochemically acceptable positions]. Bond lengths in these complexes, averaged over chemically equivalent bonds, are collected in the Table, figures in parentheses being e.s.d.'s referred to the least significant digit of the preceding bond length.

The crystal structures of the complexes *mer*-$M(PMe_2Ph)_3Cl_3$ (M = Re^{III}, Os^{III}, and Ir^{III}) are much more complex with two molecules in the asymmetric unit of a large monoclinic unit cell. A typical *X*-ray analysis of one of these complexes was based on *ca.* 4000 independent reflexions with convergence to an unweighted discrepancy index of 0·05; bond lengths and their e.s.d.'s are again collected in the Table.

These results are conveniently summarised in the Figure and a number of points deserve comment at this stage.

(i) Change of electronic configuration has little effect on the M–Cl bond lengths but a much greater influence on the M–P bonds. For unit increase in electronic configuration, the M–Cl bonds contract by at most 0·01 Å, whereas the M–P bonds contract by *ca.* 0·05Å.

(ii) The M^{IV}–Cl and M^{III}–Cl bond distances for a given configuration differ by 0·03 Å, whereas the M^{IV}–P and M^{III}–P distances are nearly coincident (in the 3+ complexes, one is referring to the M–Cl bonds *trans* to another chlorine and the M–P bonds *trans* to another phosphine ligand). The interpretation of this result seems straightforward and intuitively obvious: the more ionic M–Cl bonds are much more sensitive to the formal oxidation state of the metal than their more covalent metal–phosphorus counterparts.

(iii) The *trans*-influence of a co-ordinated tertiary phosphine ligand on an M–Cl bond length in an octahedral complex is *ca.* 0·1 Å, a value comparable to that which we have discussed for planar d^8 complexes and a number of six-co-ordinate species.[2]

(iv) There is considerable anisotropy in the σ-covalent radius of the earlier metals. For example, the covalent radius of W^{IV}, judged from the M–Cl distance, is 1·35 Å while the value derived from the M–P distance is 1·49 Å. Even allowing for some correction for varying ionic character, these values suggested that the axial metal–phosphorus bonds contain much more '*s*' electron character than the equatorial metal–chlorine bonds. The centroids of electron density,

$$\bar{r}_{6s} = \frac{\int r|\psi|^2 d\tau}{\int |\psi|^2 d\tau}$$

for the Basch–Gray wavefunctions[3] are 1·52 Å (W^{IV}), 1·48 Å (Re^{IV}), 1·45 Å (Os^{IV}), 1·42 Å (Ir^{IV}), and 1·39 Å (Pt^{IV}). These theoretical radii are quite close in absolute value and in their variation from element to element to the observed covalent radii derived from the metal–phosphorus bond lengths. We are presently investigating theoretical radii of

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† Present address: Chemistry Department, Moscow State University, Moscow, U.S.S.R.

hybrid orbitals for we do not, as yet, have a quantitative explanation for the small variations in the M–Cl bond distances. There is additional evidence to support the view that the metal–phosphorus bond lengths are particularly sensitive to their '*s*' electron character. In $OsH_4(PEt_2Ph)_3$, the average Os–P bond length[4] is 2·311 Å which is 0·14 Å less than that observed in $OsCl_4(PMe_2Ph)_2$. The mutually ***trans***-metal–phosphorus bonds in the hydrido-complex average 2·296(4) Å in length compared with the value of 2·339 Å for the remaining Os–P bond length. With equivalent σ-hybrid orbitals in a seven-co-ordinate species, it follows that the M–P bonds must have less '*s*' electron character compared with their counterparts in the MCl_4P_2 species. The covalent radius of Os^{IV} in the hydrido-species is 1·25 ± 0·03 Å compared with 1·33 and 1·39 Å derived from the M–Cl and M–P bond lengths, respectively, in $OsCl_4(PMe_2Ph)_2$.

(v) It was not possible to analyse the structure of the complex, $PtCl_4(PMe_2Ph)_2$, on account of its instability. The metal–phosphorus and, to a much less significant extent, the metal–chlorine bond lengths in $PtCl_4(PEt_3)_2$ show a discontinuity from an otherwise systematic trend; this may be related simply to the change of substituents on the phosphine ligands although the Figure shows some indication, albeit hardly significant, of a comparable situation in the M^{III} complexes.

(vi) While the $(M–X_4)e_u$ stretching frequencies[1] fall in the series Pt > > Ir > Os > Re, the metal–chlorine bond lengths show no large variations which could reasonably be attributed to high ligand-field stabilisation energy in the d^6 complex.

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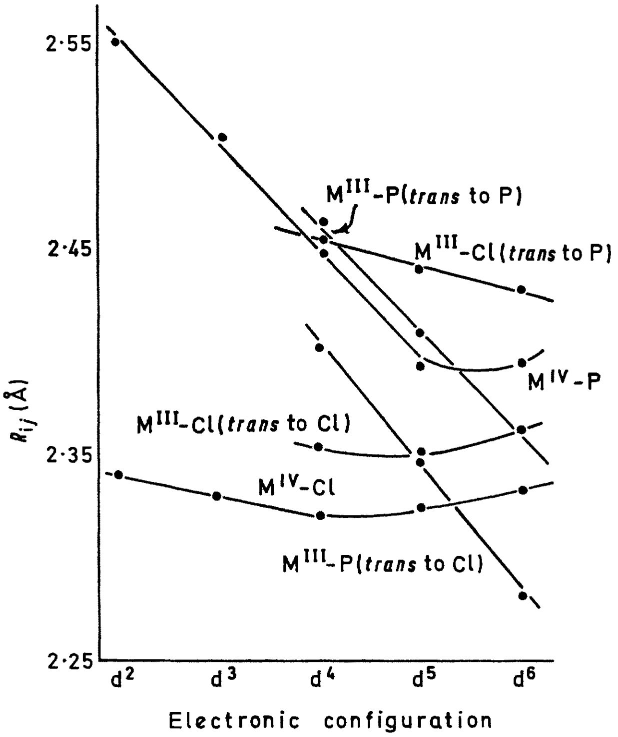

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