# Five-co-ordinate Iridium(III) Hydrides with Hydride Resonances at $\tau$ 60

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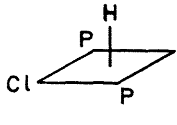
*Summary* Some purple hydrides of the type $[IrHCl_2(PBu^t_2R)_2]$ (R = Me, Et, or Pr$^n$) are described for which the hydride ligands have the largest $\tau$-values yet observed (*ca.* 60); the influence of bulky phosphines on products is discussed briefly.

WE find that the hexachloroiridite ion when heated with an excess of di-t-butyl(alkyl)phosphines in isopropyl alcohol for *ca.* 15 h gives five-co-ordinate iridium(III) hydrides, $[IrHCl_2(PBu^t_2R)_2]$; R = Me, Et, or Pr$^n$, configuration (**1**) as stable purple crystals. Steric effects and the strong *trans*-bond weakening effect of the hydride ligand are probably both important in preventing co-ordination of a third $PBu^t_2R$ (which is extremely bulky). In six-co-ordinate iridium hydrides $[IrHCl_2L_2Q]$ of configuration (**2**) (L, Q = tertiary phosphine) the tertiary phosphine (Q) *trans* to hydrogen is much more labile and is probably much less strongly co-ordinated than the other two phosphines (L).[1]

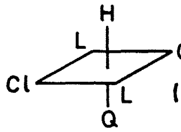
The suggested square pyramidal geometry for these complexes $[IrHCl_2L_2]$ is confirmed by their physical properties and by analogy with corresponding rhodium complexes $[RhHCl_2L_2]$, for which the *trans*-planar arrangement of the Cl and L ligands has been established by *X*-ray diffraction, for L = $PBu^tPr^n_2$.[2]

These complexes of type $[IrHCl_2(PBu^t_2R)_2]$ show only one band (at *ca.* 315 cm$^{-1}$) due to an iridium–chlorine stretching vibration, indicating that the chlorines are mutually *trans.* $\nu$(Ir–H) occurs at *ca.* 2000 cm$^{-1}$. In the $^1$H n.m.r. spectrum the t-butyl resonance forms a well defined 1 : 2 : 1 triplet showing that $|^2J(P\text{–}P)|$ is large[3] and the phosphines are probably *trans.*[4] The complexes show a triplet hydride resonance at exceptionally high $\tau$-values, 60·5 (Me), 59·6 (Et) and 60·0 (Pr$^n$). These are the highest $\tau$-values yet observed for diamagnetic compounds. The high $\tau$-values for transition metal hydride ligand have been attributed to paramagnetic shielding by valence *d*-electrons of the metal;[5,6] the shielding would then increase as the separation between the ground and electronically excited states decreases and/or the metal–hydrogen distance decreases. Our five-co-ordinate iridium(III) hydrides show electronic absorption maxima at exceptionally low frequencies for hydrides {*e.g.* $[IrHCl_2(PBu^t_2Et)_2]$ has $\lambda_{max}$ nm ($\epsilon$) at 568(420), 529(350), 461(570), and 433(469)} and there could be an unusual amount of 'mixing in' of the excited states under the influence of a magnetic field. This could be the major cause of high $\tau$-values. An unusually short iridium–hydrogen distance, which might be expected from the absence of a *trans*-ligand, could also contribute towards a high $\tau$-value.

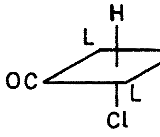
The complexes $[IrHCl_2(PBu^t_2R)_2]$ are co-ordinately unsaturated and although a third $PBu^t_2R$ ligand is too large to become co-ordinated, smaller ligands (Q) such as CO, MeNC, pyridine, 4-methylpyridine, dimethyl sulphide, *etc.* are taken up to give yellow complexes $[IrHCl_2(PBu^t_2R)_2Q]$ of configuration (**2**). The hydride chemical shifts for these complexes are quite low $\tau$ 20—25.



(1)



(2)



(3)

On heating $[IrHCl_2(PBu^t_2Pr^n)_2]$ in boiling 2-methoxyethanol for 15 h it gives (>90%) *trans*-$[IrCl(CO)(PBu^t_2Pr^n)_2]$. The hexachloroiridite ion when heated with tertiary t-butylphosphines (L) in 2-methoxyethanol gives complexes of the type *trans*-$[IrCl(CO)L_2]$, or their adducts with hydrogen chloride, $[IrHCl_2(CO)L_2]$, configuration (**3**). Thus $PBu^t_2Ph$ gives *trans*-$[IrCl(CO)(PBu^t_2Ph)_2]$ (100%); $PBu^tEt_2$ gives $[IrHCl_2(CO)(PBu^tEt_2)_2]$, configuration (**3**) (>90%), and $PBu^tPr^n_2$ gives a mixture of both.

Thus when the hexachloroiridite ion (or iridium trichloride) reacts with bulky phosphines (L) especially those with t-butyl substituents simple substitution products $[IrCl_3L_3]$ such as one gets with triethylphosphine or dimethylphenylphosphine[7] are not formed. It seems likely that hydrides or carbonyls are produced because in this way steric strain is reduced. When triphenylphosphine reacts with iridium trichloride a hydride, $[IrHCl_2(PPh_3)_3]$, or a carbonyl, *trans*-$[IrCl(CO)(PPh_3)_2]$, is formed rather than $[IrCl_3(PPh_3)]_3$.[8,9] We suggest that this is due to steric rather than electronic factors.

We thank the S.R.C. and Imperial Chemical Industries Ltd. for financial support.

(*Received, December* 21*st*, 1970; *Com.* 2194.)

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