Assignments of Metal–Ligand Vibrations for Triphenylphosphine Complexes

By G. B. DEACON* and J. H. S. GREEN†

(*Department of Chemistry, Monash University, Clayton, Victoria, Australia; †Chemical Standards Division, National Physical Laboratory, Teddington, Middlesex)

METAL–PHOSPHORUS stretching frequencies have been assigned for complexes of trialkylphosphines,[1–3] and it has been suggested[1] that ν(Pt–P) may be at 424 cm.$^{-1}$ in Pt^0(Ph$_3$P)$_4$. However no definite assignments of ν(M–P) for triphenylphosphine complexes have been reported. We have recorded the spectra (380—40 cm.$^{-1}$)[4] of the complexes (Ph$_3$P)$_2$MX$_2$ (M = Zn, Cd, or Hg; X = Cl, Br, or I), and have assigned ν(M–P) to bands in the 166—98 cm.$^{-1}$ region. Assignments have also been made for the ν(M–X) vibrations.

(a) *Metal–phosphorus stretching frequencies*

Absorption bands of (Ph$_3$P)$_2$MX$_2$ complexes above 180 cm.$^{-1}$ can be assigned either to modes of triphenylphosphine or to ν(M–X) vibrations. Triphenylphosphine has no absorption bands in the region 180—40 cm.$^{-1}$, but the following bands, essentially independent of the mass of the halogen, are observed in the spectra of the complexes below 180 cm.$^{-1}$, and can be assigned to metal–phosphorus stretching modes (Table 1). Although the complexes probably have tetrahedral structure,[5,6] only the mercury complexes show the pair of ν(M–P) frequencies expected for this structure. The δ(PMP) modes are evident below 40 cm.$^{-1}$, as no other bands below 180 cm.$^{-1}$ were independent of the mass of the halogen.

TABLE 1

	X = Cl	Br	I
M=Zn	166	157	153
Cd	136	134	133
Hg	137	132	133
	108	104	98

Although the ν(M–P) frequencies for (Ph$_3$P)$_2$MX$_2$ complexes are much lower than those given for (Et$_3$P)$_2$PtX$_2$ complexes (440—400 cm.$^{-1}$),[1] there is not necessarily a conflict between these observations. It is difficult to make a meaningful comparison between the two sets of assignments, owing to the different stereochemistries of the complexes and the different electronic configurations of the metals. However, two factors contributing to the frequency difference can be identified: Pt–P bonding is stronger owing to π-bonding than M–P bonding, in which a significant π-bonding contribution is unlikely, and the mass of triphenylphosphine is considerably larger than that of triethylphosphine.

(b) *Metal–halogen frequencies*

The following absorption frequencies, which move to lower values as the mass of the halogen is increased, are assigned to metal–halogen stretching modes (Table 2). The frequency ratios, ν(M–Br)/ν(M–Cl) = 0·68—0·71 and ν(M–I)/ν(M–Cl) = 0·56—0·60 [using average ν(M–X) frequencies for each complex] are virtually independent of change in metal. Two ν(M–X) frequencies are generally observed in accordance with the probable tetrahedral structure. The complexes also show a further set of halogen-mass-sensitive absorption bands at lower frequencies which can be assigned to δ(XMX), *e.g.*, at 79, 56, and 42 cm.$^{-1}$ for $(Ph_3P)_2HgCl_2$, $(Ph_3P)_2HgBr_2$, and $(Ph_3P)_2HgI_2$, respectively.

TABLE 2

	X = Cl	Br	I
M = Zn	316*	236*	198
	297	200	173
Cd	268	195	166
	261	176	145
Hg	232	153	127
	221		

* Values agree with those previously reported (ref. 5).

(*Received, April 22nd*, 1966; *Com.* 261.)

---

[1] D. M. Adams and P. J. Chandler, *Chem. Comm.*, 1966, 69.

[2] P. Goggin and R. J. Goodfellow, quoted by D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5275.

[3] G. E. Coates and C. Parkin. *J. Chem. Soc.*, 1963, 421.

[4] Higher-frequency spectra of the complexes have been discussed, G. B. Deacon and J. H. S. Green, *Chem. and Ind.*, 1965, 1031.

[5] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1964, 166.

[6] R. C. Evans, F. G. Mann, H. S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1940, 1209.