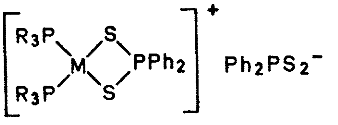
Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II). A Correction

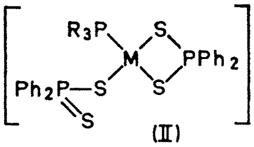
By (MISS) J. M. C. ALISON and T. A. STEPHENSON*
(*Department of Chemistry, University of Edinburgh, Edinburgh* EH9 3JJ)

Summary The 1 : 1 and 1 : 2 tertiary phosphine adducts of $Pd(S_2PPh_2)_2$, originally formulated as five- and six-co-ordinate complexes, respectively, are probably both four-co-ordinate.

RECENTLY evidence was reported for 1 : 1 and 1 : 2 tertiary phosphine adducts of $Pd(S_2PPh_2)_2$ which were tentatively formulated as five- and six-co-ordinate complexes, respectively.[1] Further work on these and the isomorphous platinum(II) complexes has now indicated that this formulation is incorrect and that the "six-co-ordinate" complexes are in fact four-co-ordinate ionic species (I) and the "five-co-ordinate" complexes are probably the four-co-ordinate species (II).



(I)



(II)

(M = Pd,Pt)

The evidence for the revised structures is as follows: (a) As discussed previously,[1] the 1 : 2 complexes rapidly dissociate to 1 : 1 complexes in benzene and carbon disulphide. However, in more polar solvents such as dichloromethane the 1 : 2 complexes are stabilized and conductivity measurements (Table 1) are consistent with those expected for 1 : 1 electrolytes in this solvent.

TABLE 1

Equivalent conductivities (25°) *of some* 1 : 1 *and* 1 : 2 *complexes in* CH_2Cl_2

Compound	Concn. (10^{-4}M)	Λ^a	Λ^a (plus excess of PR_3)
$Bu^n{}_4NClO_4$	10·1	22·7	—
$Pd(S_2PPh_2)_2(PEt_3)_2$	8·3	25	—
$Pd(S_2PPh_2)_2(PMe_2Ph)_2$	12	24·4	—
$Pd(S_2PPh_2)_2(PMe_2Ph)$	13·7	2·5	26·4
$Pt(S_2PPh_2)_2(PPh_3)_2$	8·8	26·6	—
$Pt(S_2PPh_2)_2(PPh_3)$	9·4	0·72	32·35
$Pt(S_2PPh_2)_2(PMePh_2)_2$	8·6	30·2	—
$Pt(S_2PPh_2)_2(PMePh_2)$	8·1	1·18	29·77

[a] $cm^2\ ohm^{-1} mole^{-1}$.

(b) Addition of an excess of tertiary phosphine to the 1 : 1 complexes (non-electrolytes) in CH_2Cl_2 produces an increase in conductivity consistent with the formation of 1 : 1 electrolytes (Table 1).

(c) ^1H n.m.r. data on 1 : 2 platinum(II) complexes of $MePh_2P$ and Me_2PhP in deuteriochloroform (Table 2) indicate a *cis*-arrangement of tertiary phosphine groups (no virtual coupling[2]).

(d) An *X*-ray structural analysis[3] on $[Pd(S_2PPh_2)_2(PEt_3)_2]$ is sufficiently advanced to verify the authenticity of structure (I). The mull and solution i.r. spectra of these 1 : 2 complexes are identical, suggesting the same species is retained in solution, and this is supported by ^1H n.m.r. and conductimetric data.

The reformulation of the 1 : 2 complexes as the ionic species (I) and their ready interconversion with the 1 : 1 complexes casts doubt on the validity of the five-co-ordinate structure postulated earlier for the latter.[1] No direct evidence is yet available to support (II) (a crystal structure of $[Pd(S_2PPh_2)_2(PPh_3)]$ is in progress) but an analogous structure has been postulated by Tebbe and Muetterties[4] for 1 : 1 tertiary phosphine complexes of palladium(II) difluorodithiophosphate on the basis of i.r. and ^{19}F n.m.r. evidence.

TABLE 2

^1H *n.m.r. data* (*methyl region*) *for some platinum tertiary phosphine complexes in* $CDCl_3$

Compound	τ value[a]	Multiplicity and *J* value (Hz)[b]
$[Pt(S_2PPh_2)_2(PMe_2Ph)_2]$	8·27	three doublets *J*(P–H) 12·6 *J*(Pt–H) 49
$[Pt(S_2PPh_2)_2(PMePh_2)_2]$	7·99	three doublets *J*(P–H) 13·2 *J*(Pt–H) 49·5
$[Pt(S_2PPh_2)_2(PMePh_2)]$	7·67	three doublets *J*(P–H) 11·3 *J*(Pt–H) 37·5

[a] ±0·01. [b] *J*(P–H) ± 0·2 Hz; *J*(Pt–H) ± 0·5 Hz.

If (II) is correct, the best explanation for the "isomers" of $[Pd(S_2PPh_2)_2PPh_3]$[1] is probably different orientations of the unidentate diphenylphosphinodithioato-group with respect to the bulky triphenylphosphine ligand.

Finally, preliminary studies on tertiary phosphine complexes of platinum(II) dithiocarbamates[5] suggest that 1 : 1 and 1 : 2 adducts with analogous structures to (I) and (II) are formed.

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