Effect of Mutual Attraction of Aromatic Ligands on Bond Angles in Metal Complexes: Structures of Dibromotris-(5-alkyl-5*H*-dibenzophosphole)-palladium(II) [or platinum(II)] Compounds

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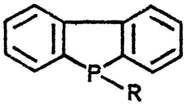
Summary In compounds ML_3X_2 (M = Ni, Pd, Pt; L = 5-alkyl-5*H*-dibenzophosphole) two only of the ligands L have their aromatic ring systems parallel plane-to-plane, close and geometrically overlapping; in six such molecules, of varied stereochemistry, an attraction between the two ligands is shown by their P–M–P angles which are less than the corresponding angles for non-parallel ligand pairs.

In three molecules of formula $NiL_3(CN)_2$ where L is 5-alkyl-5*H*-dibenzophosphole (**1**), two of the ligands, identified by their phosphorus atoms P(2) and P(3) have their ring systems nearly parallel plane-to-plane and geometrically overlapping to a considerable extent.[1] The separation 3·57—3·79 Å of the planes in the overlapping regions is comparable to that between aromatic molecules in crystals



(**1**)

or in crystalline molecular compounds. Atomic dimensions and bond angles forbid such overlapping of all three ligands. They allow, but do not require, the proximity and parallel nature of the two ligands, which could be explained by an attractive interaction. The two overlapping ligands are distinguished by their phosphorus atoms P(2) and P(3) chosen so that angle P(2)–M–P(1) $<$ P(3)–M–P(1) (M = metal). This choice does not require angle A [P(2)–M–P(3)] to be greater than angle B [P(2)–M–P(1)] or the converse, but ensures that A and B are stereochemically comparable.

Crystal structures (diffractometer data, R values $<10\%$) have now been determined for a further three related compounds ML_3X_2 in which palladium or platinum replaces nickel, and Br is substituted for CN.[2] They all show two ligands in similar close and nearly parallel arrangement. The effect occurs irrespective of the stereochemistry which, among the six compounds, has three different forms: (a) a distorted tetragonal pyramid with P(2) apical and P(1) and P(3) *trans* basal, (b) a distorted trigonal bipyramid with all phosphorus atoms equatorial, and (c) a distorted tetragonal pyramid with all phosphorus atoms basal. Even if no selective interaction between the ligands is assumed, the angles A and B will not necessarily be equal since in polyatomic molecules a particular angle may be influenced by many factors. The difference (A − B) might be expected to be one or two orders of magnitude less than A and, for a series of such molecules, to be distributed around zero. Instead the negative values shown in the Table demonstrate the attraction between the ligands (2) and (3). For the trigonal bipyramidal form (b) all three P–M–P angles are stereochemically comparable (ideally 120°). The figures in brackets are for angles P(1)–M–P(3) and the difference between A and this angle.

TABLE

M	R	X	Stereochemistry	A(°)	B(°)	(A−B)(°)
Ni	Me	CN	a	98·1	100·7	−2·6
Ni	Me	CN	b	110·8	116·3	−5·5
					(132·8)	(−22·0)
Ni	Et	CN	b	111·8	121·8	−10·0
					(126·4)	(−14·6)
Pd	Et	Br	c	92·8	98·0	−5·2
Pt	Me	Br	c	92·6	98·4	−5·8
Pt	Et	Br	c	93·0	98·6	−5·6

In the trigonal bipyramids the angle A is less than the ideal 120° which could be achieved without steric difficulty if the molecules had C_{3h} symmetry with no two ring systems plane-to-plane. In the tetragonal pyramids of type (c) all the angles P–M–P are greater than the ideal 90° owing to steric reasons.

It appears that, whatever other factors affect the bond angles, the attraction between two ligands makes one angle smaller than another though it does not determine the magnitude of either. It does not correlate directly with stereochemical form, as is clear from the first two molecules in the table which are allogon isomers, but it will influence all the bond angles at the central atom.

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[2] D. W. Allen, I. T. Miller, and F. G. Mann, *J. Chem. Soc.* (*A*), 1969, 1101.