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# A Method to Measure the Size of Phosphorus Ligands in Coordination Complexes

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The relevance of steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis has been recently reviewed by Tolman [1]. This author has proposed a method for quantitative evaluation of electronic and steric properties of phosphorus ligands based respectively on carbonyl stretching frequencies of $Ni(CO)_3L$ complexes [2] (L = phosphorus ligand) and the "ligand cone angle" measured by using space filling molecular models [3]. However, when several conformations are accessible to the coordinated ligand, the use of molecular models may give uncertain results. Therefore we have recently proposed [4] to exploit, if available, X-ray structural data to measure ligand cone angles.*

Furthermore, it has been pointed out that the bulky phosphines, even though symmetrically substituted, may adopt unsymmetrical conformations. As a consequence, in some crowded complexes such as $Pt(PCy_3)_3$ a remarkable intermeshing ability of the ligand has been observed [4]. This suggests that the circular cone approach may be substantially improved by taking into account the dependence of the ligand angular encumbrance ($\frac{1}{2}\theta$) on the orientation of the ligand itself about the metal–phosphorus bond ($\phi$, see Figure, A and B).

The set of $\frac{1}{2}\theta$ values, with $0 < \phi < 360°$, gives rise to a generalized non-circular cone whose solid angle is:

$$\Omega = \int_{\phi=0}^{2\pi} (1 - \cos\tfrac{1}{2}\theta)\,d\phi$$

Here we report (see Table) the $\Omega$ values obtained for 27 structures containing 8 different tertiary phosphines. In addition we give the angle $\bar{\Theta} = 2\text{-arcos}(1 - \Omega/2\pi)$, the aperture of a circular cone having an equivalent solid angle $\Omega$. The angular parameter $\bar{\Theta}$ should be comparable with the ligand cone angle $\Theta$ as defined by Tolman. The structures examined include, on purpose, some crowded molecules in order to test the influence of the crowding on the solid angle of a given ligand. The listed values, albeit still limited, allow some preliminary observations: i) if several crystallographically independent ligands of the same species are present in the same complex (possibly with different conformations) the solid angles $\Omega$ are strictly similar; ii) among the complexes containing the same ligand, $\Omega$ decreases if the crowding around the metal increases. From the data given in the Table the following ligand compressibility values are observed: 16% for $PEt_3$, 7% for $PMe_2Ph$, 12% for $PPh_2Me$, 11% for $PPh_3$, 9% for $PCy_3$, 8% for $PBu^t_2Ph$; iii) when phosphines are the only bulky ligand present in the complexes (see cases 2, 5, 17, 21, 24, 25, 27) the sum of $\Omega$'s for each ligand is less or slightly greater than $4\pi$, the spherical solid angle; iv) the $\bar{\Theta}$ values given in the table are systematically lower than Tolman's $\Theta$, especially for the bulkiest ligands.

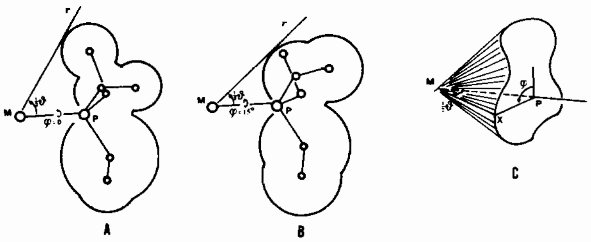

Figure. Dependence of the angular encumbrance of a coordinated phosphorus ligand ($PEt_3$ as a working example) on the ligand orientation. Hydrogen atoms are omitted for sake of clarity. In A and B the curved line indicates the section in the plane of the drawing of the space filling molecular model (carbon radius 1.8 Å). For each orientation $\phi$ the $\frac{1}{2}\theta$ angle is defined by the straight line $r$ tangent to the model in the plane of the figure. C represents the generalized non-circular cone described by $r$ on changing $\phi$ and $\frac{1}{2}\theta$ angles. X, a point of $r$ at an arbitrary fixed distance from M, describes a closed non-circular line belonging to a sphere centered on M.

These preliminary results stimulate a further and widespread analysis of X-ray structures available in order to test the reliability of the solid angle approach to measure the ligand size in coordination complexes.

We wish to thank Dr. C. A. Tolman for giving us a copy of his review [1] before publication and Professor G. Ferguson for a preprint of his article [6].

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*The convenience of considering the dependence of $\frac{1}{2}\theta$ on $\phi$ has been also pointed out by Ferguson [5], who has introduced the term "ligand profile". In a recent paper [6] the profile of $[Hg(NO_2)_2PCy_3]_2$ complex has been discussed.

1 C. A. Tolman, *Chem. Reviews*, in the press.
2 C. A. Tolman, *J. Am. Chem. Soc., 92,* 2953 (1970).
3 C. A. Tolman, *J. Am. Chem. Soc., 92,* 2956 (1970).
4 A. Immirzi, A. Musco and B. E. Mann, *Inorg. Chim. Acta, 21,* L37 (1977).
5 G. Ferguson, E. C. Alyea, R. J. Restivo and P. J. Roberts, *A.C.A. Spring Meeting,* Asilomar (1977) paper HN8.
6 E. C. Alyea, S. A. Dias, G. Ferguson and R. J. Restivo, *Inorg. Chem.*, in the press.
7 M. L. Schneider and H. M. N. Shearer, *J. Chem. Soc. Dalton,* 354 (1973).
8 A. Musco, W. Porzio and A. Immirzi, *unpublished values.*

TABLE. Solid Cone Angles (Ω) for Some Tertiary Phosphines Based on X-ray Structures of Metal Complexes. Tolman's ligand cone angles (Θ) and values of $\bar{\Theta} = 2\text{-arcos}(1 - \Omega/2\pi)$ (see text) are also listed. Hydrogen atom positions have been calculated by assuming C–H bond lengths 1.08 Å, H–C–H angles 109°, local $C_{2v}$ symmetry on each C atom and staggered conformations of C–C bonds for saturated carbons. Methyl groups bonded to phosphorus are assumed staggered with respect to M–P bond. Following Tolman [3], the M–P distance is assumed in all cases 2.30 Å, shifting the metal along M–P if necessary. Van der Waals radii are: $R_P = 1.80$, $R_C = 1.80$, $R_H = 1.17$ Å When several crystallographically independent ligands are present, all Ω values are listed.

| No. | Ligand | Complex | Ω | $\bar{\Theta}$° | Θ° | Ref. |
|---|---|---|---|---|---|---|
| 1 | $PEt_3$ | *trans*-$HPdClL_2$ | 3.60 3.72 | 129.5 131.8 | 132 | 7 |
| 2 | $PEt_3$ | $PtL_4$ | 3.09 3.14 | 118.9 119.9 | 132 | 8 |
| 3 | $PMe_2Ph$ | $[Ir(CO)_3L_2]^+ClO_4^-$ | 3.06 3.03 | 118.3 117.7 | 122 | 9 |
| 4 | $PMe_2Ph$ | *cis*-$PdCl_2L_2$ | 2.90 | 125.0 | 122 | 10 |
| 5 | $PMe_2Ph$ | $PtL_4$ | 2.82 2.81 | 113.1 113.1 | 122 | 8 |
| | | | 2.79 2.88 | 112.4 114.6 | | |
| 6 | $PPh_2Me$ | $[AuL_2]^+PF_6^-$ | 3.44 | 126.2 | 136 | 11 |
| 7 | $PPh_2Me$ | $MoH_4L_4$ | 2.99 2.99 | 116.7 116.8 | 136 | 12 |
| | | | 3.05 3.10 | 118.1 119.1 | | |
| 8 | $PPh_2Me$ | $[IrL_4]^+BF_4^-$ | 3.31 3.27 | 123.4 122.6 | 136 | 13 |
| 9 | $PPh_3$ | $AuCl_3L$ | 3.75 | 132.4 | 145 | 14 |
| 10 | $PPh_3$ | $Co(CO)_2NOL$ | 3.58 | 129.0 | 145 | 15 |
| 11 | $PPh_3$ | $[CuClL]_2$ | 3.57 | 128.8 | 145 | 16 |
| 12 | $PPh_3$ | $Rh(C_2H_4)(pmcp)L^a$ | 3.54 | 128.2 | 145 | 17 |
| 13 | $PPh_3$ | *cis*-$PtCl(dtt)L_2{}^b$ | 3.82 3.72 | 133.8 131.8 | 145 | 18 |
| 14 | $PPh_3$ | $CuClL_3$ | 3.70 | 131.5 | 145 | 19 |
| 15 | $PPh_3$ | $Ir(NO)L_3$ | 3.59 | 129.2 | 145 | 20 |
| 16 | $PPh_3$ | $[CuL_3]^+BF_4^-$ | 3.77 | 132.9 | 145 | 21 |
| 17 | $PPh_3$ | $PdL_4$ | 3.44 3.43 | 126.2 125.9 | 145 | 22 |
| 18 | $PPh_3$ | $RuH_2L_4$ | 3.31 3.32 | 123.5 123.7 | 145 | 23 |
| | | | 3.35 3.38 | 124.4 124.9 | 145 | |
| 19 | $PPr^i_3$ | $IrHL_2(C_4H_6)$ | 3.89 3.96 | 135.2 136.7 | 160 | 24 |
| 20 | $PPr^i_3$ | $IrL_2(C_3H_5)$ | 4.02 | 137.8 | 160 | 25 |
| 21 | $PCy_3$ | $PdL_2$ | 4.48 | 146.7 | 170 | 26 |
| 22 | $PCy_3$ | $PtH_2L_2$(monocl.)$^c$ | 4.61 | 149.1 | 170 | 27 |
| 23 | $PCy_3$ | $PtH_2L_2$ (tricl.)$^c$ | 4.40 | 145.0 | 170 | 27 |
| 24 | $PCy_3$ | $PtL_3$ | 4.18 | 140.6 | 170 | 4 |
| 25 | $PBu^t_2Ph$ | $PdL_2$ | 4.94 | 155.3 | 170 | 26 |
| 26 | $PBu^t_2Ph$ | *cis*-$PtCl_2L_2$ | 4.61 4.50 | 149.1 147.0 | 170 | 8 |
| 27 | $PMen_2Pr^i$ | $PdL_2$ | 6.09 | 176.5 | 209$^e$ | 8 |

[a] pmcp = pentamethylcyclopentadienyl. [b] dtt = di-*p*-tolyltriazenido. [c] Conformational analysis and solid state molecular volumes indicate the triclinic as the more stable form. The Ω value 4.61, surprisingly greater than 4.48 (case 21) is probably due to a strained conformation induced by the crystal packing. [d] Men = menthyl. [e] Our evaluation using Tolman's formula.

9 G. Raper and W. S. McDonald, *Acta Cryst., B29,* 2013 (1973).

10 L. L. Martin and R. A. Jacobson, *Inorg. Chem., 10,* 1795 (1971).

11 J. J. Guy and P. G. Jones, *Acta Crystall., B32,* 1937 (1976).

12 L. J. Guggenberger, *Inorg. Chem., 12,* 2295 (1973).

13 G. R. Vlark, C. A. Reed, W. R. Roper, B. W. Skelton and T. N. Waters, *J. Chem. Soc. D,* 758 (1971).

14 G. Bandoli, D. A. Clemente and G. Marangoni, *J. Chem. Soc. Dalton,* 886 (1973).

15 D. L. Ward, G. N. Gaughlan, G. E. Voecks and P. W. Jennings, *Acta Cryst., B28,* 1949 (1972).

16 W. R. Clayton and S. G. Shore, *Cryst. Struct. Comm., 2,* 605 (1973).

17 W. Porzio and M. Zocchi, to be published.

18 G. Bombieri, A. Immirzi and L. Toniolo, *Transition Metal Chem., 1,* 130 (1976).

19 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Bartow, D. Stovens and S. J. Lippard, *Inorg. Chem., 15,* 1155 (1976).

20 V. G. Albano, P. Bellon and M. Sansoni, *J. Chem. Soc. A,* 2420 (1971).

21 A. P. Gaughan, Z. Dori and J. A. Ibers, *Inorg. Chem., 13,* 1657 (1974).

22 V. G. Andrianov, I. S. Akhrem, N. M. Chistovalova and Yu. T. Struchkov, *J. Struct. Chem., 17,* 112 (1976).

23 A. Immirzi and A. Lucherini, *Cryst. Struct. Comm., 1,* 317 (1972).

24 G. Perego, G. Del Piero and M. Cesari, *Gazzetta Chim. Ital., 105,* 529 (1975).

25 G. Perego, G. Del Piero and M. Cesari, *Cryst. Struct. Comm., 3,* 721 (1974).

26 A. Immirzi and A. Musco, *Chem. Comm.,* 400 (1974).

27 A. Immirzi, A. Musco, G. Carturan and U. Belluco, *Inorg. Chim. Acta, 12,* L23 (1975).