

Factors Influencing the Formation of Eight-co-ordinate Metal Complexes: An Eight-co-ordinate Phosphine Complex of Titanium(IV)

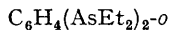
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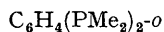
SINCE the isolation of the first eight-co-ordinate derivative of titanium(IV) *i.e.*, the complex $\text{TiCl}_4 \cdot 2\text{diarsine}^1$ [diarsine = *o*-phenylenebisdimethylarsine = (I)] many other attempts have been made to reach this unusual co-ordination number for the metal. The studies have involved the reactions of bidentate nitrogen-, phosphorus-, arsenic-, oxygen-, and sulphur-donor ligands with titanium tetrachloride, but in no case has the co-ordination number of the metal been shown to increase beyond six.² In particular, the ethyldiphosphine (IV)³ and the ethyldiarsine (II),⁴ analogous to the original diarsine (I), yield only 1:1 adducts with titanium tetrachloride.



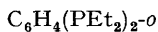
(I)



(II)



(III)

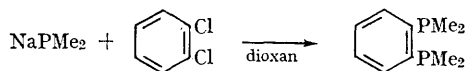
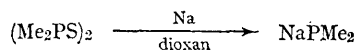


(IV)

It is therefore of interest to investigate whether these results are a consequence of the differing

sizes and inductive properties of methyl and ethyl groups or of differing intrinsic donor properties of arsines as compared with phosphines towards titanium(IV).

To resolve this problem we have synthesised the methyldiphosphine (III)⁵ by the improved route



It is a colourless liquid which is highly unstable in air, b.p. 92° c at 0.4—0.5 mm. Hg. Titanium tetrachloride (0.2 ml) in rigorously anhydrous cyclohexane (5 ml.) reacts immediately with this ligand (0.6 ml.) in the same solvent (5 ml.) under a nitrogen atmosphere to form an orange precipitate for which complete analytical data indicate the

formation of a 1:2 adduct. It is rapidly hydrolysed in moist air, and begins to decompose at $\sim 205^\circ\text{C}$. An X-ray powder photograph of the complex unambiguously demonstrates that it is isomorphous with the known eight-co-ordinate complex $\text{TiCl}_4 \cdot 2\text{diarsine}$,¹ and hence that it is eight-co-ordinate with the full dodecahedral (D_{2d}) symmetry.

The infrared spectrum of the complex is consistent with the presence of co-ordinated diphosphine, and in particular the infrared-active TiCl stretching vibrations ($b_2 + e$) occur as a strong broad band at 312 cm^{-1} *i.e.*, at almost exactly the frequency of the corresponding vibrations⁶ in the complex $\text{TiCl}_4 \cdot 2\text{diarsine}$ (317 cm^{-1}), and $\sim 60\text{ cm}^{-1}$ below the strongest TiCl stretching vibrations in six-co-ordinate adducts of titanium(IV).⁶

The first charge-transfer band in the diffuse reflectance spectrum of the complex occurs at

$21,100\text{ cm}^{-1}$ *i.e.*, $1,500\text{ cm}^{-1}$ above the corresponding band in the spectrum of the analogous arsine complex.¹

We conclude, therefore, that the principal factor determining whether titanium achieves the co-ordination number of eight rather than six in this series is not associated with the relative donor properties of phosphines and arsines, but with the steric and inductive properties of methyl as compared with ethyl substituents on the donor atoms. However, it is noteworthy that neither of the two aliphatic phosphines $\text{R}_2\text{P}[\text{CH}_2]_2\text{PR}_2$ ($\text{R} = \text{Me}, \text{Et}$) yield other than 1:1 adducts with titanium tetrachloride.³ While the difference in behaviour between these ligands and ligands (III) and (IV) is probably also steric in origin, the benzene rings of the aromatic ligands may be playing an important role.

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¹ R. J. H. Clark, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1962, 2460.

² R. J. H. Clark and W. Errington, *Inorg. Chem.*, 1966, 5, 650, and references therein.

³ J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1963, 1343.

⁴ R. J. H. Clark, *J. Chem. Soc.*, 1965, 5699.

⁵ F. A. Hart, *J. Chem. Soc.*, 1960, 3324.

⁶ R. J. H. Clark, *Spectrochim. Acta*, 1965, 21, 955.