X-Ray Crystal Structure and Interconversions of Three Isomeric Platinum Complexes containing Metallated t-Butyl-di-*o*-tolylphosphine Ligands

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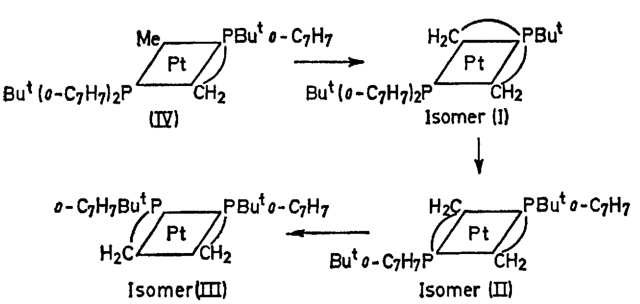
Summary Internal metallation in [PtMe{$CH_2{\cdot}C_6H_4PBu^t$(*o*-tolyl)}{PBu^t(*o*-tolyl)$_2$}] gives three isomeric products whose *X*-ray structures and stereospecific interconversions are reported.

WE have reported[1] previously that bulky substituents on tertiary phosphines promote internal metallation, *e.g.*, one of the *o*-tolyl methyl groups of a PBu^t(*o*-tolyl)$_2$ ligand can be readily metallated by platinum to give[2] a chelate system. We now find that the methylplatinum complex [PtMe{$CH_2{\cdot}C_6H_4PBu^t$(*o*-tolyl)}{(PBu^t(*o*-tolyl)$_2$}] (IV) on heating in boiling toluene for 30 min gives [Pt{$CH_2C_6H_4P(Bu^t)C_6H_4$-CH_2}{PBu^t(*o*-tolyl)$_2$}] (I). This compound contains the first example of a dimetallated tridentate ligand. When (I) is heated at 135° for 7 h (refluxing xylene) it isomerises to (±)-*trans*-[Pt($CH_2{\cdot}C_6H_4PBu^t$-*o*-tolyl)$_2$] (II) containing a small amount of the (±)-*cis*-isomer (III). Prolonged heating (135° for 23 h in refluxing xylene) increases the proportion of the *cis*-isomer to *ca.* 20%. Thus the isomers are formed in the sequence (I) → (II) → (III). We have reported on compounds (II) and (III) previously,[2] but not on their relative stabilities and detailed structures.



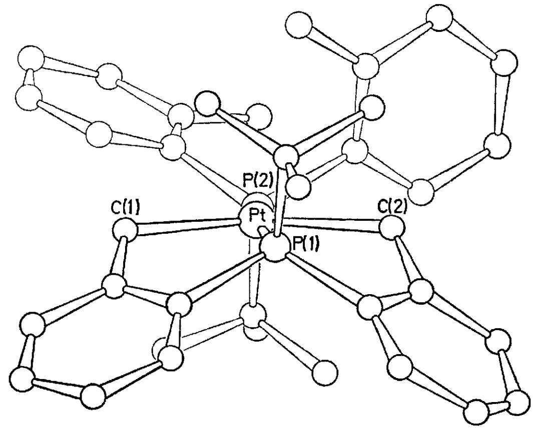


FIGURE 1. *Isomer* (I): Pt–P(1) 2·232(4), Pt–P(2) 2·331(4), Pt–C(1) 2·12(2), Pt–C(2) 2·11(2) Å. ∠ P(1)–Pt–C(1) 82·0(5)°, P(1)–Pt–C(2) = 81·3(5)°.

The structures of the three isomers have been determined by *X*-ray diffraction: crystallographic data are in the Table and the molecular structures are shown in Figures 1—3.

Isomers (II) and (III) are each of the ($\pm$)- rather than the *meso*-configuration, and both have site symmetry C_2. In isomer (I) a methyl group of the unmetallated ligand is close to the axial position of the platinum, with a non-bonded Pt–C distance of 3·36 Å, corresponding to a Pt–H distance of 2·4—2·8 Å depending on the orientation of the methyl hydrogens. Molecular models suggest that steric hindrance prevents this methyl group from occupying any alternative position.

TABLE. *Crystallographic data*

	Isomer (I)	Isomer (II)	Isomer (III)
a/Å	18·54(2)	12·59(2)	11·98(1)
b/Å	11·68(2)	10·69(2)	17·63(2)
c/Å	16·30(2)	12·44(2)	15·39(2)
β	114·8°(1)	103·7°(1)	97·0°(1)
Z	4	2	4
Space group	$P2_1/c$	$P2/n$	$C2/c$
No. of independent F_0	6434	3239	1819
Residual, R	0·109	0·109	0·096

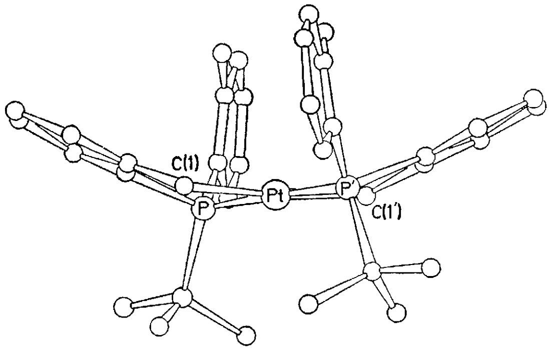


FIGURE 2. *Isomer* (II): Pt–P 2·238(4), Pt–C 2·15(2) Å. ∠P–Pt–C(1) 82·6(6)°.

It is possible that in (IV) the *o*-methyl group of the metallated phosphine is similarly held in the axial position of the platinum, thus leading to preferential formation of (I) rather than (II).

Models of (II) and (III) indicate that the alternative *meso–trans*-isomer is not excessively hindered, but that the *meso–cis*-isomer would require prohibitively close contact between the two t-butyl groups. Thus the stereospecific conversion of (I) into ($\pm$)-(II) is probably controlled by steric interactions in the transition state rather than by the relative stabilities of ($\pm$)-(II) and *meso*-(II).

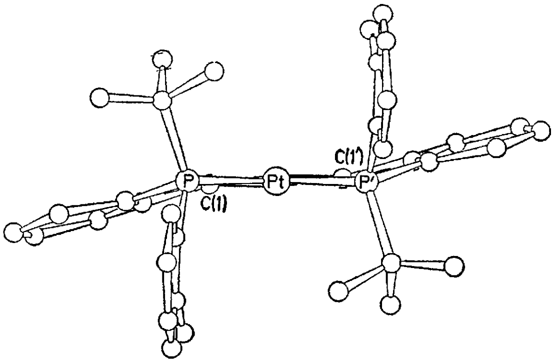


FIGURE 3. *Isomer* (III): Pt–P 2·295(6), Pt–C 2·08(3) Å. ∠P–Pt–C 83·3(7)°, P–Pt–P' 109·5(2)°, C–Pt–C' 84·1(9)°.

There are at least two mechanisms[3] by which a transition metal can metallate a ligand: in one of these the metal acts as an electrophile and in the other as a nucleophile (by oxidative addition). In the above compounds the platinum has low electronegativity ligands and it seems likely that it is acting as a nucleophile in the metallations.

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[2] A. J. Cheney and B. L. Shaw, *J.C.S. Dalton*, 1972, 754.

[3] G. W. Parshall, *Accounts Chem. Res.*, 1970, 3, 139.