

## Intramolecular Metal-Carbon Bond Formation in Some Triaryl Phosphite Complexes of Platinum(II) and Palladium(II)

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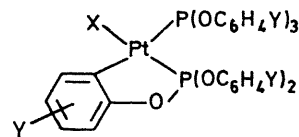
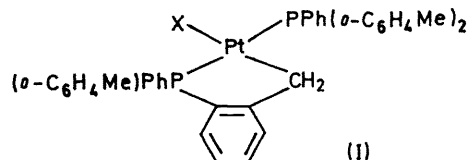
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**Summary** Platinum(II) and palladium(II) triaryl phosphite complexes in boiling decalin undergo reactions leading to formation of products containing intramolecular metal-carbon bonds; the influence of chelate ring size on the course of these reactions is discussed.

THE conversion of *o*-tolylphosphine complexes of platinum(II), *trans*-PtX<sub>2</sub>[PPh(*o*-C<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>]<sub>2</sub>, into metal-carbon bonded complexes (I) by intramolecular attack at the *o*-methyl group in preference to the aromatic CH group of the coordinated *o*-tolylphosphine ligand has recently been disclosed.<sup>1</sup> We now report a similar series of reactions involving co-ordinated triaryl phosphites, including tri-*o*-tolyl phosphite, in which the reverse situation prevails; the attack occurring exclusively at the aromatic CH group.

On heating *cis*-PtCl<sub>2</sub>[P(OPh)<sub>3</sub>]<sub>2</sub> in boiling decalin for *ca.* 3 h elimination of hydrogen chloride is observed and the metal-*ortho*-carbon bonded complex PtCl[P(OC<sub>6</sub>H<sub>4</sub>)(OPh)<sub>2</sub>]-[P(OPh)<sub>3</sub>] (IIa) may be isolated from the reaction mixture in high yield as a white, air stable, solid. The related tri-*o*-tolyl-, tri-*m*-tolyl-, and tri-*p*-tolyl phosphite complexes, PtCl<sub>2</sub>[P(OC<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>]<sub>2</sub>, undergo similar reactions to yield white, solid complexes (II B, C, and D, respectively) of formula PtCl[P(OC<sub>6</sub>H<sub>3</sub>Me)(OC<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>][P(OC<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>]. The n.m.r. spectra of these three products are very similar, in particular each shows in the region  $\tau$  7-9, three sharp singlets of relative intensity 1:2:3 attributable to the methyl groups, six in all, in three different chemical environments (II; Y = Me). There is no evidence for the presence of a metal-bonded methylene group in any of the spectra. We conclude therefore that all six methyl groups are intact in each complex and that the metal-carbon bond formation reaction involves the *ortho*-CH group of a tolyl moiety.

The difference in behaviour between the *ortho*-tolylphosphine and phosphite complexes in these reactions may be rationalised in terms of the steric requirements of the resultant chelate ring. Thus, reactions of the two types of



(II) A; Y = H  
 B; Y = *o*-Me  
 C; Y = *m*-Me  
 D; Y = *p*-Me

X may be Cl, Br, or I.

complex, while following different paths, both give rise to products with sterically favoured five-membered chelate rings. The alternative paths for these reactions, involving attack at the aromatic CH group of *o*-tolylphosphine ligands or the methyl group of *o*-tolyl phosphite ligands, would give rise to less sterically favourable four- and six-membered chelate rings, respectively. This illustrates the importance

of stereochemical factors in promoting and directing these reactions.

Similar reactions have been performed with the corresponding bromo- and iodo-complexes,  $\text{PtX}_2[\text{P}(\text{OR})_3]_2$ , and with the analogous palladium derivatives,  $\text{PdX}_2[\text{P}(\text{OR})_3]_2$ , [R = Ph, *o*-, *m*-, or *p*-tolyl]. We observe that the ease with which the metal-carbon bond formation reactions occur decreases  $\text{Cl} > \text{Br} \gg \text{I}$  and  $\text{Pt} > \text{Pd}$ ; in the extreme case of  $\text{PdI}_2[\text{P}(\text{OPh})_3]_2$  only analytically pure starting material is recovered after a 3 h reaction. The palladium reactions are also accompanied by deposition of metal and yields of complexed palladium recovered rarely exceed 50%. No evidence for formation of hydridic products was observed.

If, as suggested elsewhere,<sup>2</sup> reactions of the type under discussion occur by an initial oxidative addition of the C-H group across the metal atom then the reluctance of the palladium(II) complexes to react may arise from the relative inaccessibility of the oxidation state  $\text{Pd}^{\text{IV}}$ .

The products formed from triphenyl and tri-*p*-tolyl phosphite complexes show the expected i.r. bands at 1100, 800 and 1120, 750  $\text{cm}^{-1}$ , respectively, typical of the metal-*ortho*-carbon bonded groups derived from these ligands.<sup>3</sup> Good analytical data [C, H, P, and halogen] have been obtained for all products; M. W. data (osmometric,  $\text{C}_6\text{H}_6$  solution) on selected products confirm that they are monomeric.

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<sup>1</sup> A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *Chem. Comm.*, 1970, 1176.

<sup>2</sup> G. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

<sup>3</sup> E. W. Ainscough and S. D. Robinson, *Chem. Comm.*, 1970, 863. One of the key metal-*ortho*-carbon bonded structures suggested in ref. 3, on the basis of similar i.r. data, has now been confirmed by a full X-ray crystal structure determination: J. M. Guss and R. Mason, *Chem. Comm.*, 1970, 58.