Intramolecular Platinum–Carbon Bond Formation Promoted by Steric Hindrance

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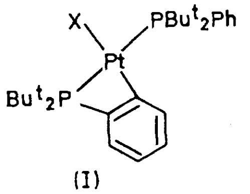
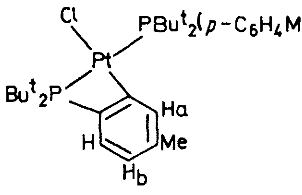
Summary Bulky substituents on tertiary phosphine ligands co-ordinated to platinum(II) are shown to promote internal platinum–carbon bond formation.

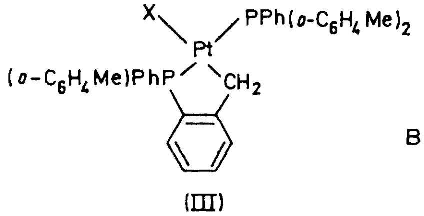
THERE are many examples of internal transition metal–carbon bond formation involving nitrogen- or phosphorus-donor ligands,[1] but little is known about the factors which promote such metal–carbon bond formation. We have now found that bulky substituents on a tertiary phosphine ligand promote internal metal–carbon bond formation in some platinum(II) complexes. The bulky substituents studied are t-butyl and *o*-tolyl.



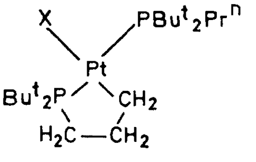
(I)



(II)



(III)



(IV)

Thus, *trans*-$\mathrm{PtCl_2(PBu^t_2Ph)_2}$ when heated under reflux for 12 h in 2-methoxyethanol solution gives $\mathrm{PtX(C_6H_4PBu^t_2)(PBu^t_2Ph)}$ (I; X = Cl); the corresponding bromo- or iodo-complexes, (I; X = Br or I), are formed from *trans*-$\mathrm{PtCl_2(PBu^t_2Ph)_2}$ by heating under reflux for 12 h in 2-methoxyethanol with lithium bromide or sodium iodide, respectively. The complex $\mathrm{PtCl(C_6H_4PBu^t_2)(PBu^t_2Ph)}$ is non-conducting in nitrobenzene solution and monomeric in benzene. The ^{31}P n.m.r. spectrum (with random noise decoupling of the protons) consists of an AB pattern, with platinum satellites, and the large value of J_{PP} (388 ± 5 Hz) is indicative of phosphorus ligand atoms in mutually *trans*-positions.[2]

In contrast, the dimethylphenylphosphine complex *cis*-$\mathrm{PtCl_2(PMe_2Ph)_2}$ when heated under reflux with sodium iodide in 2-methoxyethanol for 51 h gives only *cis*-$\mathrm{PtI_2(PMe_2Ph)_2}$. Similar treatment of *cis*-$\mathrm{PtCl_2(PMePh_2)_2}$ for 97 h gave a mixture of *cis*- and *trans*- $\mathrm{PtI_2(PMePh_2)_2}$; no ring-closed compounds could be detected.

trans-$\mathrm{PtCl_2[PBu^t_2(}p\mathrm{-C_6H_4Me)]_2}$ when heated under reflux in 2-methoxyethanol forms the cyclised compound, $\mathrm{PtCl[MeC_6H_3PBu^t_2][PBu^t_2\,(}p\mathrm{-C_6H_4Me)]}$, (II) more rapidly (6—8 h) than does the corresponding complex from $\mathrm{PBu^t_2Ph}$.

It is known that *p*-tolylphosphine ligands undergo *ortho*-attack more rapidly than phenylphosphine ligands.[1] The ^{1}H n.m.r. pattern of (II) is completely consistent with the assigned structure; in particular, proton $\mathrm{H_a}$ forms a doublet with platinum satellites at τ 4·51, $J_{\mathrm{a,b}}$ 5·6, $J(\mathrm{H_a{-}Pt})$ 66·6 Hz.

trans-$\mathrm{PtCl_2(PBu^tPh_2)_2}$ will also undergo similar ring formation when heated under reflux in 2-methoxyethanol, but more slowly than the above-mentioned complexes. The cyclised complex, $\mathrm{PtCl(C_6H_4PBu^tPh)(PBu^tPh_2)}$ is the minor product, the major product is the hydride, *trans*-$\mathrm{PtHCl(PBu^tPh_2)_2}$. The corresponding bromides or iodides are made similarly; the tendency to ring close rather than form a hydride increasing in the order Cl < Br < I. *trans*-$\mathrm{PtCl_2[PBu^t(}p\mathrm{-C_6H_4Me)_2]_2}$ when heated with lithium bromide in 2-methoxyethanol gives a similarly ring-closed product, $\mathrm{PtBr[MeC_6H_3PBu^t(}p\mathrm{-C_6H_4Me)][PBu^t\text{-}(}p\mathrm{-C_6H_4Me)_2]}$.

The *o*-methyl group of an *o*-tolylphosphine can also be involved in ring formation. Thus when *trans*-$\mathrm{PtCl_2[P(}o\mathrm{-C_6H_4Me)_2Ph]_2}$ is heated in 2-methoxyethanol either alone or with an alkali metal halide (LiBr or NaI), ring-closed complexes of type $\mathrm{PtX[(}o\mathrm{-C_6H_4CH_2{-})PPh(}o\mathrm{-C_6H_4Me)][P(}o\mathrm{-C_6H_4Me)_2Ph]}$ (III) are formed; as before, the rate of ring formation increases in the order Cl < Br < I. Similar ring formation involving a methyl group of di-*o*-tolylphenylphosphine has previously been observed with rhodium but the product, $\mathrm{RhCl_2[(}o\mathrm{-C_6H_4CH_2{-})PPh(}o\mathrm{-C_6H_4Me)]}$, was not obtained pure.[3] The crystal structure of dichlorodipyridine-[*o*-(di-*o*-tolylphosphino)benzyl]rhodium(III), formed from tri-*o*-tolylphosphine and rhodium trichloride with subsequent treatment with pyridine, has been reported recently.[4]

It is also possible to induce ring formation involving aliphatic chains; thus when *trans*-$\mathrm{PtCl_2(PBu^t_2Pr^n)_2}$ is heated with 2-methoxyethanol either alone or with lithium bromide ring closed complexes are formed. The ^{1}H n.m.r. spectra of these complexes show the t-butyl groups to be intact, *i.e.* an n-propyl group is involved in ring formation. We prefer to formulate these complexes as $\mathrm{PtX({-}CH_2CH_2CH_2PBu^t_2)(PBu^t_2Pr^n)}$ (IV), X = Cl or Br, *i.e.* with five-membered rings rather than four-membered rings because of the extra stability normally associated with five-membered rings. When *trans*-$\mathrm{PtCl_2(PBu^tPr^n_2)_2}$ is heated with lithium bromide in 2-methoxyethanol the ring-closed compound $\mathrm{PtBr({-}CH_2CH_2CH_2PBu^tPr^n)(PBu^tPr^n_2)}$ is formed together with *trans*-$\mathrm{PtBr_2(PBu^tPr^n_2)_2}$ and a trace of the hydride, *trans*-$\mathrm{PtHBr(PBu^tPr^n_2)_2}$. The ^{31}P n.m.r spectrum (with random noise decoupling of the protons) of $\mathrm{PtBr({-}CH_2CH_2CH_2PBu^tPr^n)(PBu^tPr^n_2)}$ shows J_{PP} to be large (396·3 Hz), indicative of *trans*-phosphines. Ring closure of triethylphosphine to platinum(II) is thought to occur when *trans*-$\mathrm{PtCl_2(PEt_3)_2}$ is treated with lithium derivatives of carboranes.[5]

Our results show that bulky substituents on tertiary phosphines promote internal metal–carbon bond formation. Phosphine ligands with two t-butyl groups undergo ring closure more readily than phosphines with only one t-butyl group and tertiary phosphines with smaller steric requirements such as dimethylphenylphosphine show no tendency to ring close. In complexes such as *trans*-$PtCl_2(PBu^t{}_2Ph)_2$ the environment of the platinum is very crowded but by elimination of chloride, in a ring closure reaction the environment of the platinum becomes less crowded. Steric factors may also lower the activation energy of the metal–carbon bond-forming reaction by forcing the metal and the carbon–hydrogen bond on the ligand closer together. In $PdI_2(PMe_2Ph)_2$ *ortho*-hydrogens of the phenyl groups are only 2·8 Å from the centre of the metal[6] and in $RuCl_2(PPh_3)_3$ only 2·6 Å;[7] with more sterically-hindered phosphines the distance could be even less.

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