Hydrogen–Deuterium Exchange at a Saturated Carbon Atom in Tertiary Phosphine Complexes of Platinum(II)

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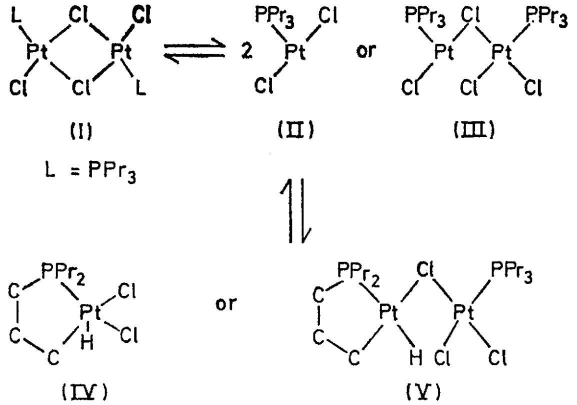
Summary Complexes of the type $Pt_2Cl_4L_2$, where L = PPr_3 or PBu_3, undergo hydrogen–deuterium exchange in solution to give complexes containing deuterium in the tertiary phosphine, specifically at C-3 of the alkyl group.

INTERACTIONS between transition metals and carbon–hydrogen bonds of co-ordinated ligands have been widely studied.[1-4] Such interactions are well established in complexes containing arylphosphine or arylphosphite ligands,[1,2] but only a few examples[3,4] are known of such interactions in transition-metal complexes containing monodentate tertiary alkylphosphines as ligands. We have found that dimeric platinum(II) complexes of the type (I), where L = PPr_3 or PBu_3, undergo a hydrogen–deuterium exchange in $MeCO_2D$–D_2O containing perchloric acid to give the complexes (I) with deuteriated tertiary-phosphine ligands. Thus, shaking a 0·02M-solution of (I) (L = PPr_3) in D_2O-$MeCO_2D$ (1 : 6) containing 0·23M-perchloric acid for 2 h at 100° resulted in 31 ± 5% deuterium incorporation into the complex. The ^1H n.m.r. spectrum of the complex showed that only the terminal methyl groups of the tri-n-propylphosphine ligands had been deuteriated (78 ± 5%). With L = PBu_3, under the same conditions, 22 ± 5% deuteriation of the tri-n-butylphosphine ligands was found.


(I) L = PPr_3
(II)
(III)
(IV)
(V)

The ^{13}C n.m.r. spectrum (with complete proton decoupling) of the deuteriated complex indicated that the deuterium was situated predominantly ($> 80\%$) at C-3 of the butyl group. Apart from the deuteriation, the complexes were recovered unchanged after the reaction. With $L = PEt_3$ no deuterium incorporation was found. The exchange of hydrogen for deuterium in *cis*- and *trans*-$PtCl_2(PBu_3)_2$ was attempted. With these complexes, even after a reaction time of 24 h at 100°, $< 5\%$ deuterium incorporation was observed. It therefore appears necessary to use a bridged platinum complex of the type (I). It is probable that the first stage of the reaction involves bridge fission to produce a formally co-ordinatively unsaturated complex of the type (II) or (III). Subsequent insertion of the platinum into a C–H bond on C-3 of the tertiary-phosphine ligand yields (IV) or (V), which then exchanges H for D in the medium.

These results support the suggestion previously made[3,6] that five-membered rings are of importance in internal-metallation reactions of platinum. They also show that tertiary-alkylphosphine ligands are capable of interacting with platinum under relatively mild conditions. This observation is of considerable significance since tertiary-phosphine ligands are used to modify the properties of transition-metal catalysts in a wide range of catalytic reactions.[7]

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