Metallation of an Aliphatic Carbon–Hydrogen Bond: Synthesis and X-Ray Structure of $[PtCl(PBu^t_2CH_2CMe_2CH_2)]_2$

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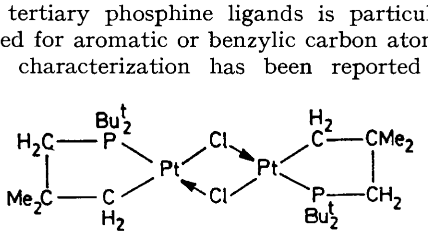
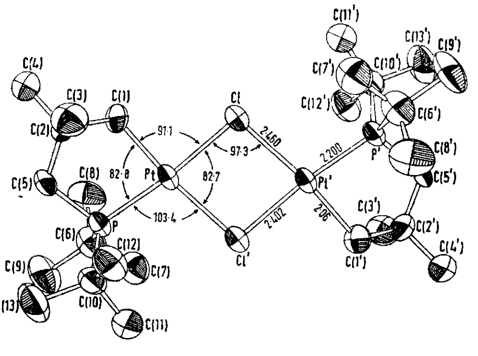
Summary The reaction of $[PtCl_2(NCPh)_2]$ with $(Me_3C{\cdot}CH_2)$-PBu^t_2 provides $[PtCl(PBu^t_2CH_2CMe_2CH_2)]_2$, a binuclear complex characterised by X-ray diffraction methods as containing metallated neopentyl groups.

THE oxidative addition of metals to carbon–hydrogen bonds has been studied extensively over the last five years; intramolecular oxidative addition to *ortho*-carbon–hydrogen bonds of tertiary phosphine ligands is particularly well documented for aromatic or benzylic carbon atoms but no structural characterization has been reported where a purely aliphatic chain has been metallated. Treatment of $[PtCl_2(NCPh)_2]$ with di-t-butyl(neopentyl)phosphine (1 : 1 mol per platinum atom) in dichloromethane at 20 °C gives, after a few minutes, a white binuclear complex which molecular weight measurements and i.r., ^1H, and ^{31}P n.m.r. data suggested was (**1**).



(1)



Crystal data: $C_{26}H_{56}Cl_2P_2Pt_2$, triclinic, $a = 8{\cdot}411(4)$, $b = 10{\cdot}948(7)$, $c = 9{\cdot}106(4)$ Å; $\alpha = 102{\cdot}86(4)°$, $\beta = 90{\cdot}64(4)°$, $\gamma = 97{\cdot}95(5)°$; $Z = 1$. The dimer has crystallographic C_i symmetry in the space group $P\bar{1}$. 1259 reflexion intensities [Cu-K_α; four-circle diffractometry: geometrical and absorption corrections; $I_{obs} > 3\sigma\ (I_{obs})$] formed the basis of the X-ray structure analysis (heavy atom methods; full-matrix least-squares analysis of positional and anisotropic thermal parameters) which converged to $R_F = 0{\cdot}047$; a difference electron density synthesis indicated the position of all hydrogen atoms and including their contributions to the structure factor calculations provided $R_F = 0{\cdot}043$ (weighted $R = 0{\cdot}052$). The structure is shown in the Figure together with some relevant bond lengths and bond angles.

The co-ordination geometry of the platinum atom is planar (±0·01 Å), the chelate ring having an envelope conformation. The relative *trans*-influence of a σ-bonded carbon atom and co-ordinated phosphorus is reflected in the non-equivalent metal–chlorine bridge bonds, the average length of which is, as expected, *ca.* 0·05 Å greater than terminal bonds in related complexes such as *cis*-[$PtCl_2(PMe_3)_2$].[2]

While PBu^t_2(neopentyl) is metallated readily when treated with [$PtCl_2(NCPh)_2$], the corresponding n-propyl phosphine, $PBu^t_2Pr^n$, gives, under similar conditions, only a mixture of the *cis*- and *trans*-[$PtCl_2(NCPh)(PBu^t_2Pr^n)$] complexes with no metallation. The complex [$PtCl_2(NCBu^t)(PBu^t_2Pr^n)$] was similarly prepared and, when heated under reflux in toluene for 10 min, provides a virtually quantitative yield of [$Pt_2Cl_4(PBu^t_2Pr^n)_2$] which on further heating tends to give platinum metal but no metallation. Kiffen *et al.*[3] have shown that [$Pt_2Cl_4(PBu^t_2Pr^n)_2$] undergoes slow hydrogen–deuterium exchange, at the 3-position of the n-propyl group, in strong acid media. We believe the main reason for the difference in metallation rates to be the proximity to the metal into which the carbon–hydrogen bond is forced by steric overcrowding at the tertiary phosphine and, in particular, by favourable conformational and entropy factors promoted by the *gem*-t-butyl and *gem*-dimethyl groups.[4]

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