The Formation and Structure of a Platinum(IV) Complex Containing a Metal–Carbon σ-Bond

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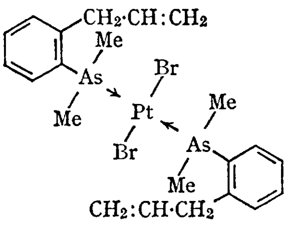
As part of an investigation of the reactivity of co-ordinated olefinic ligands, we have studied the bromination of the square planar platinum(II) complex $PtBr_2(oA)_2$ ($oA = o$-allylphenyldimethylarsine) (I). The infrared spectrum of this complex contains a band at 1640 cm.$^{-1}$ and no band at *ca.* 1500 cm.$^{-1}$, showing that the double bonds are not co-ordinated to the metal.[1]


(I)

The product of reaction with 1 mol. of bromine is a yellow monomeric complex $PtBr_4(oA)_2$, which, on refluxing in ethanol, forms a yellow, monomeric ethoxy-derivative $PtBr_3OEt(oA)_2$. Octahedral tetrabromoplatinum(IV) complexes of the type $PtBr_4(\text{arsine})_2$ are usually orange–red,[2] and indeed such compounds are formed by treating 1 mol. of bromine with the complexes $PtBr_2(mA)_2$ and $PtBr_2(pA)_2$ (mA and pA being the isomeric allylphenyldimethylarsines). Chemical and spectral evidence summarised elsewhere[1] suggests that $PtBr_4(oA)_2$ is not a square planar platinum(II) complex obtained by adding bromine to one double bond of (I), but an octahedral platinum(IV) complex with a metal–carbon σ-bond to one of the allyl side-chains. This suggestion is confirmed by an *X*-ray analysis of the structure of $PtBr_3OEt(oA)_2$ whose stereochemistry is shown in Figure 1. Metal–ligand bond lengths are given in Figure 2. The average e.s.d.'s of the Pt–Br and Pt–As lengths are 0·01 Å and of the Pt–C 0·08 Å, and correspond to a least-squares analysis of 1730 independent reflexions for which the present discrepancy factor, *R*, is 0·13.

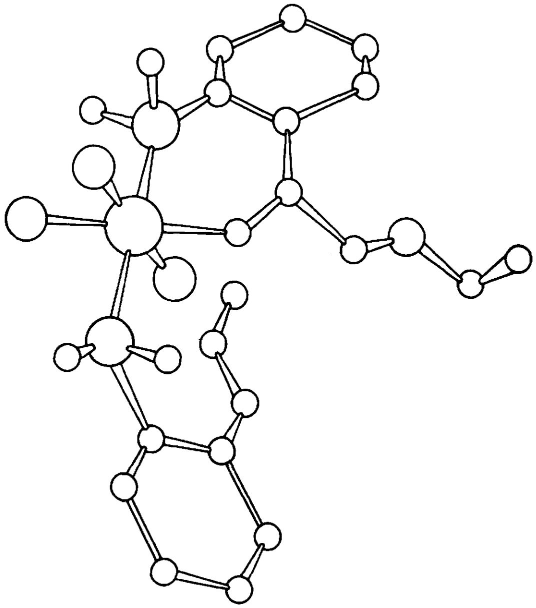


FIGURE 1

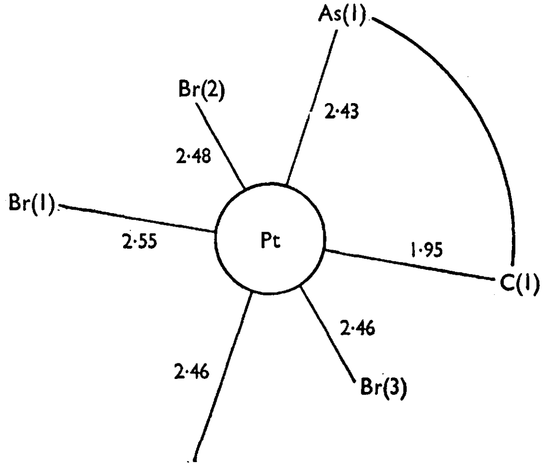


FIGURE 2

The σ-bonded carbon atom forms part of a six-membered chelate ring which has a chair conformation. The ethoxymethylene substituent occupies an equatorial position. The platinum–bromine bond *trans* to the σ-bonded carbon is significantly (6σ) longer than the two remaining Pt–Br bonds ($\bar{l} = 2{\cdot}47$ Å). The rearrangement of the σ-bonded fragment suggests the possibility of a metal-stabilised carbonium ion intermediate in the ready alcoholysis of $PtBr_4(oA)_2$.

The metal–carbon σ-bonds in $PtBr_4(oA)_2$ and $PtBr_3OEt(oA)_2$ show remarkable chemical stability. For example, bromine adds to the free double bond of $PtBr_4(oA)_2$ leaving the metal–carbon bond intact; this is broken only by heating with an excess of bromine, giving the usual tetrabromoplatinum(IV) complex of the fully brominated ligand.

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[1] The same ligand forms a chelate complex $PtBr_2oA$, in which the double bond is co-ordinated to the metal, and ν_{C-C} is 1500 cm.$^{-1}$; (M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, to be published.)

[2] R. S. Nyholm, *J. Chem. Soc.*, 1950, 843; J. Chatt, *ibid.*, p. 2301.