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Preliminary communication

Metallation of a phenyl group in a platinum(II) carbene complex during oxidation to platinum(IV)

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SUMMARY

Reaction of chlorine with *cis*-$[PtCl_2\{C(NHR)(NHR')\}PEt_3]$ and *trans*-$[PtCl\{C(NHR)(NHR')\}(PEt_3)_2]ClO_4$ gives analogous platinum(IV) carbene complexes when R = R′ = Me; but when R = Me or Et and R′ = Ph, 2-metallation and 4-chlorine substitution of the phenyl group occurs, shown by the X-ray structure of $[PtCl_2\{C(Cl{\cdot}C_6H_3NH)(NHMe)\}(PEt_3)_2]ClO_4$.

The metallation of aromatic groups in ligands occurs in complexes of transition metals in their lower oxidation states and is sometimes induced by reduction[1]. We now report a metallation which is induced by oxidation.

The reaction of the complexes *trans*-$[PtCl\{C(NHR)(NHPh)\}(PEt_3)_2]ClO_4$ (R = Me or Et)[2] with chlorine leads to oxidation of the platinum, together with 2-metallation and 4-chlorination of the phenyl rings. The white, chlorinated derivative from *trans*-$[PtCl\{C(NHMe)(NHPh)\}(PEt_3)_2]ClO_4$ (I) is $[PtCl_2\{C(4\text{-}ClC_6H_3NH)(NHMe)\}(PEt_3)_2]ClO_4$ (II), the structure of which is shown in Fig.1. (R = 0.051 and R_w = 0.072 over 3811 independent intensities).

The five-membered ring and the carbon and nitrogen atoms of the NHMe side chain are coplanar to within 0.03 Å. The short N–C(2) distances imply substantial multiple character for these bonds but the Pt–C(2) distance (only 0.048(21) Å shorter than the formally single Pt–C(1) distance) is essentially that of a single Pt–C bond, as is normally found in carbene complexes[3,4].

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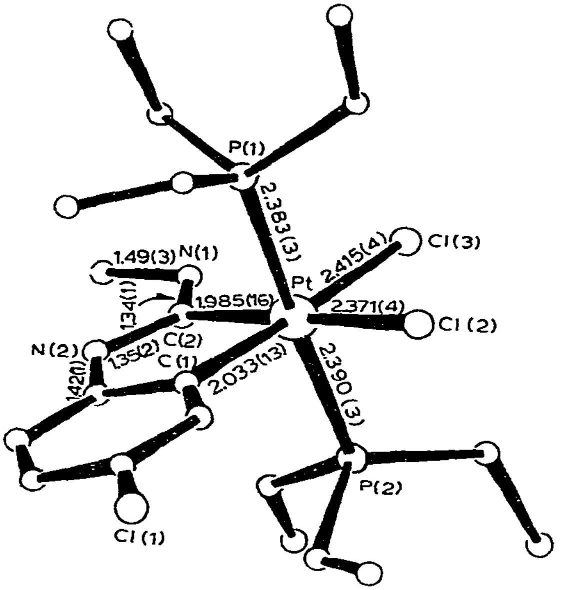

Fig. 1. Perspective view of the $[PtCl_2(C_8H_8N_2Cl)(PEt_3)_2]^+$ cation.

The Pt—Cl distances, together with those of 2.332(5) in *trans*-$[PtCl_4(PEt_3)_2]$[5] indicate the relative order of *trans*-influences $Ph^- >$ carbene $> Cl^-$ for platinum(IV) complexes, in accord with that established for platinum(II) complexes, where carbene lies close to PEt_3, between σ-alkyl and chloride[3,4,6].

To determine whether the metallation involves insertion of metal into a C—Cl bond pre-formed by ring chlorination, we have studied reactions of ring-chlorinated derivatives of (I). With dichlorine, the 4-chloro derivative gave (II) but the 2,6-dichloro compound did not metallate. The 2,4-dichloro derivative did not metallate even when refluxed in 2-methoxyethanol. Thus platinum does not insert into a pre-formed C—Cl bond and further studies on the reaction mechanism are in hand.

Since the ethyl analogue of (II) has a closely similar phenyl ^1H NMR spectrum, it is metallated at the phenyl group. With dichlorine, the compounds *cis*-$[PtCl_2\{C(OR)(NHPh)\}PEt_3]$ (R = Me or Et)[2] give metallated products but the entirely aliphatic *cis*-$[PtCl_2\{C(NHMe)_2\}PEt_3]$ and *trans*-$[PtCl\{C(NHMe)_2\}(PEt_3)_2]ClO_4$ give only the simple Pt^{IV} complexes, analogues of those reported with aliphatic chelate-carbene ligands[7].

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