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Electroneutral Alkoxy(organo)carbene Complexes of Platinum(II); a Metal–Hydrogen Non-Primary Valence Interaction in *cis*-[$PtCl_2(PMe_2Ph)${C(OEt)-CH_2Ph}]

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Although synthetic routes to cationic platinum(II) complexes containing alkoxy(organo)carbene ligands are well established [1], electroneutral platinum(II) complexes containing these ligands have so far not been described. We now report the preparation and spectroscopic examination of a series of related, electroneutral alkoxy(organo)carbene–platinum(II) species and the X-ray structure determination of *cis*-[$PtCl_2(PMe_2Ph)${C(OEt)CH_2Ph}], a typical member of the series.

The complexes *cis*-[PtX_2L{C(OR')CH_2R}] are formed in yields of 30–70% when chloroform solutions of the halogen-bridged dimer [$L_2Pt_2X_4$] (L = PMe_2Ph, PEt_3; X = Cl, Br, I) are treated with monosubstituted acetylenes. RC≡CH (R = Ph, Me, Et), and alcohols, R'OH (R' = Me, Et, Pr^n), at room temperature. They are colourless, crystalline solids, stable to air and moisture, and readily soluble in chloroform and methylene chloride; the solutions display little decomposition when kept for several days at room temperature. The complexes have been characterised analytically, and by i.r. and ^1H and ^{31}P n.m.r. techniques which indicate a *cis*-configuration for each compound.

Crystals of *cis*-[$PtCl_2(PMe_2Ph)${C(OEt)CH_2Ph}] are monoclinic, space group $P2_1/n$, with four molecules in a cell of dimensions a = 15.084(2), b = 8.419(3), c = 15.801(3) Å, β = 92.93(2)°. The structure analysis was based on 2166 diffractometric intensity data corrected for absorption. Full-matrix least-squares refinement of the parameters of all atoms, including hydrogens, led to R = 0.036.

The crystal structure is built from discrete molecules which display the expected *cis*-square planar coordination around the platinum atom (Figure).

The rotational orientation of the carbenoid ligand around the Pt–C bond is similar to that observed in *cis*-[$PtCl_2(PEt_3)${C(OEt)NHPh}] [2]: the three bonds involving the carbenoid carbon atom lie in a plane which is approximately normal to the coordination plane of platinum (dihedral angle 85°). The Pt–C distance found here [1.920(9) Å] may be compared with values of 1.96(2) and 2.009(13) Å in the complexes *cis*-[$PtCl_2(PEt_3)L$], where L = C(OEt)NHPh [2] and $\overline{\mathrm{CN(Ph)CH_2CH_2N}}$Ph [3], respectively. The latter two ligands are believed to be stabilised mainly by donation of lone pair electron density from nitrogen to the carbenoid carbon atom [2, 3]. Such a possibility does not exist for the C(OEt)CH_2Ph ligand and enhanced Pt → C back bonding, reflected in a shorter bond, is the evident result. It should also be noted that the C–O distance found here [1.283(11) Å], slightly shorter than that [1.33(2) Å] in the complex with L = C(OEt)NHPh [2], indicates some enhancement of the multiple bond character of the C–O bond as well.

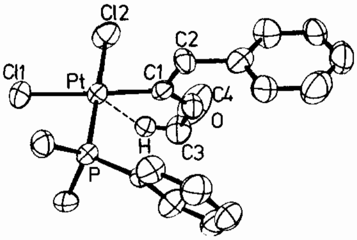

Figure. Molecular structure of *cis*-[$PtCl_2(PMe_2Ph)${C(OEt)-CH_2Ph}]. Thermal motion ellipsoids enclose 50% probability. The only hydrogen atom indicated is that involved in the intramolecular Pt···H contact of 2.6(1) Å. Important bond lengths are: Pt–Cl(1) 2.375(3), Pt–Cl(2) 2.355(3), Pt–P 2.240(3), C(1)–C(2) 1.490(15), and O–C(3) 1.509(15) Å.

The Pt–Cl distances in the C(OEt)CH_2Ph complex are nearly equal and are in good agreement with corresponding values in the C(OEt)NHPh and $\overline{\mathrm{CN(Ph)CH_2CH_2N}}$Ph complexes. Despite the differences in the Pt–C bonding, the three carbene ligands exert similar *trans*-influence on Pt–Cl bond lengths, and are comparable in this respect with monotertiary phosphines.

The most noteworthy structural feature is the short intramolecular Pt···H contact, of 2.6(1) Å, involving an ethoxy methylene hydrogen atom (Figure). The geometry of the carbene ligand is such that this contact is nearly minimised: the Pt–C–O–CH_2 and C–O–CH_2–CH_3 torsion angles are respectively –2 and 119°. The contact is longer than the Mo···H distances of *ca.* 2.0 Å found in pyrazolyborate complexes [4]. Nevertheless, it is shorter than the *ortho*-hydrogen–metal distances of *ca.* 2.8 Å, observed in the two isomers of [$RhCl(PPh_3)_3$], for which the term *non-primary valence interaction* has been suggested [5].

The ^1H n.m.r. spectrum of this complex shows AB patterns for both carbene methylene groups, but the chemical shifts of the alkoxy methylene protons (5.73 and 5.11 δ, in ppm downfield of TMS in $CDCl_3$

solution) indicate greater differences in magnetic environment than those experienced by the α-carbene protons (4.11 and 3.77δ). This suggests that the solid state conformation persists in solution at room temperature. Furthermore, the n.m.r. spectra of the other electroneutral (though not the cationic) ethoxy(organo)carbene platinum(II) complexes are similar in this respect, and suggest that a short Pt···H contact is a general phenomenon in these molecules.

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