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Preliminary communication

STERICALLY CROWDED PLATINUM(II) PHOSPHINE CATIONS

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Summary

Cationic platinum(II) hydrides $[HPtL_2L']^+$ (L = phosphines) have been prepared and the ligand steric effects studied; the crystal and molecular structure of *trans*-$[PtH(PCy_3)_2PPh_3]$ PF_6 is described.

The importance of the steric properties of ligands in determining the chemical behaviour of metal complexes is well appreciated. There is much less understanding of the real demand for space that each ligand makes. A commonly used approach is that developed by Tolman [1], and known as the cone angle concept. The uses of it have been reviewed recently by Tolman [2], although both Tolman and others [3] have stressed that cone angles may measure only relative sizes of ligands. Cone angles do not allow for the intermeshing effects of ligands (e.g. of the organic substituents of a tertiary phosphine) and hence do not describe the intimate details of ligand shapes and sizes. More refined models have been described recently by Payne and Stephaniak [4], Ferguson et al. [5], and Immirzi and Musco [6].

Because of our interest [7] in ligand steric effects on the chemistry of platinum(II) species, we have now prepared a series of cationic platinum(II) hydrides, $[HPtL_2L']^+$, L = tricyclohexylphosphine, L′ = tertiary phosphine, from the reaction of *trans*-$[PtH(solvent)(PCy_3)_2]^+$ PF_6^- [8] with L′ at 0—25°C in dichloromethane. Air stable, white crystals of *trans*-$[PtH(PCy_3)_2L']^+$ PF_6^- have thus been obtained for L′ = PEt_3, PPh_3, PPh_2Me, $PPhMe_2$, PPh_2Cy, $PPhCy_2$, PCy_3, P-i-Pr_3, P-n-Bu_3, $P(4\text{-}CH_3C_6H_4)_3$, $P(3\text{-}CH_3C_6H_4)_3$, $P(2\text{-}CH_3C_6H_4)_3$, $AsPh_3$, or $SbPh_3$. All compounds have been fully characterized analytically, and by infrared, ^1H and ^{31}P NMR spectroscopy; the spectroscopic results will be discussed fully elsewhere.

The cation *trans*-$[PtH(PPh_3)_3]^+$ has been described previously [9], but these new analogues containing three tertiary phosphines two of which are tricyclohexylphosphine are unexpected and must be highly strained sterically. Tricyclohexylphosphine has a cone angle of ca. 170°, and hence, on this basis, these hydridoplatinum(II) cations should not exist. Certainly, both the existence and stability of *trans*-$[PtH(PCy_3)_3]^+$ are surprising, even allowing for the intermeshing of the cyclohexyl substituents which must be even more significant than in the zerovalent complex $Pt(PCy_3)_3$ [10].

To investigate the way in which such steric crowding can be accommodated, the crystal and molecular structures of *trans*-$[PtH(PCy_3)_2PPh_3]PF_6$ (I) have been determined.

Crystals of I from $CH_2Cl_2/(C_2H_5)_2O$ are monoclinic, $P2_1/n$ with a 11.323(1), b 27.240(3), c 18.191(1) Å, β 96.93(1)° and $Z = 4$. Of the 6998 reflections measured with Cu-K_α radiation, 6197 possessed intensities significantly above background and were used in the solution and refinement of the structure. The standard corrections for α_1—α_2 splitting, Lorentz and polarization effects and absorption as a function of crystal shape were applied to the intensities. The structure was solved by the heavy atom method, the Pt and the four P atoms having been located from a Patterson map, and has been refined (phenyls treated as rigid bodies) to a conventional R of 0.073. During the latter refinement cycles the hydride ligand was included at its idealized position (opposite the centroid defined by the three Pt-bound P atoms with a Pt—H distance equal to the sum of the Van der Waals' radii of the atoms) and not refined. The geometry of the cation is shown in Fig. 1 and consists of a virtually planar arrangement of the atoms bonded to Pt. The PCy_3 ligands are *trans* to one another. Each cyclohexyl ring is in a chair conformation. The three bulky phosphine ligands intermesh, leaving a cavity occupied by the hydride ligand. Average values for bond distances are: C—C(cyclohexyl) 1.54(3) Å, P—F(PF_6^-) 1.54(4) Å, P—C(cyclohexyl) 1.858(6) Å and P—C(phenyl) 1.85(1) Å. Other pertinent distances are: Pt—H 1.596 Å, Pt—P(1) 2.359(3) Å, Pt—P(2) 2.346(3) Å, and Pt—P(3) 2.325(3) Å. Selected bond angles are H—Pt—P(1) 178.9(1)°, H—Pt—P(2) 77.7(1)°, H—Pt—P(3) 77.6(1)°, P(1)—Pt—P(2) 102.8(1)°, P(1)—Pt—P(3) 101.9(1)°, and P(2)—Pt—P(3) 155.2(1)°.

The bond lengths and bond angles for the PCy_3 ligands are similar to related values in other complexes [11, 12]. Moreover, calculations of the "ligand profiles" of the PCy_3 ligands in I and in $(PCy_3)_2Pt(CF_3C{\equiv}CCF_3)$ [12] by the method of Ferguson et al. [5] reveal differences that reflect the ability of the

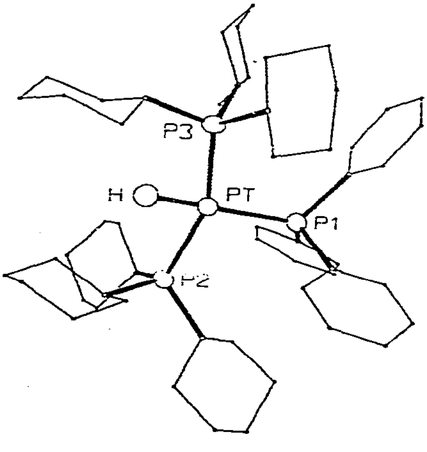

Fig. 1. Geometric structure of the cation *trans*-$[PtH(PCy_3)_2PPh_3]^+$.

flexible cyclohexyl rings to adopt alternative conformations, thereby facilitating the intermeshing of the nine bulky organic substituents of I.

It is thus clear that the existence of these unexpected cations can be attributed to (a) the substantial intermeshing of the cyclohexyl groups, as shown in Fig. 1 and (b) the remarkably small P(2)—Pt—P(3) angle of 155.2°. Although it is thus possible to accommodate the four ligands in a planar geometry about platinum, not surprisingly such distortions from the regular square arrangement will be reflected in spectroscopic parameters. For example, the $^{31}P\{^{1}H\}$ spectrum of *trans*-$PtH[P(o\text{-tolyl})_3](PCy_3)_2PF_6$ shows a PCy_3 resonance consisting of an eight line pattern centred at δ −26.4 ppm, attributable to magnetic non-equivalence of the PCy_3 ligands. The steric bulk of the $P(o\text{-tolyl})_3$ ligand presumably causes a similar distortion of the square planar arrangement, and thus produces this magnetic non-equivalence.

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