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Preliminary communication

PREPARATION AND X-RAY CRYSTAL STRUCTURE OF BIS{BIS(DIPHENYLPHOSPHINO)METHANIDO}PLATINUM(II), $[Pt(Ph_2PCHPPh_2)_2]$

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Summary

$[Pt(Ph_2PCHPPh_2)_2]$, the first homoleptic complex containing the chelated bis(diphenylphosphino)methanide ligand, has been synthesised by reaction of $K_2[PtCl_4]$ and $Ph_2PCH_2PPh_2$ with KOH in ethanol, and characterised by ^1H and ^{31}P NMR spectroscopy and X-ray crystallography.

The only known homoleptic complexes of the bis(diphenylphosphino)methanide anion $[Ph_2PCHPPh_2]^-$ (which was first reported in 1970 [1]), are binuclear $[Au_2(\mu\text{-}Ph_2PCHPPh_2)_2]$ [2] and trinuclear $[Cu_3(\mu\text{-}Ph_2PCHPPh_2)_3]$ [3], in which the ligand is bridging. We now report the preparation and full characterisation of $[Pt(Ph_2PCHPPh_2)_2]$ (I), the first homoleptic complex to be described in which the ligand displays a chelating configuration, a configuration previously only found in the mixed ligand complexes II [4] and III [5]. Products of composition $[M(Ph_2PCHPPh_2)_2]$ (M = Pd or Pt) have previously been obtained, but were apparently intractable and thought to be polymeric [4].

Complex I was obtained in ca. 70% yield as air-stable, pale yellow crystals by slow addition of an aqueous solution of $K_2[PtCl_4]$ to a solution of dppm ($Ph_2PCH_2PPh_2$) and KOH in ethanol at 70°C (i.e. a reaction analogous to the standard preparation of $[Pt(PPh_3)_4]$ [6]). The complex is insoluble in most common solvents but is sufficiently soluble (ca. 0.5% w/w) in benzene to permit ^1H and ^{31}P NMR spectra to be obtained: it may also be readily recrystallized as a benzene solvate from this solvent. The NMR data obtained are: ^1H,

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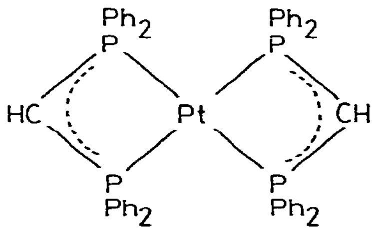
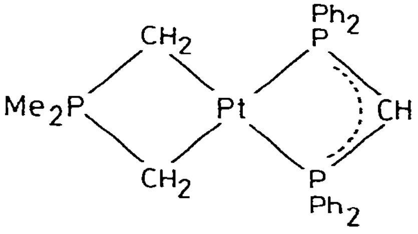
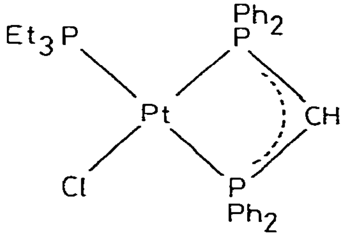


(I)



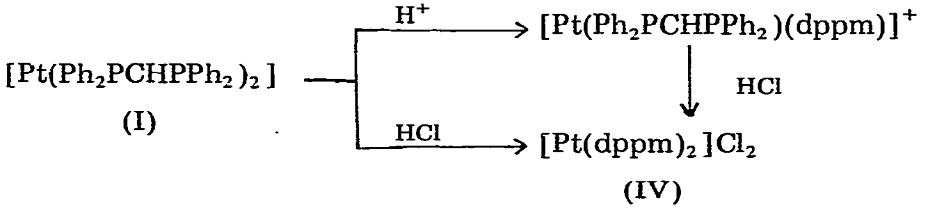
(II)



(III)

δ(PCHP) 4.16 ppm, J(Pt—H) 139 Hz (coupling to ^{31}P is not observed); ^{31}P, $\delta(^{31}P)$ −46.0 ppm (relative to trimethylphosphate), J(Pt—P) 1887 Hz.

Protonation of I gives salts of the known cationic complex $[Pt(dppm)_2]^{2+}$, e.g. excess HCl in $C_2H_2Cl_4$ gives the dichloride salt IV [7]. Stepwise protonation via a stable intermediate, $[Pt(Ph_2PCHPPh_2)(dppm)]^+$, appears to have occurred during attempts to record the ^{31}P NMR spectrum of I in $C_2H_2Cl_4$, and the nature of this interesting intermediate mixed-ligand species is being further investigated.



(IV)

We have shown by an X-ray crystal structure analysis that I can be unequivocably formulated as $[Pt^{II}(Ph_2PCHPPh_2)_2]$. The crystals obtained from a benzene solution are characterised by a triclinic unit cell of dimensions a 9.780(1), b 9.817(1), c 12.898(1) Å, α 93.09(1), β 109.51(1), γ 95.68(1)°, containing one $[Pt^{II}(Ph_2PCHPPh_2)_2]$ molecule and one benzene molecule, both constrained to exact $C_i(\bar{1})$ symmetry by the space group $P\bar{1}$. The structure was solved by the heavy atom method and refined to $R = 0.016$, $R_w = 0.021$, using 6723 independent reflections with $I > 3\sigma(I)$. All hydrogen atoms were located in electron-density syntheses and their parameters have been included in the least-squares refinement.

As in II and III, $[Ph_2PCHPPh_2]^-$ behaves as a chelating diphosphine ligand. The four Pt—P bonds are exactly coplanar (Fig. 1), in conformity with our formulation of the complex as a platinum(II) species. The Pt—P bond lengths

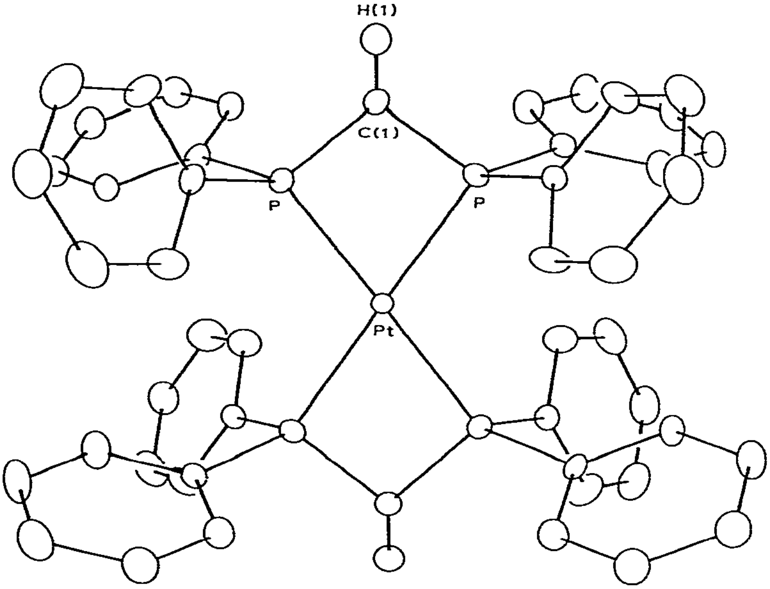


Fig. 1. The molecular structure of $[Pt(Ph_2PCHPPh_2)_2]$. Hydrogen atoms (except H(1)) are omitted. 20% probability ellipsoids are displayed.

(2.326(1), 2.321(1) Å) are also consistent with this interpretation. They may be compared with values of 2.28—2.32 Å observed in II [4] and III [5] and with the mean Pt—P distance of 2.30(1) Å in *cis*-$[PtPh_2(Ph_2PCH_2PPh_2)]$ [8]. Bond angles within the chelate ring P—Pt—P 69.1(1), Pt—P—C 95.0(1) and 95.3(1), and P—C—P 99.4(1)° agree well with corresponding ones in II and III and indeed in *cis*-$[PtPh_2(Ph_2PCH_2PPh_2)]$. Deprotonation of the methylene carbon of $Ph_2PCH_2PPh_2$ to form a delocalised P⎓C⎓P system manifests itself mainly by the P—C(1) bond lengths (1.730(2), 1.727(2) Å), which are ca. 0.1 Å shorter than the P—C(phenyl) distances (1.821(2)—1.831(2) Å). Corresponding values are found in II and III, whereas in *cis*-$[PtPh_2(Ph_2PCH_2PPh_2)]$ the mean P—CH_2 bond length is 1.86(2) Å.

In conclusion it is worth noting that known products of reactions involving reduction of platinum(II) in the presence of dppm include the diplatinum(0) complex $[Pt_2(\mu\text{-dppm})_3]$ [9], the hydridoplatinum(I) cation $[Pt_2H(\eta^1\text{-dppm})(\mu\text{-dppm})_2]^+$ [7], as well as the platinum(II) methanido complex reported herein. The reactions of I are under active investigation and it appears probable that, like the recently reported carbanions derived from $[M(CO)_4(dppm)]$ (M = Cr, Mo or W) [10], I will prove to be a versatile reagent susceptible to nucleophilic attack.

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