

Preliminary communication

**A THREE-COORDINATE CATIONIC HYDRIDOPLATINUM(II) COMPLEX
 STABILIZED BY TRI-*t*-BUTYLPHOSPHINE**

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Summary

Synthesis, characterization and some reactions of a three-coordinate hydrido-platinum(II) complex, $[(P-t-Bu_3)_2PtH]PF_6$, are reported.

A number of cationic platinum(II) hydrides of the type $[(PR_3)_2Pt(L)H]^+$ (L = a neutral ligand or a donor solvent such as acetone or methanol) have been reported recently [1]. These hydrido complexes invariably are four-coordinate even when $PR_3 = L = PCy_3$ (Cy = cyclohexyl) [1d]. The existence and stability of such complexes containing bulky phosphines [$PR_3 = PCy_3$ and L = e.g., PCy_3 , PCy_2Ph , $P-i-Pr_3$, $P(o-tolyl)_3$] is surprising in view of the large cone angle ca. 170° for tricyclohexylphosphine and has been attributed to (a) the substantial intermeshing of the cyclohexyl groups and (b) the small $PCy_3-P-PCy_3$ angle (ca. 155°) [1d]. We have recently employed tri-*t*-butylphosphine and -arsine to stabilize platinum and palladium hydrides [2–4]. *P-t-Bu_3* has a larger steric requirement [5] than PCy_3 as shown by the comparison of the X-ray diffraction data for $(PCy_3)_2Pt$ [6] and $(P-t-Bu_3)_2Pt$ [7] as well as by the fact that, unlike in the case of PCy_3 , no complex containing more than two *P-t-Bu_3* ligands bonded to a metal has been isolated [1g]. We were therefore interested in preparing the *P-t-Bu_3* analogues of *trans*- $[(PCy_3)_2Pt(L)H]^+$. In the course of this investigation we have isolated the first three-coordinate hydridoplatinum(II) complex, $[(P-t-Bu_3)_2PtH]PF_6$ (I), which has unusually high values of $\delta(Pt-H)$ and $^1J(Pt-H)$ as well as $\nu(Pt-H)$ and undergoes facile reductive elimination in the presence of bases.

The yellow complex I was prepared by the reaction of *trans*- $(P-t-Bu_3)_2PtHCl$

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with an equimolar amount of AgPF_6 in acetone or methanol. Formulation of the complex is based on analytical, IR, and ^1H NMR and ^{31}P NMR data.

The infrared spectrum of I shows a medium intensity band at 2645 cm^{-1} due to the Pt—H stretching mode and strong bands at 840 and 560 cm^{-1} due to the P—F stretching and bending modes of PF_6^- [8].

The ^{31}P - $\{^1\text{H}\}$ NMR spectrum (in CH_2Cl_2 containing 20% C_6D_6) of I consists of a singlet at 86.7 ppm [$^1J(\text{Pt}-\text{P})$ 2623 Hz] due to P-*t*-Bu₃ and a characteristic septet at -144.8 ppm [$^1J(\text{P}-\text{F})$ 710 Hz] for PF_6^- . In the ^1H NMR spectrum (in CD_2Cl_2), the *t*-Bu protons are observed as a triplet at 1.537 ($^3J(\text{P}-\text{H}) + ^5J(\text{P}-\text{H}) = 13.6\text{ Hz}$) indicating the *trans*-geometry of the *t*-Bu₃P ligands [9]. The Pt—H proton appears as a 1/2/1 triplet at $\delta -36.3$ [$^1J(\text{Pt}-\text{H})$ 2592 Hz ; $^2J(\text{P}-\text{H})$ 17.6 Hz].

The $\nu(\text{Pt}-\text{H})$ and $^1J(\text{Pt}-\text{H})$ values for the $[(\text{PR}_3)_2\text{Pt}(\text{L})\text{H}]^+$ complexes reflect the relative *trans* influence of the ligand L [1h]. For example, $\nu(\text{Pt}-\text{H})$, $\delta(\text{Pt}-\text{H})$ and $^1J(\text{Pt}-\text{H})$ for *trans*- $[(\text{PCy}_3)_2\text{Pt}(\text{L})\text{H}]\text{PF}_6$ [1c] are 2308 cm^{-1} , $\delta -27.8$ and 1590 Hz , respectively, when L = MeOH and 2170 cm^{-1} , $\delta -4.66$ and 916 Hz respectively when L = CO. The values of $\nu(\text{Pt}-\text{H})$, $\delta(\text{Pt}-\text{H})$ and $^1J(\text{Pt}-\text{H})$ for I appear to be the largest reported for a platinum(II) hydride complex. This would suggest the presence of a ligand, if any, with a *trans* influence even weaker than methanol. The presence of any other ligand except the hydride and the phosphines in the coordination sphere of platinum(II) in I is ruled out by its analytical, infrared and NMR data. On the basis of the spectral data and the diamagnetism* of the cation we propose a T-shaped structure (Fig. 1) containing three-coordinate platinum(II). A polymeric structure (Fig. 2) involving bridging hydrides can be ruled out on the basis of the

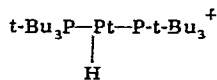


Fig. 1.

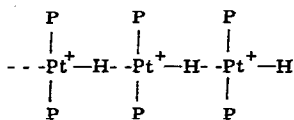


Fig. 2.

large Pt—H chemical shift and absence of $\nu(\text{Pt}-\text{H}-\text{Pt})$ in the IR spectrum.

For example, the chemical shift for the bridging hydride in the complex $\text{Ph}(\text{PEt}_3)_2\text{Pt}^{\text{a}}-\text{H}-\text{Pt}^{\text{b}}(\text{PEt}_3)_2\text{H}$ has been reported to be $\delta -9.46$ [$^1J(\text{H}-\text{Pt}^{\text{a}}) \approx ^1J(\text{H}-\text{Pt}^{\text{b}}) \approx 500\text{ Hz}$] [10]:

I reacts with L = CO, MeCN and H_2O to give the four-coordinate complexes *trans*- $[(\text{P}-\text{t-Bu}_3)_2\text{Pt}(\text{L})\text{H}]\text{PF}_6$ (II), which show markedly lower values of $\nu(\text{Pt}-\text{H})$, $\delta(\text{Pt}-\text{H})$ and $^1J(\text{Pt}-\text{H})$ than I. For example, $^1J(\text{Pt}-\text{H})$ for II ranges from 740 to 1475 Hz . No reaction is observed with ethylene or diphenylacetylene, probably due to unfavourable steric reasons [1b]. Addition of 1 mol of P-*t*-Bu₃, PCy₃ or NH_3 to I results in rapid disappearance of the yellow colour and formation of $(\text{P}-\text{t-Bu}_3)_2\text{Pt}$ in quantitative yield. Further reactions of I and II with bases are being studied with an aim to establish the mechanism of these interesting** reactions.

*In a trigonal planar structure the *d* orbitals of platinum will split in the order $d_{xz}, d_{yz} < d_z^2 < d_{xy}, d_{x^2-y^2}$ giving rise to two unpaired 5*d* electrons.

**Whereas the reaction of $[(\pi\text{-allyl})\text{Pt}(\text{PCy}_3)_2]\text{PF}_6$ with nucleophiles such as methoxide affords $(\text{PCy}_3)_2\text{PtH}_2$ [11], *trans*- $(\text{PPh}_3)_2\text{Pt}(\text{h-C}_3\text{H}_5\text{CN})\text{H}$ gives $(\text{PPh}_3)_2\text{Pt}$, $(\text{PPh}_3)\text{Pt}(\text{PPhMe}_2)_3$ or $(\text{PPh}_3)_2\text{Pt}(\text{Ph}_2\text{PCH}=\text{CHPPh}_2)_2$ with PEt_3 , PPhMe_2 or $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ [12].

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