

## Dihydro-platinum(II) and Related Complexes

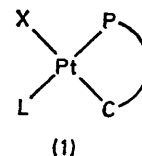
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**Summary** Stable platinum(II) dihydrides  $trans$ -[PtH<sub>2</sub>L<sub>2</sub>] and monohydrides [PtH(P—C)L] (L = a bulky tertiary phosphine, P—C = a metallated tertiary phosphine) are described; a previous claim to have made such dihydrides is shown to be wrong.

ALTHOUGH many monohydride complexes of the type  $trans$ -[PtHXL<sub>2</sub>] (L = tertiary phosphine or tertiary arsine; X = anionic ligand such as Cl, NO<sub>3</sub> etc.) are known attempts at further reduction to give dihydrides [PtH<sub>2</sub>L<sub>2</sub>] lead to decomposition when, for example, L = PEt<sub>3</sub>, AsEt<sub>3</sub>, PMe<sub>2</sub>-Ph, or PPh<sub>3</sub>. We have now prepared a series of white crystalline dihydrides,  $trans$ -[PtH<sub>2</sub>L<sub>2</sub>], with bulky tertiary phosphine ligands, L, simply by reducing either  $cis$ -[PtCl<sub>2</sub>L<sub>2</sub>] or  $trans$ -[PtHClL<sub>2</sub>] with a large excess of NaBH<sub>4</sub>

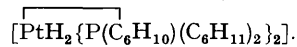
in EtOH. Dihydrides with L = PBu<sup>t</sup>Me<sub>2</sub>, PBu<sup>t</sup>Et<sub>2</sub>, PBu<sup>t</sup>Bu<sup>n</sup>, PBu<sup>t</sup>(CH<sub>2</sub>Ph)<sub>2</sub>, PBu<sup>t</sup>Pr<sup>n</sup>, PBu<sup>t</sup>CH<sub>2</sub>Ph, and P(cyclohexyl)<sub>3</sub> have been prepared, the more bulky ligands



giving the more stable compounds; *e.g.* [PtH<sub>2</sub>(PBu<sup>t</sup>CH<sub>2</sub>Ph)<sub>2</sub>] is stable for several weeks in air at room temperature whilst [PtH<sub>2</sub>(PBu<sup>t</sup>Et<sub>2</sub>)<sub>2</sub>] darkens considerably after 1 day at room temperature in air but appears to be indefinitely

stable at  $-30^{\circ}\text{C}$ . These compounds are characterized by a very intense i.r. absorption band within the range  $1710\text{--}1750\text{ cm}^{-1}$  due to  $\nu(\text{Pt-H})$  and a  $^1\text{H}$  n.m.r. resonance at very low field for a transition-metal hydride, *i.e.* within the range  $\tau$   $12\text{--}13.15$  (in benzene solution) and  $^2J(\text{P-H})$   $16\text{--}18\text{ Hz}$ ;  $^1J(\text{Pt-H})$   $780\text{--}802\text{ Hz}$ . In particular *trans*- $[\text{PtH}_2\{\text{P}(\text{cyclohexyl})_3\}_2]$ † has  $\nu(\text{Pt-H})$   $1710\text{ cm}^{-1}$  (Nujol),  $\tau_{\text{H}}$   $13.15$ ,  $^2J(\text{P-H})$   $17\text{ Hz}$ ,  $^1J(\text{Pt-H})$   $792\text{ Hz}$  (in benzene in which it is readily soluble). Previously it has been reported that the material 'X' which gradually precipitates over a period of 1 week from an ether solution containing  $[\text{Pt}(\text{acac})_2]$ ,  $\text{P}(\text{cyclohexyl})_3$ , and  $\text{Et}_3\text{Al}$  is  $[\text{PtH}_2\{\text{P}(\text{cyclohexyl})_3\}_2]$ . This could not be the structure of the material 'X' which had a value for  $\nu(\text{Pt-H})$  of  $1910\text{ cm}^{-1}$ , very high for two mutually *trans* hydride ligands,<sup>2-4</sup> and was reported to be too insoluble for  $^1\text{H}$  n.m.r. studies but was apparently monomeric in dilute solution in benzene. It reacted with  $\text{CCl}_4$  to give  $\text{CHCl}_3$  and *trans*- $[\text{PtHCl}\{\text{P}(\text{cyclohexyl})_3\}_2]$ . We have prepared this hydrochloride complex by treating *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$  with tricyclohexylphosphine and find the same properties as those reported previously.<sup>1</sup> We find that *trans*- $[\text{PtHCl}\{\text{P}(\text{cyclohexyl})_3\}_2]$  is smoothly converted into *trans*- $[\text{PtH}_2\{\text{P}(\text{cyclohexyl})_3\}_2]$  by  $\text{NaBH}_4$  in ethanol. Two other hydrides analogous to 'X' have also been described and were similarly prepared from  $[\text{Pt}(\text{acac})_2]$ ,  $\text{Et}_3\text{Al}$ , and  $\text{PEt}(\text{cyclohexyl})_2$  or  $\text{PPr}^n(\text{cyclohexyl})_2$ , but they were isolated only as viscous oils.<sup>1</sup> These two hydrides must also have been incorrectly formulated as *trans*- $[\text{PtH}_2\text{L}_2]$  since they had large values for  $\nu(\text{Pt-H})$  (*ca.*  $1910\text{ cm}^{-1}$ ) and

the  $^1\text{H}$  n.m.r. data,  $\tau_{\text{H}}$   $15.6$ ,  $^2J(\text{P-H})$   $18\text{ Hz}$ ,  $^1J(\text{Pt-H})$   $596\text{ Hz}$  for  $\text{L} = \text{PEt}(\text{cyclohexyl})_2$  and  $\tau_{\text{H}}$   $16.9$ ,  $^2J(\text{P-H})$   $20\text{ Hz}$ ,  $^1J(\text{Pt-H})$   $610\text{ Hz}$  for  $\text{L} = \text{PPr}^n(\text{cyclohexyl})_2$  are quite different from the narrow ranges of values found for our extensive series of dihydrides. Since these three hydrides have high values for  $\nu(\text{Pt-H})$  and very low values for  $^1J(\text{Pt-H})$  we tentatively suggest that they are hydrides of platinum(IV) either of type *trans*- $[\text{PtH}_4\text{L}_2]$  or containing metallated tertiary phosphine ligands, *e.g.* *trans*-



We have also made stable crystalline platinum(II) hydrides  $[\text{PtX}(\text{P-C})\text{L}]$  (**1**;  $\text{X} = \text{H}$ ) containing metallated tertiary phosphine ligands (P-C) with  $\text{L}^2 = \text{P}^t\text{Bu}(\text{o-tolyl})_2$ ,  $\text{P}^t\text{Bu}_2(\text{o-tolyl})$ , or  $\text{P}^t\text{Bu}(\text{CH}_2\text{Ph})_2$  by  $\text{NaBH}_4$  reduction of the corresponding chlorides (**1**;  $\text{X} = \text{Cl}$ ).<sup>5,6</sup> These have values of  $\nu(\text{Pt-H})$  of  $1980\text{--}1988\text{ cm}^{-1}$ ,  $\tau_{\text{H}}$   $14.3\text{--}16.3$ ,  $^2J(\text{P-H})$  *ca.*  $15\text{ Hz}$ , and  $^1J(\text{Pt-H})$   $624\text{--}717\text{ Hz}$ . These spectroscopic data are similar to those previously ascribed to the incorrectly formulated dihydrides such as 'X' discussed above. *trans*- $[\text{PtH}_2\{\text{P}(\text{cyclohexyl})_3\}_2]$  on controlled pyrolysis gave no indication of producing any other hydrides or compounds containing metallated  $\text{P}(\text{cyclohexyl})_3$  ligands.

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† S. Otsuka and Y. Yoshida reported verbally at the XVI I.C.C.C., Dublin, August 1974 that they had prepared authentic *trans*- $[\text{PtH}_2\{\text{P}(\text{cyclohexyl})_3\}_2]$  and gave properties very similar to ours.

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