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Preliminary communication

IONIC BINUCLEAR PLATINUM(II) HYDRIDES

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Summary

The new hydrides $[(L—L)_2Pt_2H_3][BF_4]$ (I: L—L = 1,2-bis(diphenylphosphino)ethane; II: L—L = 1,2-bis(diphenylarsino)ethane) were obtained by reaction of $(L—L)Pt(PzH)_2][BF_4]_2$ (PzH = 3,5-dimethylpyrazole) with KBH_4 in MeOH or EtOH.

Many platinum hydrides have been reported since the initial discovery of the stable *trans*-$(Et_3P)_2Pt(H)(Cl)$ [1]. Besides the monohydrides, the known species include several *trans*-$(R_3P)_2Pt(H)_2$ [2], a *cis*-dihydride [3], the thermally unstable five-coordinate $(Et_3P)_3Pt(H)_2$ [4], the bridging dinuclear species $[PtH(\mu\text{-}H)(PCy_3)]_2$ and $[Pt(SiEt_3)(\mu\text{-}H)(PCy_3)]_2$ [5] and the platinum(IV) dihydrides $[PtH_2(SnR_3)_2(PMe_2Ph)_2]$ [6]. In this communication a new type of hydride is reported and characterized, viz. the binuclear, cationic trihydrides $[(L—L)_2Pt_2H_3][BF_4]$ (I: L—L = 1,2-bis(diphenylphosphino)ethane; II: L—L = 1,2-bis(diphenylarsino)ethane).

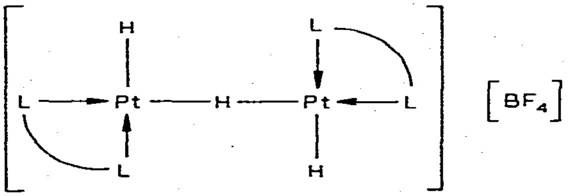
The new hydrides are obtained by reaction of $[(L—L)Pt(PzH)_2][BF_4]_2$ [7] (PzH = 3,5-dimethylpyrazole) with KBH_4 (1/1 molar ratio) in methanol or ethanol: the crude precipitate (yield > 85%) is crystallized three times from CH_2Cl_2/Et_2O. The elemental analyses (C, H, B, F, Pt), conductance in acetone solution, and molecular weight in chloroform, establish the formula $[(L—L)_2Pt_2H_x]^+[BF_4]^-$. In the IR spectra a weak band at ca. 2000 (I) and a broad band at ca. 2050 cm^{-1} (II) in nujol and correspondingly at ca. 2008 (I) and ca. 2075 cm^{-1} (II) in $CHCl_3$, indicate a terminal hydride. In the deuterium analogue of complex I, obtained by use of $NaBD_4$, the absorption at ca. 2000 cm^{-1} disappears, but ν(Pt—D), expected at ca. 1450 cm^{-1}, is obscured by phosphine vibrations. No other shift is observed upon deuteration, even around 1600 cm^{-1}, where Pt—H—Pt vibrations were reported to occur [5].

The number of hydrogens, x, is shown to be three by treatment of complex I with iodine in chloroform solution which shows the following stoicheiometry:

$$[(L-L)_2Pt_2H_3][BF_4] + 2\,I_2 \rightarrow 2\,(L-L)PtI_2 + H_2 + HBF_4$$

In the NMR spectrum of complex I ($CDCl_3$ solution) at 40°C in addition to the signals due to the phosphine, only one set of signals due to the hydride is found and the spectrum is not affected by lowering the temperature down to —50°C. At 60 MHz, the signal centered at τ 12.7 ppm is split into a triplet of quintets, while at 100 MHz, the full 25 line pattern (quintet of quintets) of the hydride signal appears. The 1/4/6/4/1 quintet with 40 Hz spacings is assigned to coupling of the hydrides to four magnetically equivalent ^{31}P nuclei by comparison with the spectrum of complex II (τ 15.8 ppm in CD_2Cl_2). The other quintet, with separation of 250 and 225 Hz for I and II, respectively, arises from coupling to ^{195}Pt nuclei (natural abundance 33.7%, nuclear spin $I = 1/2$). In a binuclear platinum complex the abundance of the species Pt—Pt, ^{195}Pt—Pt and ^{195}Pt—^{195}Pt are 43.94, 44.70 and 11.36, respectively. A system with such a distribution of NMR active and inactive nuclei requires the splitting of bridging hydride Pt—H—Pt signals, into a quintet having a 0.127/1.0/2.21/1.0/0.127 ratio, and the experimental ratios are 1.0/2.13/1.0 and 1.0/2.23/1.0 for the three central peaks of the quintet, on which reliable intensity measurements can be made. The ^{195}Pt—H coupling constants are therefore 500 and 450 Hz for I and II respectively.

In conclusion, since a formula such as $[(L-L)Pt(\mu\text{-}H)_3Pt(L-L)]^+[BF_4]^-$ in which all the hydrogens bridge the platinum nuclei is ruled out by the presence in the IR spectrum of the stretching vibrations due to terminal Pt—H bonds, we suggest that the structure of the trihydrides is:



and that the exchange between the bridging and terminal hydrides is fast on the NMR time scale in the temperature range investigated.

Work is in progress on the reactions of the new species.

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