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Preliminary communication

SOME NEW MONOHYDRIDOMONOPHOSPHIDO BRIDGED DIPLATINUM COMPLEXES

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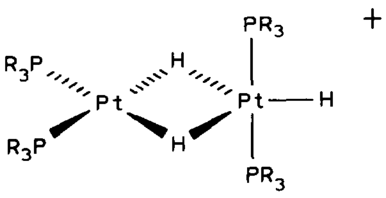
Summary

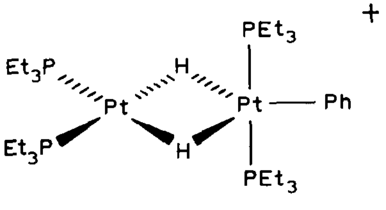
The cation $[(PPh_3)(Ph)Pt(\mu\text{-}H)(\mu\text{-}PPh_2)Pt(PPh_3)_2]^+$ (III), was obtained from the reaction of $[Pt(1,5\text{-}C_8H_{12})_2]$, *trans*-$[Pt(Ph)(acetone)(PPh_3)_2][BF_4]$, PPh_3 and H_2. The molecular structure of III is reported. It is shown that the Ph and Ph_2P fragments arise from the cleavage of one molecule of PPh_3.

Hydrido-bridged complexes have been extensively studied in recent years because of their interesting structural features [1] and their potential use as reaction intermediates in homogeneous catalysis [2].

A recent publication [3] describes the preparation of the dihydro-bridged species I and II from reaction 1.



(I)



(II)

We now find that the reaction of eq. 2 instead of giving the expected product of type (II), gives the cationic species (III).

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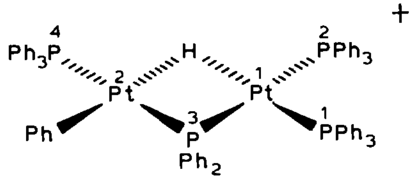
$$[\mathrm{Pt(COD)_2}] + 2\mathrm{PR_3} + \mathrm{H_2} + \textit{trans}\text{-}[\mathrm{PtY(acetone)(PR_3)_2}][\mathrm{BF_4}] \rightarrow [\mathrm{I}][\mathrm{BF_4}] \text{ or } [\mathrm{II}][\mathrm{BF_4}] \qquad (1)$$

(COD = 1,5-cyclooctadiene; for Y = H, R = Et, Ph and Cy $[\mathrm{I}]^+$; for Y = Ph, R = Et, $[\mathrm{II}]^+$)

$$[\mathrm{Pt(COD)_2}] + \mathrm{H_2} + 2\mathrm{PPh_3} + \textit{trans}\text{-}[\mathrm{Pt(Ph)(acetone)(PPh_3)_2}][\mathrm{BF_4}] \qquad (2)$$



(III)

The molecular geometry of III, as its $[\mathrm{BF_4}]$ salt, was established by X-ray diffraction [4]. A perspective view of III is shown in Fig. 1. Compound $[\mathrm{III}][\mathrm{BF_4}]$ consists of discrete cations and $[\mathrm{BF_4}]$ anions. There are two chemically equivalent but crystallographically independent molecules in the unit cell. The overall geometries of the two cations and the two anions do not differ significantly; the only relevant (ca. 11 σ) difference observed in the two independent cations is the Pt—Pt bond length which is 2.889(3) Å in one of them and 2.912(2) Å in the other. This difference may be due to packing forces. Similar effects have been observed in the anion $[(\mathrm{CO})_5\mathrm{Mo}(\mu\text{-H})\mathrm{Mo}(\mathrm{CO})_5]^-$ [5]. The coordination around each platinum atom can be described as distorted square planar if one assumes

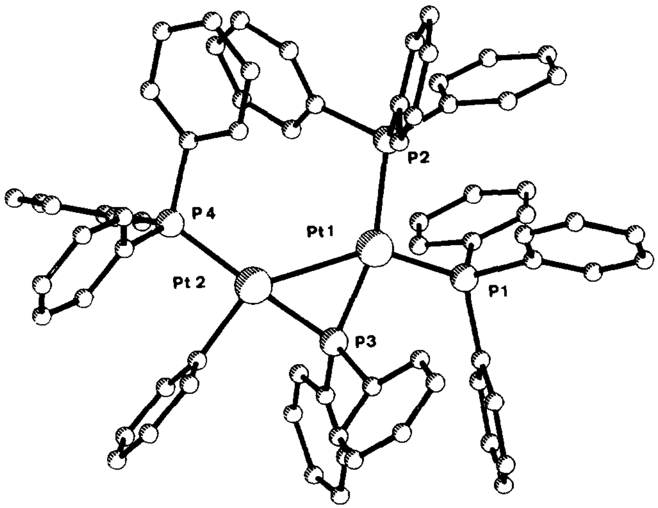


Fig. 1. A perspective view of the cation $[(\mathrm{PPh_3})(\mathrm{Ph})\mathrm{Pt}(\mu\text{-H})(\mu\text{-PPh_2})\mathrm{Pt}(\mathrm{PPh_3})_2]^+$. The Pt····Pt bond distances are 2.889(2) and 2.912(2) Å for the two independent molecules in the unit cell (see text). Other relevant (average) bond distances (Å) and angles (°) are: Pt(1)—P(1) 2.250(7), Pt(1)—P(2) 2.360(7), Pt(1)—P(3) 2.247(7), Pt(2)—P(3) 2.162(8), Pt(2)—P(4) 2.270(8), Pt(2)—C(1) 2.06(3); Pt(1)—P(3)—Pt(2) 82.3(2), P(1)—Pt(1)—P(3) 99.8(3), P(1)—Pt(1)—P(2) 98.9(3), P(4)—Pt(2)—C(1) 88.0(9), P(3)—Pt(2)—C(1) 94.6(9).

that also a hydride ligand is bridging the two platinum atoms. Although this bridging hydride ligand could not be located with certainty, its presence is confirmed by the ^1H NMR spectrum of III (see later). Three of the Pt—Pt—L bond angles (L = PPh_3 for Pt(1) and L = Ph for Pt(2)) are larger than 90°, as Pt—Pt—L angles are generally in the mononuclear complexes of the type *trans*-$[PtHL(PR_3)_2]$ [6,7], and it is noteworthy that in III they are smaller around Pt(2) which is the less crowded side of the molecule.

There are small deviations from planarity as judged from the displacements from the least squares plane through Pt, P and C(1) atoms (in the range 0.05—0.25 Å) possibly due to the presence of bulky phosphine ligands.

The Pt—Pt distance (av. 2.901(2) ± 0.012 Å) falls within the expected range if one considers that (1) on going from a dihydrido-bridged species, e.g., $[(CO)_4W(\mu\text{-}H)_2W(CO)_4]^{2-}$ (3.016 Å) [8] to the diphosphido-bridged compounds of similar structure, e.g., $[(CO)_4M(\mu\text{-}PEt_2)_2M(CO)_4]^{2-}$ (3.053 Å for M = W and 3.057 Å for M = Mo) [9] there is a lengthening of the M—M bond, (2) that a further lengthening of this bond occurs when one of the bridging ligands is a hydride and the other a phosphide, e.g., $[(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}H)(\mu\text{-}PMe_2)Mo(CO)_2(\eta^5\text{-}C_5H_5)]$ (3.267 Å) [10] vs. $[(PEt_3)(CO)_3Mo(\mu\text{-}PMe_2)_2Mo(CO)_3(PEt_3)]$ (3.089 Å) [11] and (3) that the Pt—Pt distance in $[(PCy_3)(Et_3Si)Pt(\mu\text{-}H)_2Pt(Et_3Si)(PCy_3)]$ is 2.692 Å [12].

The Pt(1)—P(3) and Pt(2)—P(3) distances, 2.247(7) and 2.162(8) Å, respectively, are much shorter than those observed in related platinum(II) complexes with phosphido bridges [13,14] and the asymmetry of the bridge may be related to the different coordination spheres of Pt(1) and Pt(2). The Pt(1)—P(3)—Pt(2) bond angle, 82°, is larger than the Pt—P—Pt bond angles found in the complexes mentioned above. Thus, the longer Pt—Pt distance is associated with shorter Pt—P bonds and a larger Pt—P—Pt bond angle. The three Pt—P bond-lengths span most of the range normally observed Pt^{II}—P bonds [15].

The ^1H, ^{31}P and ^{195}Pt NMR data for III [16] are first order, and are consistent with the crystal structure and can all be discussed using a "first-order" approximation.

The ^1H NMR spectrum of the hydride ligand (δ −6.5 ppm) appears as a doublet of multiplets flanked by three sets of ^{195}Pt-satellites arising from the isotopomers $(^{195}Pt^1)(Pt^2)^\star$(ca. 22%), $(Pt^1)^\star(^{195}Pt^2)$ (ca. 22%) and $(^{195}Pt^1)(^{195}Pt^2)$ (ca. 11%). ((Pt)* indicates a "non-magnetic" Pt-isotope)). Noteworthy are the $^1J(^{195}Pt^1,{}^1H)$ 600 Hz, and $^1J(^{195}Pt^2,{}^1H)$ 324 Hz and the $^2J(^{31}P^1,{}^1H)$ 98 Hz while $^2J(^{31}P^x,{}^1H)$ for x = 2, 3 and 4, fall in the range 7—18 Hz [17].

The ^{31}P NMR spectrum shows the four inequivalent phosphorus nuclei ($\delta(P^1)$ 18.1; $\delta(P^2)$ 15.3; $\delta(P^3)$ 121.3 and $\delta(P^4)$ 22.9 ppm) each showing coupling to both $^{195}Pt^1$ and $^{195}Pt^2$ [18]. While the chemical shifts and most of the coupling constants fall in the ranges observed in related bonding situations [18], the $^1J(^{195}Pt^1, {}^{31}P^1)$ (3785 Hz) is unusually large and comparable with $^1J(^{195}Pt,{}^{31}P)$ in compounds where the phosphorus atom in question has a weakly held electronegative ligand in *trans* position [19], e.g., X = NO_3^- in the series *cis*-$[PtX_2(P\text{-}n\text{-}Bu_3)_2]$. While it has been previously observed that the $^1J(^{195}Pt,{}^{31}P)$ value for a phosphorus atom in *trans*-position to a bridging hydride is considerably higher than that for a phosphorus atom *trans* to a terminal hydride [3], the value observed in III is unusually high and could be taken to indicate that the H—Pt^1 interaction is quite weak.

The ^{195}Pt NMR data for III [20] are consistent with the solid state structure and were particularly useful for the assignment of the $^1J(^{195}Pt,^{31}P)$ couplings.

The question of whether the phenyl group bonded to Pt^2 originates from the cation *trans*-$[Pt(Ph)(acetone)(PPh_3)_2]^+$ or from the cleaved PPh_3 was resolved by carrying out the reaction 3. As this gave III and not its *p*-tolyl analogue, we conclude that the σ-bonded phenyl group comes from the cleavage of PPh_3.

$$[Pt(COD)_2] + H_2 + 2PPh_3 + trans\text{-}[Pt(p\text{-}Tol)(acetone)(PPh_3)_2]^+ \qquad (3)$$

Similar P—C bond cleavages in PPh_3 complexes have been frequently observed [21] and such reactions are often responsible for catalyst deactivation. It should be pointed out here that the P—C bond cleavage described here occurs at ca. 0° C, while those observed earlier are reported to require higher temperatures [13]. The detailed mechanism leading to the formation of compounds of type III is currently under investigation.

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4 The crystals are triclinic, space group $P\bar{1}$; $Z = 4$, a 13.042(3), b 22.391(6), c 26.205(8) Å; α 65.03(4)°, β 76.04(5)°, γ 73.91(4)°; V 6597 $Å^3$; ρ(calc) 1.54 g cm^{-3}.
11048 independent reflexions were measured on a Nonius CAD 4 diffractometer up to $2\theta = 45°$ (graphite monochromated Mo-K_α-radiation). 7116 reflections (with $I > 3\sigma(I)$) were considered as observed and used in the subsequent analysis. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares using the X-ray 70 system of programs to the present conventional R factor of 0.091 (for the observed reflections). Anisotropic temperature factors were used for Pt and P atoms while the phenyl rings were constrained to their idealized D_{6h} geometry. A table of F_0/F_c values and a complete list of final refined coordinates may be obtained from the authors upon request.

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16 The NMR spectra were measured in dichloromethane-d_2 as indicated below: ^1H at 250.13 MHz, at 25°C, δ(ppm) rel. to TMS; $^{31}P\{^1H\}$ at 101.27 MHz at 25°C, δ(ppm) rel. to H_3PO_4; $^{195}Pt\{^1H\}$ at 53.51 MHz at −10°C, δ(ppm) rel. to 0.1 M $Na_2[PtCl_6]$ in water. A positive sign denotes a resonance to low field of the reference.

17 The *cis*-P—H coupling constants, obtained from a simulated spectrum, fall in the range in which one usually observes such *cis*-P—H couplings.

18 $^1J(^{195}Pt^1, ^{31}P^1)$ 3785 Hz, $^1J(^{195}Pt^1, ^{31}P^2)$ 2509 Hz, $^1J(^{195}Pt^1, ^{31}P^3)$ 1798 Hz, $^1J(^{195}Pt^2, ^{31}P^3)$ 2257 Hz, $^1J(^{195}Pt^2, ^{31}P^4)$ 2895 Hz, $^{2 \text{ or } 3}J(^{195}Pt^1, ^{31}P^4)$ 57.5 Hz, $^{2 \text{ or } 3}J(^{195}Pt^2, ^{31}P^1)$ 71 Hz, $^{2 \text{ or } 3}J(^{195}Pt^2, ^{31}P^2)$ 54.8 Hz, $^2J(^{31}P^1, ^{31}P^2)$ 18.3 Hz, $^2J(^{31}P^1, ^{31}P^3)$ 16.6 Hz, $^2J(^{31}P^2, ^{31}P^3)$ 245 Hz, $^2J(^{31}P^3, ^{31}P^4)$ 324 Hz.

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