

## NOTE

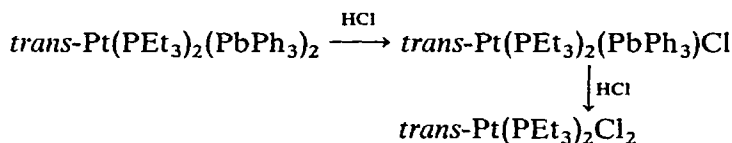
### A NOVEL ROUTE TO *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)Cl

GIULIO DEGANELLO, GIOVANNI CARTURAN AND PAOLO UGUAGLIATI

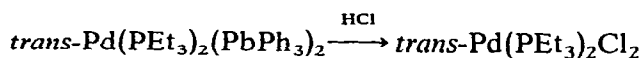
Laboratorio Chimica e Tecnologia Radioelementi del C.N.R., Padova (Italy)

(Received January 20th, 1969)

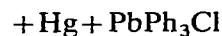
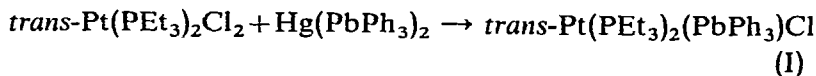
In the past decade several metal-metal bonded complexes involving organometallic IVB Group derivatives and transition metals have been described\*. We have recently prepared and characterized some Pt-Pb and Pd-Pb bonded complexes of the type *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)X (X = Cl, H) and of the type ML<sub>2</sub>(PbPh<sub>3</sub>)<sub>2</sub> (L = PEt<sub>3</sub>, AsEt<sub>3</sub>, Ph<sub>2</sub>PCH<sub>2</sub>-; M = Pt and Pd)<sup>2,3</sup>. We were not able to isolate the analogous nickel complexes probably because the stability decreases in the order Pt > Pd > Ni which applies to the corresponding metal-carbon σ bonded derivatives<sup>4</sup>. The reactions of these Pt-Pb and Pd-Pb bonded complexes with anhydrous hydrogen chloride were of particular interest. In the case of *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)<sub>2</sub> the reaction proceeds stepwise:



By contrast, the reaction of *trans*-Pd(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)<sub>2</sub> involves direct cleavage of both Pd-Pb bonds affording *trans*-Pd(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>:



The rather low yield of *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)Cl obtained by the above reaction prompted us to seek new ways of preparing it, since it is a particularly versatile intermediate in the preparation of many Pt<sup>II</sup> compounds of current interest, and we have found that it can be prepared in good yield (70%) by the reaction of *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with equimolar amounts of Hg(PbPh<sub>3</sub>)<sub>2</sub> in benzene:

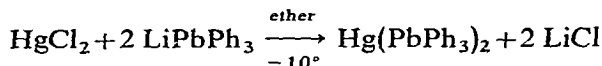


(I) is a white crystalline solid which decomposes at 120°, and is soluble in ether or benzene, but little soluble in petroleum ether and alcohol. A *trans* configuration is

\* For a survey on this subject see ref. 1.

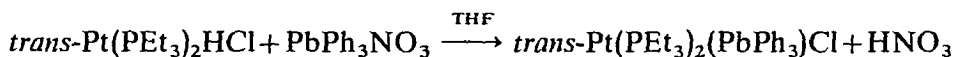
suggested by the infrared spectrum; thus, beside the bands attributed to  $\text{PEt}_3$  and  $\text{PbPh}_3$  ligands ( $1566$  and  $436\text{ cm}^{-1}$ )<sup>2</sup>, there appears a single medium band at  $415\text{ cm}^{-1}$ , which is assigned to  $\nu(\text{Pt-P})$  by analogy with other complexes of type *trans*- $\text{Pt}(\text{PEt}_3)_2\text{-XY}$ <sup>5</sup>. Further a strong band at  $285\text{ cm}^{-1}$  is assigned to  $\nu(\text{Pt-Cl})$ . The occurrence of this band at a higher frequency than in analogous complexes having  $\text{Pt-Si}$  ( $238\text{ cm}^{-1}$ )<sup>7</sup>,  $\text{Pt-Ge}$  ( $235, 255\text{ cm}^{-1}$ )<sup>7,8</sup> and  $\text{Pt-Sn}$  bonds ( $278\text{ cm}^{-1}$ )<sup>9</sup> suggests a lower *trans* influence of the  $\text{PbPh}_3$  ligand relative to other  $\text{MR}_3$  groupings of IVB Group elements.

The novel compound  $\text{Hg}(\text{PbPh}_3)_2$  employed as "metallation" agent in the above reaction was prepared by treating an ether suspension of  $\text{LiPbPh}_3$  with  $\text{HgCl}_2$  in ether at  $-10^\circ$ :



$\text{Hg}(\text{PbPh}_3)_2$  is a colorless crystalline solid melting at  $112^\circ$ , soluble in benzene, fairly soluble in ethyl or petroleum ether, insoluble in alcohol. Its infrared spectrum shows the characteristic bands of the  $\text{PbPh}_3$  group at  $1566$  and  $450\text{ cm}^{-1}$ .

We have also obtained *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{PbPh}_3)\text{Cl}$  by the reaction of  $\text{PbPh}_3\text{-NO}_3$  with *trans*- $\text{Pt}(\text{PEt}_3)_2\text{HCl}$  in tetrahydrofuran:



## EXPERIMENTAL

All the reactions were carried out in a nitrogen atmosphere.

### 1. Materials

The complexes *trans*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$ <sup>10</sup> and *trans*- $\text{Pt}(\text{PEt}_3)_2\text{HCl}$ <sup>11</sup> were prepared by standard literature methods.

*Hg(PbPh<sub>3</sub>)<sub>2</sub>*. To a vigorously stirred ether suspension of  $\text{LiPbPh}_3$  (from 10 mmoles of  $\text{PbCl}_2$  and 30 mmoles of  $\text{LiPh}$ )<sup>12</sup> was added dropwise an ether solution of 1.08 g (4 mmoles) of  $\text{HgCl}_2$  at  $-10^\circ$ . After stirring for 30 min the excess of  $\text{LiPbPh}_3$  was hydrolyzed by adding an aqueous solution of ammonium chloride. The resulting solid was filtered off and extracted with benzene. The extract, after drying over sodium sulphate, was taken to dryness under reduced pressure. The pale yellow residue was recrystallized from petroleum ether to give  $\text{Hg}(\text{PbPh}_3)_2$  as colorless needles, m.p.  $112^\circ$ . (Found: C, 39.78; H, 2.94.  $\text{C}_{36}\text{H}_{30}\text{HgPb}_2$  calcd.: C, 40.0; H, 2.77%.) A further crop may be obtained from the ether mother liquors (total yield 70%.)

### 2. Preparations

(i). *Reaction of trans-Pt(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)<sub>2</sub> with anhydrous HCl*. Hydrogen chloride (0.5 mmoles) was bubbled into a benzene solution of 0.65 g (0.5 mmole) of *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{PbPh}_3)_2$ . After stirring for a few hours the mixture was filtered and the filtrate evaporated to dryness. The white residue was washed with a little petroleum ether and recrystallized from methanol to give *trans*- $\text{Pt}(\text{PEt}_3)_2(\text{PbPh}_3)\text{Cl}$ . (Yield 40 %).

(ii). *Reaction of trans-Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> with Hg(PbPh<sub>3</sub>)<sub>2</sub>*. A solution of 0.22 g (0.2 mmole) of  $\text{Hg}(\text{PbPh}_3)_2$  in anhydrous benzene was added dropwise to a benzene solution of *trans*- $\text{Pt}(\text{PEt}_3)_2\text{Cl}_2$  (0.2 mmole). When the addition was complete the

reaction mixture was refluxed for 3 h, and activated charcoal was added. Filtration, evaporation of the filtrate, and washing of the residue with a little petroleum ether gave *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)Cl as a white solid, which was recrystallized from alcohol (Yield 70%.)

(iii). *Reaction of trans-Pt(PEt<sub>3</sub>)<sub>2</sub>HCl with PbPh<sub>3</sub>NO<sub>3</sub>*. A suspension of 0.47 g (1 mmole) of *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>HCl and 0.5 g (1 mmole) of PbPh<sub>3</sub>NO<sub>3</sub> in 30 ml of tetrahydrofuran was refluxed. The reactants dissolved and after a while a white solid began to precipitate. This was filtered off immediately and to the filtrate water was added to clouding. A pale yellow oil separated off which crystallized on cooling. The resulting solid was recrystallized from alcohol to give *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>(PbPh<sub>3</sub>)Cl. (Yield 50%.)

The products of reactions (i), (ii), (iii) had identical infrared spectra, melting points (120°, decompn.), and elemental analyses. (Found: C, 39.9; H, 5.01; Cl, 4.19. C<sub>30</sub>H<sub>45</sub>ClP<sub>2</sub>PbPt calcd.: C, 40.12; H, 5.44; Cl, 4.37%.)

#### *Infrared Spectra*

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 621 double beam spectrophotometer.

#### ACKNOWLEDGEMENTS

We thank Prof. U. BELLUCO for his interest in this work. Financial support by N.A.T.O.-Grant No. 341 is gratefully acknowledged.

#### REFERENCES

- 1 M. C. BAIRD, *Progress in Inorganic Chemistry*, Vol. 9, Interscience, New York, p. 1.
- 2 G. DEGANELLO, G. CARTURAN AND U. BELLUCO, *J. Chem. Soc., A*, (1968) 2873.
- 3 G. CARTURAN, G. DEGANELLO, T. BOSCHI AND U. BELLUCO, in press.
- 4 M. L. H. GREEN, *Organometallic Compounds, Vol. II: The Transition Elements*, Methuen, London (1968).
- 5 D. M. ADAMS AND P. J. CHANDLER, *Chem. Commun.*, (1966) 69 and references reported therein.
- 6 M. C. BAIRD, *J. Inorg. Nucl. Chem.*, 29 (1967) 367.
- 7 F. GLOCKLING AND K. A. HOOTON, *J. Chem. Soc., A*, (1967) 1066.
- 8 F. GLOCKLING AND K. A. HOOTON, *J. Chem. Soc., A*, (1968) 826.
- 9 D. J. CARDIN AND M. F. LAPPERT, *Chem. Commun.*, (1967) 506.
- 10 K. A. JENSEN, *Z. Anorg. Allg. Chem.*, 229 (1936) 225.
- 11 J. CHATT AND B. L. SHAW, *J. Chem. Soc.*, (1962) 5075.
- 12 H. GILMAN, L. SUMMERS AND R. W. LEEPER, *J. Org. Chem.*, 17 (1952) 630.