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Nucleophilic Attack on $\{(\pi\text{-allyl})Pt[P(C_6H_{11})_3]_2\}PF_6$. Preparation and X-ray Structure of *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$

A. IMMIRZI and A. MUSCO

Istituto di Chimica delle Macromolecole del C.N.R., Via Alfonso Corti 12, 20133 Milano, Italy

G. CARTURAN and U. BELLUCO

Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Calle Larga 2137, S. Marta, Venezia, Italy

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A series of tertiary phosphine Pd^0 complexes of type PdL_n (L = phosphine; n = 2,3,4) has been prepared through attack by nucleophiles such as methoxide and amines on the coordinated allyl group of compounds of the type $[(\pi\text{-2-methylallyl})PdL_2]^+$, followed by elimination of the resultant olefin moiety[1].

We have extended this preparation method to analogous platinum allyl complexes and, to our surprise, upon reacting $\{(\pi\text{-allyl})Pt[P(C_6H_{11})_3]_2\}PF_6$ with sodium methoxide in methanol a hydride species was obtained instead of the expected $Pt[P(C_6H_{11})_3]_2$. According to the ^1H NMR data (benzene solution, τ 13.16 (triplet), $^2J_{P-H}$ 17Hz, $^1J_{Pt-H}$ 794Hz) this hydride species may be formulated as *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$.

However, our NMR and IR data (see later) are inconsistent with those reported by Kudo *et al.*[2] for a series of *trans*-$[PtH_2L_2]$ complexes (including the

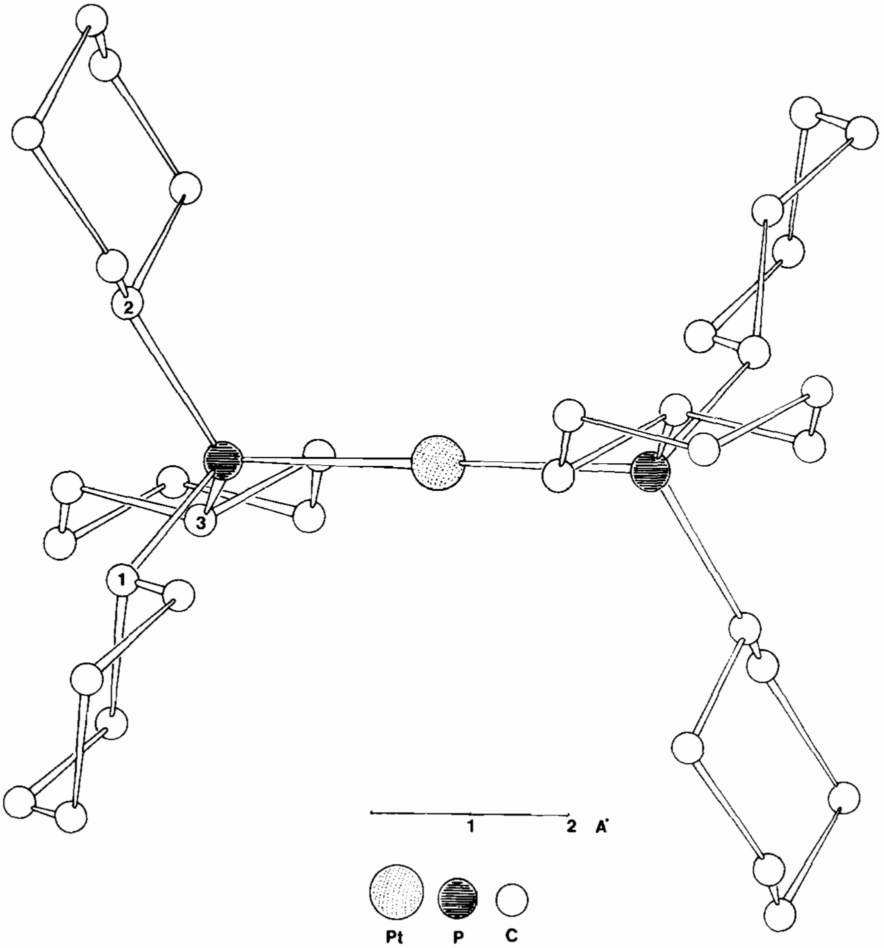

Fig. 1. Molecular structure of *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ (form II). The positions of the hydride atoms remain undetermined.

$P(C_6H_{11})_3$ derivative) which were prepared by reacting $[Pt(acac)_2]$ with $AlEt_3$ in ether in the presence of the tertiary phosphine (L).

Shaw and Uttley have recently described *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ from the reaction of *cis*-$\{PtCl_2[P(C_6H_{11})_3]_2\}$ with $NaBH_4$ in ethanol[3]. They also questioned the correctness of the formulation of Kudo's compound on spectroscopic grounds. The IR and NMR data of the compounds made by Shaw and Uttley and by us are identical, indicating that the complexes are the same chemical species. An X-ray structure determination has definitely proved that this compound is indeed *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$.

Two crystalline modifications have been obtained: **(I)**, white plates from toluene [IR, ν_{Pt-H} 1710 cm^{-1} (nujol)] and **(II)**, very pale yellow hexagonal flat prisms from heptane [IR, ν_{Pt-H} 1700 cm^{-1} (nujol)].

Crystal Data

$PtP_2C_{36}H_{66}$, M = 756.0, $\lambda = 0.7107$ Å. Form **(I)**: $a = 10.414(3)$, $b = 9.906(3)$, $c = 10.490(3)$ Å, $\alpha = 100.60(2)°$, $\beta = 112.91(2)°$, $\gamma = 89.73(2)°$, $Z = 2$, $D_c = 1.361$ g cm^{-3}, space group $P\bar{1}$; Form **(II)**: $a = 23.576(3)$, $b = 15.767(3)$, $c = 10.218(3)$ Å, $\beta = 106.93(2)°$, $Z = 4$, $D_c = 1.381$ g cm^{-3}, space group $C2/c$.

The structures have been determined from single-crystal X-ray diffraction counter data by means of the heavy atom method and refined by least-squares procedure. Actual R factors, based on 2225 **(I)** and 1875 **(II)** non-zero reflections are 0.044 for **(I)** and 0.068 for **(II)**. Further refinement with the introduction of anisotropic absorption corrections is in progress. Both forms exhibit crystallographic C_i symmetry with different conformations of the phosphine ligand, although all the C_6 rings are in a chair conformation.

The Pt–P bond lengths are quite similar [2.26(1) Å in form **(I)** and 2.25(1) Å in form **(II)**]. The $P-C_i$ bond lengths (i = 1,2,3) are in the order 1.86, 1.86, 1.85 Å (± 0.02 Å) for **(I)** and 1.88, 1.85, 1.88 Å (± 0.02 Å) for **(II)**. The $Pt-P-C_i$ angles are in the order 111, 114, 113° (± 1°) for **(I)** and 115, 120, 111° (± 1°) for **(II)**.

It is worthy of note that the Pt–P distance is significantly shorter than that found in *trans*-$\{PtI_2[P(C_6H_{11})_3]_2\}$ (2.37 Å)[4] and in *trans*-$[PtBr_2(PEt_3)_2]$ (2.31 Å). This implies a stronger $d\pi-d\pi$ interaction between P and Pt in the hydride, consistently with the suggestion that the strength of the metal–phosphorus interaction in *trans*-planar complexes increases with decreasing π-bonding capacity or increasing σ-bonding ability of the *cis* ligands. Research is in progress on the reactivity of *trans*-$\{PtH_2[P(C_6H_{11})_3]_2\}$ towards insertion reactions and/or reductive eliminations.

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