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LETTER

Binuclear phosphido-bridged platinum–platinum complex. Synthesis and X-ray structure of $[Pt(\mu\text{-}N(CH_2CH_2PPh_2)_3)\text{-}(\mu\text{-}PEt_2)Pt(PPh_3)](BPh_4)\cdot CH_2Cl_2$

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The importance of the dialkyl and diaryl phosphide groups as bridging ligands in polynuclear transition metal complexes has been widely recognized [1–10]. As a matter of fact these ligands, so strongly bridging and chemically inert, are very useful in both catalysis and organometallic synthesis. Their structural flexibility, allowing both bonding and non-bonding metal–metal arrangements, plays an important role in bond making or breaking. The M–M linkages, subtended by μ-PR_2 groups, can span distances ranging from 2.55 to 3.70 Å, while the M–(μ-PR_2)–M angles range from 67 to 120° [2].

Several homo- and hereto-polynuclear transition metal complexes which utilize μ-PR_2 as bridging ligands have been reported. Among these the homodinuclear ones containing the platinum metal are rather few [1–3] and always, as far as we know, the two platinum centers possess an analogous coordination geometry; therefore the same oxidation number can be unambiguously attributed to the metal atoms.

In this letter we report the synthesis and structural characterization of a dinuclear phosphido-bridged platinum complex of formula $[Pt(\mu\text{-}np_3)(\mu\text{-}PEt_2)Pt(PPh_3)](BPh_4)\cdot CH_2Cl_2$ (1) ($np_3 = N(CH_2CH_2PPh_2)_3$). This compound, which has been obtained by reaction of a five-coordinated platinum(II) terminal phosphide complex with a tri-coordinated platinum(0) one, retains in the dimeric unit two quite different coordination geometries.

The reaction of $[(np_3)Pt(PEt_2)](BPh_4)$ [11] with $(PPh_3)_2Pt(C_2H_4)$, under a nitrogen atmosphere, at room temperature, with the use of anhydrous thf as solvent, resulted in the formation of the new bimetallic complex **1** in high yield (88%). Orange, well-shaped crystals were obtained by recrystallization of the crude product from dichloroethane/1-butanol solution, in air.

The molecular structure of **1** was established by a single crystal X-ray analysis. The crystals are triclinic, space group $P\bar{1}$ with $a = 15.190(5)$, $b = 16.762(5)$, $c = 17.733(6)$ Å, $\alpha = 84.55(5)$, $\beta = 88.06(6)$, $\gamma = 87.25(5)°$ and $Z = 2$. Data collection was carried out on an Enraf Nonius CAD4 diffractometer using the ω–2θ scan technique and graphite monochromatized Mo Kα radiation ($\lambda = 0.7107$ Å) within $2\theta \leq 40°$. The structure was solved by the heavy atom method and refined by full-matrix least-squares refinement to the conventional R and R_w factor values both of 0.062 for 6107 absorption corrected (μ(Mo Kα) = 33.3 cm^{-1}) reflections having $I \geq 3\sigma(I)$.

The molecular structure of **1** consists of dimeric complex cations $[Pt(\mu\text{-}np_3)(\mu\text{-}PEt_2)Pt(PPh_3)]^+$, tetraphenylborate anions and methylene chloride solvent molecules interspersed in the lattice. Figure 1 shows a perspective view of the complex cation with selected bond distances and angles.

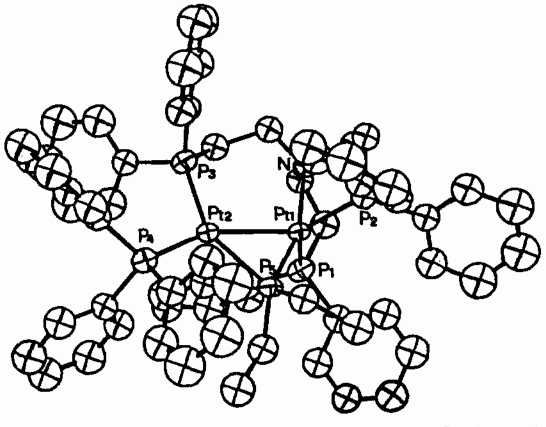

Fig. 1. Perspective view of the cation $[Pt(\mu\text{-}np_3)(\mu\text{-}PEt_2)Pt(PPh_3)]^+$. ORTEP drawing with 30% probability ellipsoids. Important selected bond distances (Å) and angles (°): Pt1–Pt2 2.824(1), Pt1–P1 2.301(6), Pt1–P2 2.297(6), Pt1–P5 2.234(5), Pt1–N 2.281(15), Pt2–P3 2.287(5), Pt2–P4 2.277(6), Pt2–P5 2.253(5), N–Pt1–P1 83.1(4), N–Pt1–P2 84.0(4), N–Pt1–P5 161.8(4), P1–Pt1–P2 127.8(2), P1–Pt1–P5 104.6(2), P2–Pt1–P5 103.1(2), P1–Pt1–Pt2 117.4(2), P2–Pt1–Pt2 114.5(2), P5–Pt1–Pt2 51.3(1), N–Pt1–Pt2 110.6(4), P3–Pt2–P4 109.6(2), P3–Pt2–P5 143.6(2), P4–Pt2–P5 106.8(2), Pt1–P5–Pt2 78.0(2), P3–Pt2–Pt1 92.9(1), P4–Pt2–Pt1 157.5(1), P5–Pt2–Pt1 50.7(1).

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In the dimeric cation the two metal centers are bridged by one diethylphosphide group and by one arm of the np_3 ligand, which utilizes two phosphorus to link one platinum (Pt1) and the third one to link the other metal center (Pt2). If we neglect the Pt–Pt bond, definitively the Pt1 is four-coordinated, being surrounded by the np_3 ligand (with two phosphorus and one nitrogen) and by the phosphide group, while the Pt2 is tri-coordinated and planar, being surrounded by one phosphorous of the np_3 ligand, the phosphide group and the triphenylphosphine moiety. Around the Pt1 center the nitrogen atom is positioned approximately *trans* to the phosphide group with the angle N–Pt1–P5 = 161.8(4)°. Around the Pt2 metal the PPh_3 is *c. trans* to the Pt1, the value of Pt1–Pt2–P4 being 157.5(1)°.

The Pt–Pt bond distance of 2.824(1) Å is definitively indicative of a single M–M bond, as required to give each metal a satisfactory electron count (18 e^-). As a matter of fact the cation could be described as having a direct covalent single M–M bond between two d^9Pt(I) centers or a polar bond between one d^{10}Pt(0) and one d^8Pt(II) center, the latter possibility being likely preferred on the basis of the different coordination number attained by the two metals.

An analogous structural array has been reported for a mixed Rh(III)–Pt(0) dinuclear phosphido-bridged complex, where the two metals are linked, besides the phosphide group, through one arm of the PNP ligand (PNP = 2-[bis(diphenylphosphino)-methyl]pyridine [5].

Even if it has been established [12] that no obvious correlations exist between the M–M distances, M–P_μ–M angles and ^{31}P NMR data in polynuclear phosphide bridged complexes, we consider it useful to emphasize the corresponding values for the title compound: Pt–Pt = 2.824(1) Å, angle M–P_μ–M = 78.0(2)°, $\delta P_\mu = 154$ ppm.

The $^{31}P\{^1H\}$ NMR spectrum of **1**, due to its complexity, deserves an accurate analysis. A preliminary inspection of the room-temperature spectrum in CD_2Cl_2 shows that: (i) the ^{31}P resonances appear as broad signals indicating a fluxional behaviour; (ii) the multiplet due to the PEt_2 group is centered at 154 ppm; (iii) the signals due to np_3 and PPh_3 appear as complex multiplets in the range 50–10 ppm.

Variable temperature spectra show that the low and fast exchange limits are reached at −50 and 120 °C, respectively. The spectrum at −50 °C appears consistent with the static structure as found in the crystal. The full simulated spectra will be reported in a successive note.

Attempts to prepare other dinuclear derivatives and to clarify the fluxionality of the system are in progress.

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