

Preliminary communication

Synthesis of the five-coordinate organoplatinum cation $[\text{PtMe}(\text{pp}_3)]^+$ ($\text{pp}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$) by oxidative addition of methyl iodide to $[\text{Pt}_2(\mu\text{-pp}_3)_2]$

Martin Peter ^a, Michael Probst ^a, Paul Peringer ^{a*} and Ernst P. Müller ^b

^a *Institut für Anorganische und Analytische Chemie der Universität Innsbruck, Innrain 52a,
 6020 Innsbruck (Austria)*

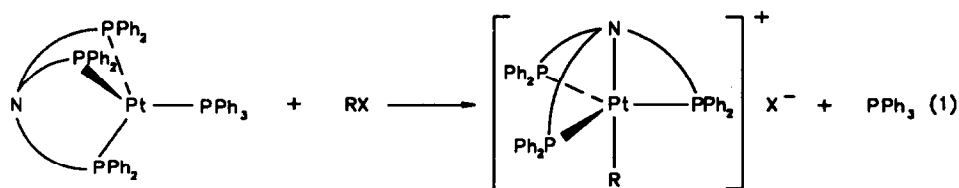
^b *Institut für Organische und Pharmazeutische Chemie der Universität Innsbruck, Innrain 52a,
 6020 Innsbruck (Austria)*

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Abstract

The complex $[\text{Pt}_2(\mu\text{-pp}_3)_2]$ ($\text{pp}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$), produced by treatment of $[\text{PtH}(\text{pp}_3)]^+$ with sodium amalgam, has been shown to react with methyl iodide to give $[\text{PtMe}(\text{pp}_3)]^+$. The new complexes have been characterized by ¹H, ³¹P and ¹⁹⁵Pt NMR spectroscopy.

Synthesis of η^1 -organoplatinum(II) complexes by oxidative addition of organic halides to zerovalent platinum complexes is well known [1]. With the usual starting materials, phosphine complexes $[\text{Pt}(\text{PR}_3)_n]$, $n = 3, 4$, or olefine complexes, e.g. $[\text{Pt}(\text{PR}_3)_2\text{C}_2\text{H}_4]$, the reaction is accompanied by the elimination of PR_3 or C_2H_4 and gives four-coordinate complexes $\text{PtR}(\text{X})(\text{PR}_3)_2$. Very recently, five-coordinate η^1 -organoplatinum complexes $[\text{PtR}(\text{np}_3\text{-N,P,P',P''})]^+$, $\text{np}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$, were obtained by the reaction depicted in eq. 1 [2].

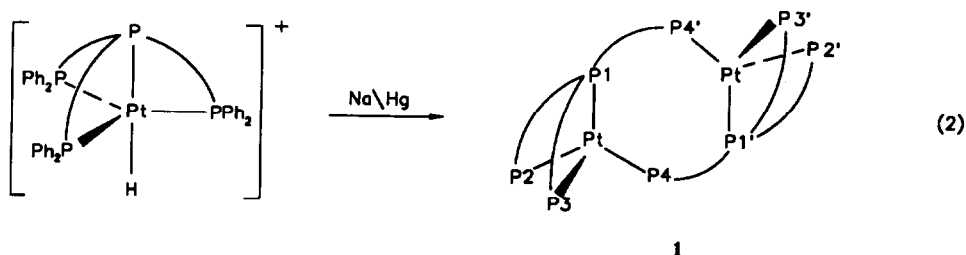


We outline here the synthesis and NMR spectroscopic characterisation of the corresponding five-coordinate polyphosphine cation $[\text{PtMe}(\text{pp}_3\text{-P,P',P'',P''',P''''})]^+$ and the zerovalent platinum precursor $[\text{Pt}_2(\mu\text{-pp}_3)_2]$.

Results and discussion

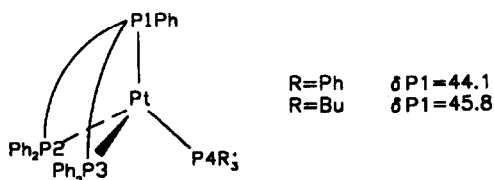
The zerovalent platinum complex **1** was prepared by treatment of $[\text{PtH}(\text{pp}_3\text{-P,P',P'',P''',P''''})]^+$ with sodium amalgam (eq. 2). Phosphorus-31 and ¹⁹⁵Pt NMR

spectroscopy indicate a dimeric structure involving two equivalent Pt atoms and pp_3 ligands, as shown in eq. 2. Each platinum atom is coordinated by the chelating



central (1 or 1') and two terminal (2, 3 or 2', 3') phosphorus atoms of one pp_3 ligand and one bridging terminal phosphorus (4 or 4') of the second pp_3 ligand. The platinum atoms, P4 and P4' are part of a 10-membered ring.

The portion of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum arising from molecules of 1 without ^{195}Pt nuclei shows three multiplets. The resonance at highest frequencies is attributed to the central phosphorus atoms (1 or 1') in accordance with ^{31}P NMR data for $[\text{Pt}(\text{PR}_3)\{\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]$ [3] shown below:



The signal consists of a first-order triplet of doublets of doublets due to coupling to the two terminal phosphorus atoms (2, 3 or 2', 3'), the bridging terminal phosphorus atom (4' or 4) of the same pp_3 ligand, and the bridging terminal phosphorus atom (4 or 4') of the other pp_3 ligand. The patterns of the chelating terminal (2, 3 or 2', 3') and bridging terminal (4 or 4') phosphorus atoms of the pp_3 ligand are second order. They are part of an $\text{AA}'\text{B}_2\text{B}_2'\text{XX}'$ spin system which was simulated [4] by using the following parameters: $\delta \text{P1} = 59.3$, $\delta \text{P2,3} = 24.6$, $\delta \text{P4} = 22.5$ (relative to 85% H_3PO_4), $J(\text{P1P2}) = 66$ Hz, $J(\text{P1P4}') = 58$ Hz, $J(\text{P1P4}) = 94$ Hz, $J(\text{P2P4}) = 53$ Hz. The signals are flanked by ^{195}Pt satellites. The magnitudes of the coupling constants are very different: $J(\text{PtP1}) = 2983$ Hz, $J(\text{PtP2,3}) = 3549$ Hz, $J(\text{PtP4}) = 4789$ Hz. Such behaviour was also observed for the complexes $[\text{Pt}(\text{PR}_3)\{\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2\}]$, and will be discussed in detail elsewhere [3].

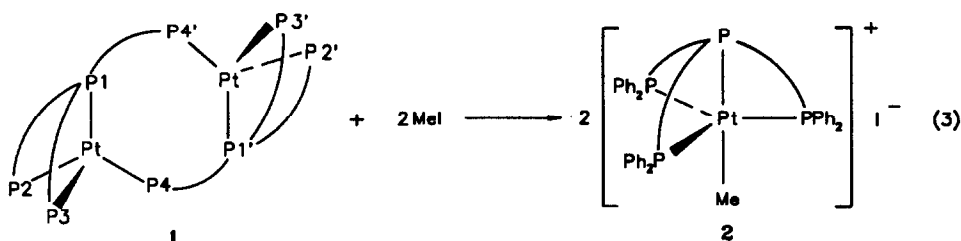
The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum of 1 is a first-order doublet of doublets of triplets at -5240 ppm relative to aqueous Na_2PtCl_6 . As in the ^{31}P NMR spectrum, no platinum-phosphorus couplings $J(\text{PtP})$ with $n > 1$ are observed.

A zerovalent complex $[\text{Pt}(pp_3)]$, prepared by treating $[\text{PtCl}(pp_3\text{-P,P',P'',P'''})]\text{Cl}$ with NaBH_4 in aqueous ethanol, has been reported [5], but the report was recently questioned because an attempt to reproduce the results although using a slightly modified procedure, gave exclusively the hydride $[\text{PtH}(pp_3\text{-P,P',P'',P'''})]^+$ [6]. We believe that $[\text{Pt}(pp_3)]$ [5] was not 1 but the corresponding hydride, since 1 readily reacts with aqueous ethanol to form $[\text{PtH}(pp_3\text{-P,P',P'',P'''})]^+$.

Complex 1 is one of few examples of dimeric platinum(0) complexes. As far as we know, only three other complexes of this type are known: $[\text{Pt}_2\{\mu\text{-CH}_2(\text{PPh}_2)_2\}_3]$

[7], $[\text{Pt}_2\{\mu\text{-CH}_2(\text{P}^t\text{Bu}_2)_2\}_2]$ [8] and $[\text{Pt}_2\{(\text{P}^t\text{Bu}_2\text{P}(\text{CH}_2)_3\text{P}^t\text{Bu}_2)\}_2]$ [9]. Structures similar to that of **1** are also found in the d^{10} metal complexes $[\text{Ni}_2(\text{pp}_3)_3]$ [10] and $[\text{Au}_2(\text{PP}_3)_2]^{2+}$ [11], the structure of the latter was established by X-ray diffraction [11].

The zerovalent platinum complex **1** undergoes oxidative addition of methyl iodide quantitatively at ambient temperature (eq. 3). Product **2** has a trigonal bipyramidal structure with the central phosphorus of the pp_3 ligand and the



methyl group in an axial position, and three terminal phosphorus atoms of the pp_3 ligand in equatorial position, as indicated in eq. 3. Complex **2** was characterized by ^1H , ^{31}P and ^{195}Pt NMR spectroscopy. The $^{195}\text{Pt}\{^1\text{H}\}$ NMR spectrum consists of a doublet (1452 Hz) of quartets (2859 Hz) at -5202 ppm, and the trigonal bipyramidal structure of **2** is confirmed by the equivalence of the three terminal phosphorus atoms of the pp_3 ligand. The small one-bond platinum–phosphorus coupling involving the central phosphorus atom indicates a P–Pt–C bond sequence, in keeping with the concept of *trans*-influence [12–14]. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows signals at 126.1 and 18.1 ppm attributable to the central and terminal phosphorus atoms of the pp_3 ligand, respectively. The ^1H NMR resonance of the methyl group appears at 1.01 ppm and is split into a doublet (5 Hz) of quartets (8 Hz) by the phosphorus atoms of the pp_3 ligand. The two-bond platinum–hydrogen coupling constant is 54.3 Hz.

As far as we know the only previously reported five-coordinate η^1 -organo-platinum(II) complex with a PtP_4C core is $[\text{PtEt}(\text{PMe}_3)_4]^+$ [15].

Preliminary studies have shown that **1** undergoes oxidative addition reactions with other organic halides and other species to give a range of five-coordinate platinum(II) complexes.

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