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Synthesis of the five-coordinate organoplatinum cation $[PtMe(pp_3)]^+$ ($pp_3 = P(CH_2CH_2PPh_2)_3$) by oxidative addition of methyl iodide to $[Pt_2(\mu\text{-}pp_3)_2]$

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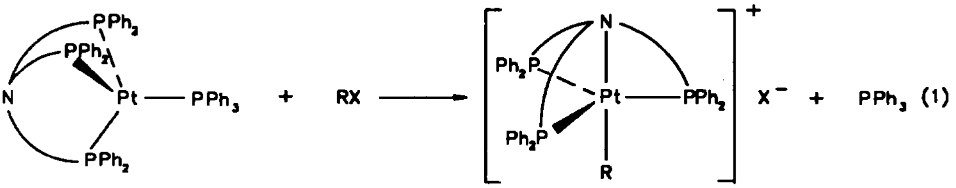
Abstract

The complex $[Pt_2(\mu\text{-}pp_3)_2]$ ($pp_3 = P(CH_2CH_2PPh_2)_3$), produced by treatment of $[PtH(pp_3)]^+$ with sodium amalgam, has been shown to react with methyl iodide to give $[PtMe(pp_3)]^+$. The new complexes have been characterized by ^1H, ^{31}P and ^{195}Pt 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 $[Pt(PR_3)_n]$, $n = 3$, 4, or olefine complexes, e.g. $[Pt(PR_3)_2C_2H_4]$, the reaction is accompanied by the elimination of PR_3 or C_2H_4 and gives four-coordinate complexes $PtR(X)(PR_3)_2$. Very recently, five-coordinate η^1-organoplatinum complexes $[PtR(np_3\text{-}N,P,P',P'')]^+$, $np_3 = N(CH_2CH_2PPh_2)_3$, were obtained by the reaction depicted in eq. 1 [2].



(1)

We outline here the synthesis and NMR spectroscopic characterisation of the corresponding five-coordinate polyphosphine cation $[PtMe(pp_3\text{-}P,P',P'',P''')]^+$ and the zerovalent platinum precursor $[Pt_2(\mu\text{-}pp_3)_2]$.

Results and discussion

The zerovalent platinum complex **1** was prepared by treatment of $[PtH(pp_3\text{-}P,P',P'',P''')]^+$ with sodium amalgam (eq. 2). Phosphorus-31 and ^{195}Pt NMR

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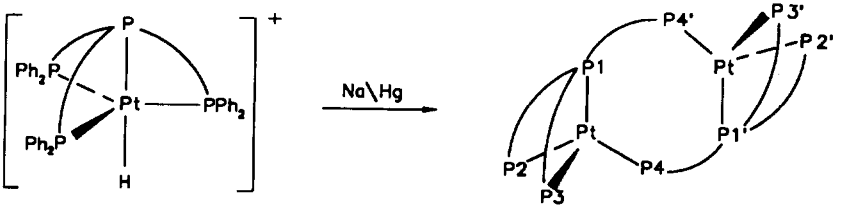
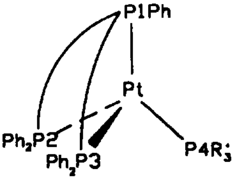
spectroscopy indicate a dimeric structure involving two equivalent Pt atoms and pp_3 ligands, as shown in eq. 2. Each platinum atom is coordinated by the chelating central (1 or 1′) and two terminal (2, 3 or 2′, 3′) phosphorus atoms of one pp_3 ligand and one bridging terminal phosphorus (4 or 4′) of the second pp_3 ligand. The platinum atoms, P4 and P4′ are part of a 10-membered ring.



(2)

1

The portion of the $^{31}P\{^1H\}$ 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 $[Pt(PR_3)\{PhP(CH_2CH_2PPh_2)_2\}]$ [3] shown below:



R=Ph δP1=44.1
R=Bu δP1=45.8

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 $AA'B_2B'_2XX'$ spin system which was simulated [4] by using the following parameters: $\delta P1 = 59.3$, $\delta P2,3 = 24.6$, $\delta P4 = 22.5$ (relative to 85% H_3PO_4), $J(P1P2) = 66$ Hz, $J(P1P4') = 58$ Hz, $J(P1P4) = 94$ Hz, $J(P2P4) = 53$ Hz. The signals are flanked by ^{195}Pt satellites. The magnitudes of the coupling constants are very different: $J(PtP1) = 2983$ Hz, $J(PtP2,3) = 3549$ Hz, $J(PtP4) = 4789$ Hz. Such behaviour was also observed for the complexes $[Pt(PR_3)\{PhP(CH_2CH_2PPh_2)_2\}]$, and will be discussed in detail elsewhere [3].

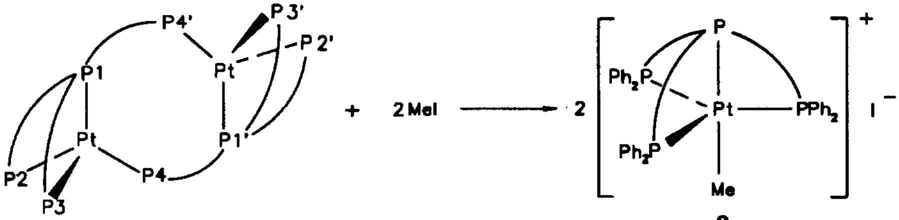
The $^{195}Pt\{^1H\}$ NMR spectrum of **1** is a first-order doublet of doublets of triplets at −5240 ppm relative to aqueous Na_2PtCl_6. As in the ^{31}P NMR spectrum, no platinum–phosphorus couplings $^nJ(PtP)$ with $n > 1$ are observed.

A zerovalent complex $[Pt(pp_3)]$, prepared by treating $[PtCl(pp_3\text{-}P,P',P'',P''')]Cl$ 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 $[PtH(pp_3\text{-}P,P',P'',P''')]^+$ [6]. We believe that $[Pt(pp_3)]$ [5] was not **1** but the corresponding hydride, since **1** readily reacts with aqueous ethanol to form $[PtH(pp_3\text{-}P,P',P'',P''')]^+$.

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: $[Pt_2\{\mu\text{-}CH_2(PPh_2)_2\}_3]$

[7], $[Pt_2\{\mu\text{-}CH_2(P^tBu_2)_2\}_2]$ [8] and $[Pt_2\{(^tBu_2P(CH_2)_3P^tBu_2)\}_2]$ [9]. Structures similar to that of **1** are also found in the d^{10} metal complexes $[Ni_2(pp_3)_3]$ [10] and $[Au_2(PP_3)_2]^{2+}$ [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 $^{195}Pt\{^1H\}$ 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 $^{31}P\{^1H\}$ 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.



1 **2** (3)

As far as we know the only previously reported five-coordinate η^1-organoplatinum(II) complex with a PtP_4C core is $[PtEt(PMe_3)_4]^+$ [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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