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Dechlorination of $ClPEt_2$ by $(np_3)Pt(PPh_3)$ ($np_3 = N(CH_2CH_2PPh_2)_3$): synthesis and characterization of $[(np_3)Pt(PEt_2)](BPh_4)$ and $[(np_3)Pt(PHEt_2)](BPh_4)_2$

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Abstract

The platinum(0) complex $(np_3)Pt(PPh_3)$ ($np_3 = N(CH_2CH_2PPh_2)_3$), undergoes oxidative addition by $ClPEt_2$, in the presence of $NaBPh_4$, to yield the five-coordinate terminal phosphide $[(np_3)Pt(PEt_2)](BPh_4)$. When the solvated compound $(np_3)Pt(PPh_3)\cdot 0.4CH_3CH_2CH_2CH_2OH$ is used as starting material, $[(np_3)Pt(PHEt_2)](BPh_4)_2$ is formed by reaction of the phosphide with HCl released by alcoholysis of $ClPEt_2$. The related complex $[(pp_3)Pt(PEt_2)](BPh_4)$ ($pp_3 = \{P(CH_2CH_2PPh_2)_3\}$) has been prepared by deprotonation of $[(pp_3)Pt(PHEt_2)](BPh_4)_2$, for comparison purposes. The complexes have been characterized by elemental analyses, conductibility measurements and ^1H and ^{31}P NMR spectra. The X-ray structural analysis of $[(np_3)Pt(PHEt_2)](BPh_4)_2$ has been carried out.

Introduction

Recently we reported that the palladium(0) and platinum(0) complexes with the tripod ligand np_3, $N(CH_2CH_2PPh_2)_3$, undergo oxidative addition by halodiorganoarsines to form five-coordinate, terminal arsenides of the divalent metals [1]. Now we report the related reactions of $ClPEt_2$ with $(np_3)Pt(PPh_3)$ (**1**) which allow the synthesis of $[(np_3)Pt(PEt_2)](BPh_4)$ (**2**), $[(np_3)Pt(PHEt_2)](BPh_4)_2$ (**3**) and the previously reported $[(np_3)PtH](BPh_4)$ (**4**) [2].

Only a few terminal phosphide complexes have been previously prepared by oxidative addition of PX_3 species (X = halogen, hydrogen) to low valent metal substrates [3]. Very recently two terminal phosphide platinum(II) complexes, with the related tripod ligand pp_3, $P(CH_2CH_2PPh_2)_3$ were isolated by deprotonation of the parent diorganophosphino complexes [4].

Experimental

All operations were carried out under an atmosphere of pure, dry nitrogen. Solvents and reagents were degassed by repeated evacuation and flushing with dry nitrogen. Benzene and tetrahydrofuran (thf) were distilled from sodium and sodium benzophenone, respectively. Diethyl chlorophosphine was purchased from Strem Chemicals and was used as received. The complex $[(C_2H_4)Pt(PPh_3)_2]$ was prepared by a published procedure [5].

The solvate complex $[(np_3)Pt(PPh_3)]\cdot 0.4CH_3CH_2CH_2CH_2OH$ was prepared as previously described [2]**. The species without alcohol was prepared by the same method by using thf/n-hexane as solvents.

^1H NMR spectra were recorded at 300 MHz on a Varian VXR-300 spectrometer; ^{31}P NMR spectra were recorded at 121.421 and 81.015 MHz on a Varian VXR 300 and a Bruker AC 200 spectrometer, respectively. Chemical shifts are relative to internal Me_4Si (^1H) or external 85% H_3PO_4 (^{31}P), with downfield values reported as positive.

Synthesis of $[(np_3)Pt(PEt_2)](BPh_4)\cdot 0.5C_4H_8O$

(a) Diethylchlorophosphine (61 μl, 63 mg, 0.5 mmol) was added to a solution of $(np_3)Pt(PPh_3)$

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**The previous reported uncorrected formulation without alcohol was in part due to the fact that the compounds $[(np_3)Pt(PPh_3)]$ and $[(np_3)Pt(PPh_3)]\cdot 0.4CH_3CH_2CH_2CH_2OH$ contain the same percentage of carbon; the amount of solvent in the solvated derivative was determined by the ^1H NMR spectrum.

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(374 mg, 0.5 mmol) in 30 ml of benzene. Sodium tetraphenylborate (180 mg, 0.53 mmol) in 10 ml of thf was added. The resulting solution was heated at 40 °C till a yellow powder precipitated. The precipitate was filtered off and evaporation of the filtrate in a current of nitrogen gave thin pale yellow crystals. The complex was collected on a sintered-glass frit, washed with benzene and dried in a current of nitrogen; yield 64%.

Anal. Found: C, 66.04; H, 5.98; N, 1.12. Calc. for $C_{72}H_{76}BNO_{0.5}P_4Pt$: C, 66.87; H, 5.92; N, 1.08%.

^1H NMR (CD_2Cl_2): δ 7.6–6.8 (m, B(C_6H_5) and –P(C_6H_5), 50H), 3.68 (m, thf, 2H), 2.25–2.50 (m, P–CH_2–CH_2–N), 12H), 1.83 (m, thf, 2H), 1.27 (m, P–CH_2–CH_3, 4H), 0.78 (dt, $^3J_{HH}$ = 8 Hz, $^3J_{PH}$ = 16 Hz, P–CH_2–CH_3, 6H).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 56.7 (s, $^1J_{PtP}$ = 884 Hz, 1P), 9.39 (s, $^1J_{PtP}$ = 3277 Hz, 3P).

The yellow powder separated during the first step of the reaction is essentially constituted by the complex [(np_3)Pt($PHEt_2$)](BPh_4)$_2$ (*vide infra*), with traces of [(np_3)PtH](BPh_4). The amount of this byproduct is related to the amount of adventitious moisture present in the system. If traces of D_2O are added to thf, [(np_3)Pt($PDEt_2$)](BPh_4)$_2$ is also isolated.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –22.7 (111 tq, $^1J_{PD}$ = 61 Hz, $^2J_{PP}$ = 24 Hz, $^1J_{PtP}$ = 2326 Hz, 1P), 19.5 (d, $^1J_{PtP}$ = 2467 Hz, 3P).

(b) A 5mm NMR tube was charged with [(np_3)Pt($PHEt_2$)](BPh_4)$_2$·$(CH_3)_2CO$ (50 mg, 0.03 mmol) and CD_2Cl_2 (0.7 ml). Then DBU (4.55 μl, 4.65 mg, 0.03 mmol) was added and the $^{31}P\{^1H\}$ NMR spectrum was recorded. The spectrum was identical to that of the isolated **2**.

Synthesis of [(np_3)Pt($PHEt_2$)](BPh_4)$_2$·$(CH_3)_2CO$

(a) Diethylchlorophosphine (61 μl, 63 mg, 0.5 mmol) was added to a solution of (np_3)Pt(PPh_3)·0.4$CH_3CH_2CH_2CH_2OH$ (389 mg, 0.5 mmol) in 30 ml of thf. To the resulting solution solid sodium tetraphenylborate (240 mg, 0.7 mmol) was added and bright yellow crystals precipitated. The complex was filtered, washed with thf and dried in a current of nitrogen; yield 32%. Large well-shaped crystals were obtained by recrystallization from acetone–ethanol.

Anal. Found: C, 71.61; H, 6.05; N, 0.80. Calc. for $C_{97}H_{99}B_2NOP_4Pt$: C, 71.23; H, 6.10; N, 0.85%.

^1H NMR (CD_2Cl_2): δ 7.7–6.8 (m, B(C_6H_5) and P(C_6H_5), 70H), 4.6 (dm, $^1J_{PH}$ = 405 Hz, P–*H*, 1H), 2.15–2.30 (m, P–CH_2–CH_2–N, 12H), 2.10 (s, CH_3COCH_3, 6H), 1.52 (m, P–CH_2–CH_3, 4H), 0.84 (dt, $^3J_{HH}$ = 8 Hz, $^3J_{PH}$ = 20 Hz, P–CH_2–CH_3, 6H).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –21.9 (q, $^2J_{PP}$ = 24 Hz, $^1J_{PtP}$ = 2326 Hz, 1P), 19.5 (d, $^1J_{PtP}$ = 2467 Hz, 3P); ^{31}P NMR (CD_2Cl_2): δ –21.9 (br d, $^1J_{PH}$ = 405 Hz, $^1J_{PtP}$ = 2326 Hz, 1P), 19.5 (br s, $^1J_{PtP}$ = 2467 Hz, 3P). The $^{31}P\{^1H\}$ NMR spectrum of the filtrate shows the presence of **2** and **4**.

(b) A 5 mm NMR tube was charged with [(np_3)Pt(PEt_2)]·0.5C_4H_8O (50 mg, 0.04 mmol) and CD_2Cl_2 (0.7 ml). Then CF_3COOH (3.00 μl, 4.56 mg, 0.04 mmol) was added and the $^{31}P\{^1H\}$ NMR spectrum was recorded. The spectrum was identical to that of the isolated **3**.

Synthesis of [(np_3)Pt($PMeEt_2$)](BPh_4)I

A 5 mm NMR tube was charged with [(np_3)Pt(PEt_2)](BPh_4)·0.5C_4H_8O (50 mg, 0.04 mmol) and CD_2Cl_2 (0.7 ml). Then CH_3I (2.50 μl, 5.68 mg, 0.04 mmol) was added and the $^{31}P\{^1H\}$ NMR spectrum was recorded.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –12.2 (q, $^2J_{PP}$ = 17 Hz, $^1J_{PtP}$ = 2042 Hz, 1P), 14.85 (br s, $^1J_{PtP}$ = 1794 Hz, 3P).

Synthesis of [(pp_3)Pt($PHEt_2$)](PF_6)$_2$

The complex was prepared by the method previously described for the corresponding [(pp_3)Pt($PHCy_2$)](BF_4)$_2$ [4].

Anal. Found: C, 45.00; H, 4.34. Calc. for $C_{46}H_{53}P_7PtF_{12}$: C, 44.35; H, 4.29%.

^1H NMR (CD_2Cl_2): δ 7.8–7.2 (m, P(C_6H_5), 30H), 5.18 (dm, $^1J_{PH}$ = 381 Hz, P–*H*, 1H), 2.9–2.5 (m, P–CH_2–CH_2–P, 12H), 1.42 (dm, P–CH_2–CH_3, 4H), 0.86 (dt, $^3J_{PH}$ = 18 Hz, $^3J_{HH}$ = 7 Hz, P–CH_2–CH_3, 6H).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –36.9 (dq, $^2J_{P(PHEt_2)P(Pap)}$ = 275 Hz, $^2J_{P(PHEt_2)P(PPht_2)}$ = 33 Hz, $^1J_{PtP(PHEt_2)}$ = 1866 Hz, *P*Et_2, 1P), 29.0 (dd, $^2J_{P(PPht_2)P(Pap)}$ = 5 Hz, $^1J_{PtP(PPht_2)}$ = 2422 Hz, P–CH_2–CH_2–*P*Ph_2, 3P), 133.18 (dq, $^1J_{PtP(Pap)}$ = 1698 Hz, *P*–CH_2–CH_2–PPh_2).

Synthesis of [(pp_3)Pt(PEt_2)](PF_6)

A 5 mm NMR tube was charged with [(pp_3)Pt($PHEt_2$)](PF_6)$_2$ (50 mg, 0.04 mmol) and CD_2Cl_2 (0.7 ml). Then DBU (5.97 μl, 6.1 mg, 0.04 mmol) was added and the $^{31}P\{^1H\}$ NMR spectrum was recorded.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –32.81 (d, $^2J_{P(PEt_2)P(Pap)}$ = 40 Hz, $^1J_{PtP(PEt_2)}$ = 767 Hz, P*H*Et_2, 1P), 16.88 (d, $^2J_{P(PPht_2)P(Pap)}$ = 11 Hz, $^1J_{PtP(PPht_2)}$ = 2975 Hz, P–CH_2–CH_2–*P*Ph_2, 3P), 117.9 (dq, $^1J_{PtP(Pap)}$ = 1419 Hz, *P*–CH_2–CH_2–PPh_2, 1P).

Crystallography

Crystal data for

[(np_3)Pt($PHEt_2$)](BPh_4)$_2$·$(CH_3)_2CO$

M = 1635.5, triclinic, $P\bar{1}$, a = 18.286(8), b = 16.402(6), c = 15.337(6) Å, α = 106.9(1), β = 113.1(1), γ = 85.1(1)°, V = 4046.1 Å^3, Z = 2, D_c = 1.342 g cm^{-3},

monochromatic Mo Kα radiation, $\lambda = 0.7107$ Å, μ(Mo Kα) = 18.8 cm^{-1}. Intensity data were collected at room temperature on a Philips PW 1100 diffractometer within $2\theta < 40°$ using the ω–2θ technique. The intensities after correction for background were corrected for Lorentz–polarization effects and for absorption [6]. The intensities were assigned a standard deviation $\sigma(I)$, calculated according to ref. 7 by using an instability factor k of 0.03.

Solution and refinement of the structure

All the calculations were performed by using the SHELX 76 [8] and ORTEP [9] programs on a SEL 32/77 computer. Atomic scattering factors for the appropriate neutral atoms were taken from ref. 10 for non-hydrogen atoms and from ref. 11 for hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all non-hydrogen atoms [12]. During the refinement the function $\Sigma w(|F_o|-|F_c|)^2$ was minimized, the weights w being defined as $w = 1/\sigma^2(F_o)$. The structure was solved by the heavy atom method and refined by full-matrix least-squares procedures. The phenyl rings were treated as rigid groups and the hydrogen atoms were introduced in calculated positions but not refined. The hydrogen atom of the $PHEt_2$ phosphine was detected in a ΔF Fourier map, although not refined. At convergence the R and R_w factors are both 0.050 for 5564 reflections having $I > 3\sigma(I)$. The final positional parameters are given in Table 1.

Results and discussion

The complex **1** rapidly reacts, at room temperature, in anhydrous thf/benzene solution, with an equimolar amount of $ClPEt_2$, in the presence of $NaBPh_4$, to form the diethylphosphide **2**. However if traces of moisture or alcohol are present in the reaction system small amounts of compounds **3** and **4** are also formed. Complex **3**, which is practically insoluble in thf and benzene, easily precipitates. If traces of D_2O are added $[(np_3)Pt(PDEt_2)](BPh_4)_2$ is also formed. In particular when the complex $(np_3)Pt(PPh_3)\cdot 0.4CH_3CH_2CH_2CH_2OH$ is used as the starting reagent, in thf solution, complex **3** crystallizes in appreciable yield (*c.* 30%); minor amounts of the soluble species **2** and **4** can be characterized in the filtrate solution by ^{31}P NMR spectra. Finally when large amounts of H_2O or ROH in comparison with the amounts of $ClPEt_2$ and **1** are present at the start of the reaction, only complex **4** together with unidentified materials are obtained.

Complex **2**, which decomposes immediately in air and rather rapidly also under nitrogen atmosphere (0.5 h in solution, 4 h the solid), behaves as a 1:1

TABLE 1. Positional parameters ($\times 10^4$) for $[(np_3)Pt(PEt_2H)](BPh_4)_2\cdot(CH_3)_2CO$

Atom	*x*	*y*	*z*
Pt	2201(1)	1990(1)	2967(1)
P1	1558(2)	630(2)	2554(2)
P2	3303(2)	2075(2)	2540(2)
P3	2000(2)	3129(2)	4239(2)
P4	1360(2)	2414(2)	1657(2)
N	3083(5)	1587(6)	4214(7)
C1	2972(6)	651(7)	4073(8)
C2	2100(6)	380(8)	3721(8)
C3	3909(6)	1743(7)	4314(8)
C4	4020(7)	1493(7)	3357(8)
C5	3009(7)	2048(7)	5168(9)
C6	2882(7)	2989(8)	5291(9)
C7	401(7)	2793(8)	1615(10)
C8	134(10)	3518(10)	1076(12)
C9	1180(7)	1605(7)	487(8)
C10	793(8)	1920(9)	−424(10)
C11	4425(12)	4822(14)	8412(15)
C12	4787(12)	4125(12)	7868(15)
C13	5525(13)	3719(14)	8383(16)
O1	4496(9)	3894(10)	6972(12)
C1.1	515(4)	441(5)	2284(5)
C2.1	270(4)	174(5)	2914(5)
C3.1	−539(4)	66(5)	2689(5)
C4.1	−1103(4)	226(5)	1833(5)
C5.1	−858(4)	493(5)	1202(5)
C6.1	−49(4)	601(5)	1428(5)
C1.2	1754(4)	−304(4)	1705(6)
C2.2	2322(4)	−249(4)	1327(6)
C3.2	2527(4)	−979(4)	741(6)
C4.2	2164(4)	−1765(4)	535(6)
C5.2	1596(4)	−1821(4)	914(6)
C6.2	1391(4)	−1090(4)	1499(6)
C1.3	3315(4)	1615(4)	1315(5)
C2.3	2940(4)	2057(4)	612(5)
C3.3	2878(4)	1703(4)	−360(5)
C4.3	3191(4)	907(4)	−628(5)
C5.3	3565(4)	465(4)	75(5)
C6.3	3627(4)	820(4)	1046(5)
C1.4	3778(4)	3105(4)	2872(5)
C2.4	4400(4)	3185(4)	2589(5)
C3.4	4802(4)	3969(4)	2910(5)
C4.4	4583(4)	4673(4)	3515(5)
C5.4	3961(4)	4593(4)	3798(5)
C6.4	3559(4)	3809(4)	3477(5)
C1.5	2040(4)	4273(5)	4386(5)
C2.5	2670(4)	4801(5)	5132(5)
C3.5	2678(4)	5672(5)	5221(5)
C4.5	2055(4)	6014(5)	4564(5)
C5.5	1425(4)	5486(5)	3818(5)
C6.5	1417(4)	4616(5)	3729(5)
C1.6	1152(5)	3017(5)	4534(6)
C2.6	1076(5)	3577(5)	5372(6)
C3.6	430(5)	3483(5)	5606(6)
C4.6	−140(5)	2830(5)	5004(6)
C5.6	−63(5)	2270(5)	4167(6)
C6.6	583(5)	2364(5)	3932(6)
C1.7	6434(4)	1617(5)	4411(4)

(*continued*)

TABLE 1. (*continued*)

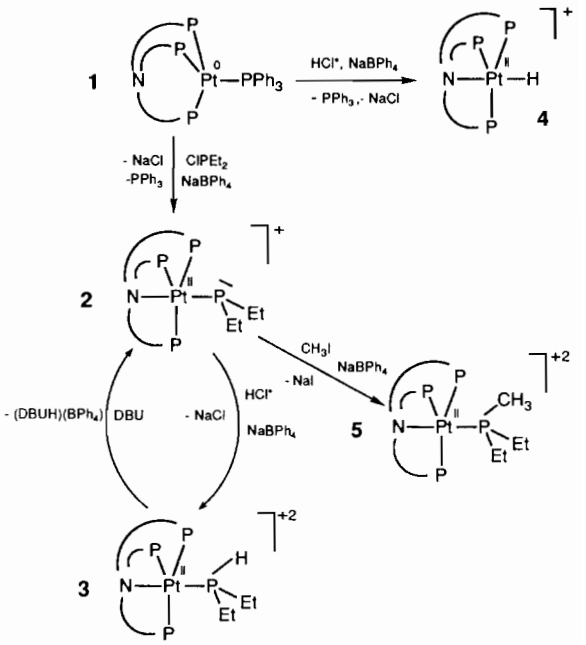
Atom	*x*	*y*	*z*
C2.7	6010(4)	2334(5)	4209(4)
C3.7	5840(4)	2942(5)	4950(4)
C4.7	6095(4)	2833(5)	5893(4)
C5.7	6519(4)	2116(5)	6095(4)
C6.7	6688(4)	1508(5)	5354(4)
C1.8	6463(3)	1182(5)	2567(5)
C2.8	7153(3)	1415(5)	2506(5)
C3.8	7100(3)	1804(5)	1786(5)
C4.8	6356(3)	1959(5)	1128(5)
C5.8	5665(3)	1725(5)	1189(5)
C6.8	5719(3)	1337(5)	1909(5)
C1.9	7370(4)	320(3)	3887(5)
C2.9	8056(4)	815(3)	4536(5)
C3.9	8790(4)	430(3)	4827(5)
C4.9	8837(4)	−450(3)	4468(5)
C5.9	8151(4)	−944(3)	3818(5)
C6.9	7418(4)	−559(3)	3527(5)
C110	5745(4)	100(5)	3128(5)
C210	5443(4)	−417(5)	2155(5)
C310	4838(4)	−1023(5)	1857(5)
C410	4535(4)	−1112(5)	2530(5)
C510	4837(4)	−595(5)	3502(5)
C610	5442(4)	11(5)	3801(5)
C111	2660(4)	3812(5)	8970(5)
C211	2688(4)	3334(5)	8069(5)
C311	3350(4)	2852(5)	8048(5)
C411	3985(4)	2847(5)	8930(5)
C511	3958(4)	3325(5)	9831(5)
C611	3295(4)	3808(5)	9851(5)
C112	1739(4)	5036(5)	8246(6)
C212	991(4)	5208(5)	7612(6)
C312	925(4)	5752(5)	7036(6)
C412	1607(4)	6123(5)	7095(6)
C512	2355(4)	5951(5)	7729(6)
C612	2421(4)	5407(5)	8305(6)
C113	1018(5)	3772(5)	8516(6)
C213	931(5)	2963(5)	7854(6)
C313	210(5)	2504(5)	7449(6)
C413	−424(5)	2855(5)	7707(6)
C513	−337(5)	3665(5)	8369(6)
C613	384(5)	4123(5)	8773(6)
C114	2004(5)	4949(4)	10113(6)
C214	1962(5)	4509(4)	10747(6)
C314	2156(5)	4930(4)	11745(6)
C414	2391(5)	5790(4)	12109(6)
C514	2433(5)	6230(4)	11475(6)
C614	2239(5)	5809(4)	10477(6)
B1	6500(7)	800(8)	3487(9)
B2	1841(8)	4373(9)	8945(11)

electrolyte in CH_2Cl_2 solution. Complex **3** is air stable and a 1:2 electrolyte.

^1H and ^{31}P NMR spectra (see 'Experimental') are consistent with the proposed formulation and indicate a five-coordinate geometry. The equivalence of the three phosphorus atoms of np_3 in the ^{31}P NMR spectrum of **3** clearly indicates a rapid rotation of the $-PHEt_2$ group, at room temperature.

A complete X-ray structural analysis of **3** revealed that the structure consists of complex cations $[(np_3)Pt(PHEt_2)]^+$, and tetraphenylborate anions, with interspersed acetone solvent molecules. Figure 1 shows a perspective view of the complex cation, with selected important bond distances and angles. The metal centre displays a slightly distorted trigonal bipyramidal geometry, being surrounded by the phosphorus and the nitrogen atoms of the np_3 ligand, in equatorial and apical sites, respectively. The fifth position, *trans* to the central nitrogen, is occupied by a phosphine moiety, $PHEt_2$. Bond distances and angles in the coordination polyhedron resemble the values previously found in a series of $Pt(II)np_3$ five-coordinated complexes, structurally characterized [1, 2]. The $Pt–P_{equal}$, ranging from 2.376(4)–2.409(3) Å, are somewhat larger than the corresponding Pt–P axial bond (2.256(3) Å), as expected in d^8 five-coordinated trigonal bipyramidal complexes [13].

The diethylphosphide complex $[(np_3)Pt(PEt_2)]^+$ is a strong nucleophilic agent, immediately reacting with HCl or CF_3COOH and CH_3I to yield $[(np_3)Pt(PHEt_2)]^{2+}$ and $[(np_3)Pt(PMeEt_2)]^{2+}$, respectively. Complex **3** is easily deprotonated by DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene(1,5-5)) in CH_2Cl_2 to reform **2**. On account of the high reactivity of both $ClPEt_2$ and terminal platinum(II) phosphide, **2**, we can rationalize the reported reactions: in



Scheme 1.

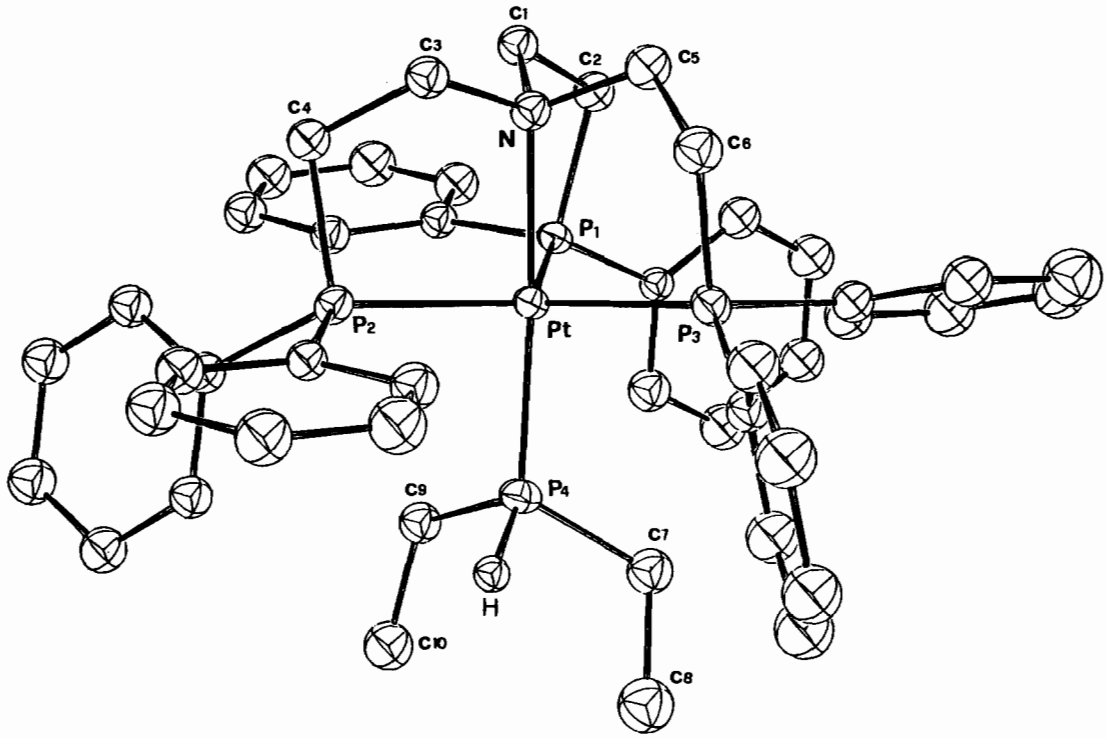


Fig. 1. Perspective view of the complex cation $[(np_3)Pt(PHEt_2)]^+$. ORTEP drawing with 30% probability ellipsoids. Important selected bond distances (Å) and angles (°): Pt–P1 2.409(3), Pt–P2 2.376(4), Pt–P3 2.399(3), Pt–P4 2.256(3), Pt–N 2.196(9), P1–Pt–P2 120.0(1), P1–Pt–P3 117.5(1), P2–Pt–P3 119.5(1), P1–Pt–P4 97.7(1), P2–Pt–P4 91.9(1), P3–Pt–P4 97.8(1), P1–Pt–N 84.3(2), P2–Pt–N 84.4(3), P3–Pt–N 83.9(2), P4–Pt–N 176.3(2).

absolutely anhydrous conditions $ClPEt_2$ cleanly reacts with **1** and $NaBPh_4$ to yield **2**; in the presence of traces of H_2O or ROH, $ClPEt_2$ first undergoes hydrolysis or alcoholysis to release HCl [14], then the remaining chlorophosphine reacts with **1** to form **2** which in turn is attacked by HCl to yield **3**; eventually HCl can also react with **1** allowing the formation of **4**. The overall process is summarized in Scheme 1.

Regarding the ^{31}P NMR spectra it is of interest to notice that the magnitude of $^1J_{Pt-P(PEt_2)}$ (884 Hz) is reduced from that of the corresponding protonated one, $^1J_{Pt-P(PHEt_2)}$ (2326 Hz). Accordingly no $^2J_{P-P}$ is observed in **2**. This behaviour, previously observed in other terminal phosphide complexes [15], supports a pyramidal geometry, in agreement with the X-ray structure of the related arsenide $[(np_3)Pt(AsPh_2)]^+$ [1]. The $\delta(PEt_2)$ at high frequencies (56.7 ppm), which has been assumed to indicate a metal–phosphorus bond order greater than one [4, 15a], seems to contrast the above suggestion. However the chemical shifts of these compounds depend on several factors: for instance the ^{31}P NMR spectrum of the likely isostructural complex $[(pp_3)Pt(PEt_2)]^+$ (**7**) [14] with a reduced $^1J_{Pt-P(PEt_2)}$ (767 Hz versus 1866 Hz for the protonated one) but a low frequency chemical shift (δ −32.8 ppm), clearly shows the importance of different donor atoms sets.

The preparation of different series of isostructural phosphides and systematic X-ray crystal structure determinations could clarify this matter.

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