# (Phosphido)platinum Complexes by Sodium-Promoted Reaction of *cis*-$PtCl_2(PHCy_2)_2$ − Synthesis and Crystal Structure of [*trans*-$Pt(PCy_2H)_2(PCy_2)Cl$], a Rare Example of a Terminal (Phosphido)platinum(II) Complex

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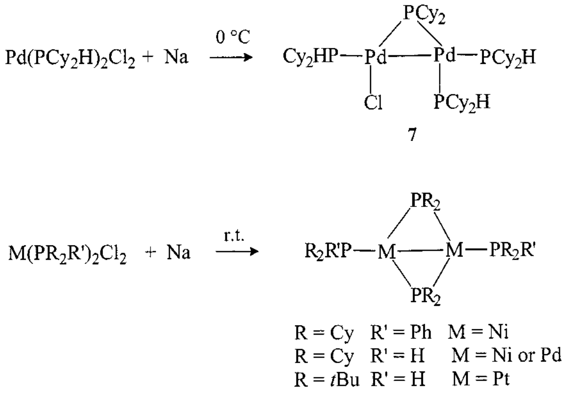
**Keywords:** Platinum / P ligands / Terminal phosphides / Hydrides / Small ring systems

*cis*-$PtCl_2(PHCy_2)_2$ (**1**) reacts at 0 °C in toluene with sodium metal to give the dinuclear $Pt^I$ complexes *cis*-[$(PHCy_2)(H)Pt(\mu\text{-}PCy_2)$]$_2$ (**2**) and [$(PHCy_2)(Cl)Pt(\mu\text{-}PCy_2)Pt(PHCy_2)_2$](*Pt–Pt*) (**3**). On standing in solution, complex **3** isomerizes to *trans*-[$(PHCy_2)(Cl)Pt(\mu\text{-}PCy_2)_2Pt(PHCy_2)(H)$] (**4**). When treated with sodium at room temperature, complex **3** transforms into [$Pt(\mu\text{-}PCy_2)(PHCy_2)$]$_2$(*Pt–Pt*) (**5**). The sodium reduction of **1** carried out at room temperature leads to the direct formation of the phosphido bridged dinuclear complex [$Pt(\mu\text{-}PCy_2)(PHCy_2)$]$_2$(*Pt–Pt*) (**5**) along with the mononuclear platinum(II) complex [*trans*-$Pt(PCy_2H)_2(PCy_2)Cl$] (**6**). Complex **6**, which has also been obtained by reaction of **1** with $LiPCy_2$, unambiguously shows by single-crystal X-ray diffraction the presence of a pyramidal terminal phosphido ligand.

## Introduction

The reaction of sodium metal with phosphanyl divalent group-10 halide complexes has been widely used to access molecules in which a transition metal atom exhibits a low-valent and somehow unusual oxidation state. In particular, $NiP_2X_2$ (P = $PEt_3$, $PnBu_3$, $PEt_2Ph$; X = Cl, Br) was reduced under argon to the zero-valent tetracoordinated species $NiP_4$, whereas $Ni(PCy_3)_2X_2$ (X = Cl, Br) gave $Ni(PCy_3)_3$ or [$NiX(PCy_3)_2$]$_2$.[1] The chelating diphosphane complexes $Ni(dp)Cl_2$ [dp = 1,2-bis(diphenylphosphanyl)ethane (dppe), 1,2-bis(diethylphosphanyl)ethane (depe), 1,2-bis(dicyclohexylphosphanyl)ethane (dcpe), 1,3-bis(dicyclohexylphosphanyl)propane (dcpp), 1,4-bis(dicyclohexylphosphanyl)butane (dcpb)] afforded the 14- (dp = dcpe, dcpp, dcpb), 16- (dp = dcpe, dcpb), or 18-electron (dp = dppe, depe, dcpe) complexes Ni(dp), $Ni_2(dp)_3$, and $Ni(dp)_2$, respectively, depending on the diphosphane and on the reaction conditions.[2] Phosphido-bridged dinuclear metal(I) complexes have been accessed by sodium reduction of $Ni(PCy_2Ph)_2Cl_2$,[3] $Pt(PHtBu_2)_2Cl_2$,[4] and $M(PHCy_2)_2Cl_2$ (M = Ni, Pd).[5] Moreover, when the sodium reaction of $Pd(PHCy_2)_2Cl_2$ was carried out at 0 °C, the isolation of [$(PHCy_2)(Cl)Pd(\mu\text{-}PCy_2)Pd(PHCy_2)_2$](*Pd−Pd*) (**7**) was achieved (Scheme 1).



Scheme 1

In this paper we describe the reactivity of *cis*-$Pt(PHCy_2)_2Cl_2$ (**1**) towards sodium metal which was found to depend on the reaction temperature. At 0 °C the phosphido-bridged dinuclear platinum species *cis*-[$(PHCy_2)(H)Pt(\mu\text{-}PCy_2)$]$_2$ (**2**) and [$(PHCy_2)(Cl)Pt(\mu$-

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$PCy_2)Pt(PHCy_2)_2]$(*Pt−Pt*) (**3**) were formed, whereas a mixture of $[Pt(\mu\text{-}PCy_2)(PHCy_2)]_2$(*Pt−Pt*) (**5**) and the mononuclear (phosphido)platinum(II) complex [*trans*-$Pt(PHCy_2)_2(PCy_2)Cl$] (**6**) was obtained when the reaction was carried out at room temperature.

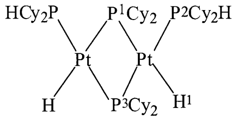
## Results and Discussion

The reaction of *cis*-$PtCl_2(PHCy_2)_2$ (**1**) with sodium metal carried out in toluene at 0 °C resulted in the formation of two dinuclear complexes **2** and **3** in an approximately 4:1 ratio. Complex **2** is fairly stable in the air but air-sensitive in aromatic solvents, where it easily dissolves. Taking advantage of insolubility in alcohols it was isolated as a white powder from the reaction mixture by treatment with methanol.

Complex **2** exhibits in the IR spectrum two characteristic bands at 2299 and 1940 $cm^{-1}$ due to P−H and Pt−H stretching, respectively. The $^{31}P\{^1H\}$ NMR spectrum of **2** recorded at room temperature consists of three signals, all flanked by $^{195}Pt$ satellites: two doublets (δ = 24.8 and δ = −170.6) and a triplet of doublets (δ = −123.0). The high-field signals at δ = −123.0 and δ = −170.6, which are mutually coupled [$^2J$(P-P) = 104 Hz], are typical for bridging phosphides involved in four-membered rings,[6] and strongly support a dinuclear structure for **2**, with two inequivalent phosphide groups bound to two platinum atoms without *Pt−Pt* linkage. Moreover, the pattern of the phosphide $^{31}P$ signals (triplet of doublets and doublet) and the value of the coupling constant between the phosphorus signal at δ = −123.0 and that at δ = 24.8 [*J*(P-P) = 308 Hz] both suggest a symmetrical dimeric structure in which two platinum atoms, each bearing a dicyclohexylphosphane ligand are bridged by two dicyclohexylphosphide groups. In the dimer the dicyclohexylphosphane ligands are *cis* with respect to each other and *trans* with respect to the bridging phosphide group resonating at δ = −123.0. $^1H$ and proton-coupled $^{31}P$ NMR spectroscopy experiments together with IR data indicate that, on each platinum atom, the *cis* positions with respect to the terminal dicyclohexylphosphane ligands are occupied by terminal hydride ligands. In addition to the resonances of aliphatic protons and a broad doublet which can be attributed to the hydrogen atom directly bound to P in the coordinated dicyclohexylphosphane [δ = 4.50; $^1J$(P-H) = 317 Hz], the $^1H$ NMR spectrum shows a doublet of doublet of doublets [*J*(P-H) = 143, 20, and 9 Hz] with $^{195}Pt$ satellites centred at δ = −3.84 [$^1J$(Pt-H) = 905 Hz]. This latter signal could be attributed to two equivalent terminal hydride ligands, *cis* with respect to each other and *trans* with respect to the bridging phosphide group resonating at δ = −170.6 as suggested by the high value of $^2J$(P-H) (143 Hz).

In the proton-coupled $^{31}P$ NMR spectrum the signal at δ = −123.0 (phosphide $P^3Cy_2$, see Table 1 for numbering) remains substantially unchanged while the signal at δ = 24.8 (phosphanes $P^2Cy_2H$) splits into a pseudo-triplet due to the additional direct coupling $^1J$(P-H) = 317 Hz, and the signal at δ = −170.6 (phosphide $P^1Cy_2$) splits into a triplet of doublets due to the additional coupling with the *trans* hydride ligands [$^2J$(P-H) = 143 Hz].

Table 1. NMR parameters for complex **2** ([$D_6$]benzene, 295 K); chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz



2

| | $P^1$ | $P^2$ | $P^3$ | $H^1$ | Pt |
|---|---|---|---|---|---|
| $P^1$ | **−170.6** | ca. 0 | 104 | 143 | 1322 |
| $P^2$ | ca. 0 | **24.8** | 308 | 20 | 1968 |
| $P^3$ | 104 | 308 | **−123.0** | 9 | 2118 |
| $H^1$ | 143 | 20 | 9 | −3.84 | 905 |
| Pt | 1322 | 1968 | 2118 | 905 | −4441 |

Finally, the value of $^1J$(Pt-H) (905 Hz) and the position of the Pt−H stretching band in the IR spectrum both indicate terminal coordination for the hydride ligands. The dimeric structure of **2** formulated as *cis*-$[(PHCy_2)(H)Pt(\mu\text{-}PCy_2)]_2$ was also confirmed by the $^{195}Pt\{^1H\}$ NMR spectrum which consists of a doublet of doublets of doublets centred at δ = −4441 [$^1J$(Pt-$P^1$) = 1322, $^1J$(Pt-$P^2$) = 1968 Hz, and $^1J$(Pt-$P^3$) = 2118 Hz].

The minor product obtained in the sodium reduction of **1** at 0 °C, is a yellow-orange solid, the spectroscopic features and elemental analysis of which indicate the phosphido-bridged platinum(I) complex $[(PHCy_2)(Cl)Pt(\mu\text{-}PCy_2)Pt(PHCy_2)_2]$(*Pt−Pt*) (**3**), and represents the Pt analogue of the palladium complex **7**. In the region of the P−H stretching the IR spectrum of **3** shows the convolution of two bands of relative intensities 2:1 centred at 2295 $cm^{-1}$ and 2255 $cm^{-1}$. The Pt−Cl band was found at 301 $cm^{-1}$. The $^{31}P\{^1H\}$ NMR spectrum of **3** recorded at room temp. shows signals centred at δ = 185.5, 37, and 16 and is reminiscent of that of **7**.

Among these signals, the only well-resolved one is that centred at δ = 185.5 (Figure 1) which does not significantly split in the proton coupled spectrum. This signal can be attributed to a bridging phosphide group involved in a three-membered $Pt_2P$ ring[7] in which the two platinum atoms are inequivalent. The spectrum consists of a central doublet of triplets due to isotopomer **A**, which does not contain $^{195}Pt$ (43.8%) flanked by three different sets of satellites, two arising from isotopomers **B** and **C** (22.4% each), which contain only one $^{195}Pt$ nucleus and one due to isotopomer **D** (11.4%) which contains two $^{195}Pt$ nuclei. The coupling constants $^2J$(P-P) = 231 and 26 Hz, which are clearly seen in the signal of isotopomer **A**, indicate that the phosphorus atom of the bridging phosphide group is coupled with a pseudo-*trans*- and two pseudo-*cis*-oriented phosphorus nuclei. The sets of satellites arising from both isotopomers **B** and **C** appear as doublets of doublets of doublets. The couplings of $P^1$ with the two inequivalent platinum atoms gives the constants $^1J(Pt^2\text{-}P^1) = 3072$ Hz and $^1J(Pt^1\text{-}P^1) = 3911$ Hz whereas the coupling with $P^2$ and $P^4$ gives $^2J(P^1\text{-}P^2) = 34$ Hz and $^2J(P^1\text{-}P^4) = 22$ Hz (see Table 2 for P and Pt numbering). The third subset of signals due to the isotopomer **D** consists of a doublet of doublets of doublets of multiplets. The relevant coupling constants are $^1J(Pt^2\text{-}P^1) = 3080$ Hz and $^1J(Pt^1\text{-}P^1) = 3916$ Hz. Interestingly, the central signal appears as a doublet of triplets (instead of the expected ddd). This can be explained in terms of the isotopomer **A** having either coincident $^2J_{P,P}$ or a greater linewidth of the signal with respect to **B**, **C**, and **D**, due to difference in relaxation efficiency in different isotopomers. The latter explanation is in agreement with high-temperature spectra (82 °C) that also show the expected ddd for isotopomer **A**.[8]

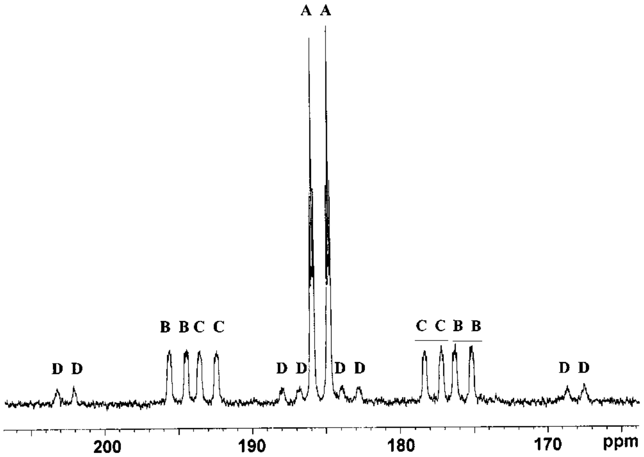
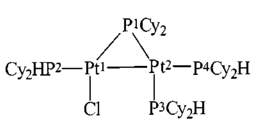


Figure 1. Phosphide region of the $^{31}P\{^1H\}$ NMR spectrum of **3** ([D$_8$]toluene, 202 MHz, 295 K); **A**: isotopomer with no $^{195}Pt$ atoms; **B**: isotopomer with NMR-active $Pt^1$; **C**: isotopomer with NMR-active $Pt^2$; **D**: isotopomer with NMR-active $Pt^1$ and $Pt^2$

Table 2. NMR parameters for complex **3** ([D$_8$]toluene, 295 K); chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz



3

| | $P^1$ | $P^2$ | $P^3$ | $P^4$ |
|---|---|---|---|---|
| $P^1$ | **185.5** | 34 | 231 | 22 |
| $P^2$ | 34 | **16.3** | 16 | 154 |
| $P^3$ | 231 | 16 | **37** | 12 |
| $P^4$ | 22 | 154 | 12 | **15.8** |

The other $^{31}P\{^1H\}$ NMR resonances of **3** are a very broad signal centred at δ = 37 and a broad multiplet centred at δ = 16. The signal at δ = 37 can be attributed to $P^3$ of the dicyclohexylphosphane pseudo-*trans* to the phosphide group. Dynamic $^{31}P\{^1H\}$ NMR spectroscopic experiments showed that the signal at δ = 37, which does not change significantly by lowering the temperature down to −38°C, splits into a broad doublet [$^2J(P^1\text{-}P^3) = 231$ Hz] at high temperatures (> 50 °C) due to the coupling with the bridging phosphide group. The broadness of this signal at or below room temperature, can therefore be explained in terms of hindered rotation around the $P^3{-}Pt$ bond originating in a set of slowly interconverting rotamers.

For the related palladium complex **7** the signal of the $PHCy_2$ ligand *trans* to the bridging phosphide group is already a broad doublet at room temperature[5] and becomes a very broad singlet by lowering the temperature down to −38 °C (Figure 2). This is in agreement with a more pronounced fluxionality of palladium with respect to platinum complexes.

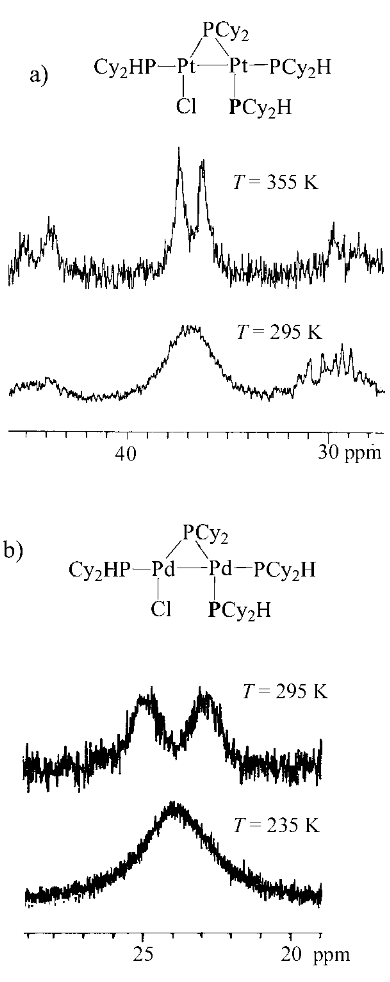
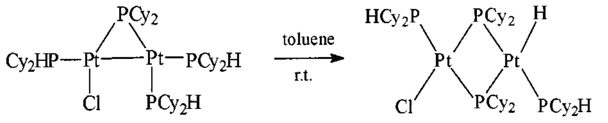


Figure 2. VT $^{31}P\{^1H\}$ NMR spectra of **3** and **7** in [D$_8$]toluene; (a) 202 MHz; (b) 81 MHz

In the case of complex **3**, $P^2$ and $P^4$ (the two phosphorus atoms of the phosphane ligands *cis* to the bridging phosphide group) belong to a second-order spin system and a direct analysis of the spectrum was not obtained. The $^{31}P\{^1H\}$ NMR spectrum simulation for the isotopomer containing no $^{195}Pt$ (ABMX spin system, A and B being $P^2$ and $P^4$) agrees well with the experimental data for the following parameters: $\delta(P^2) = 16.3$, $\delta(P^4) = 15.8$, $^3J(P^2\text{-}P^4) = 154$, $^3J(P^2\text{-}P^3) = 16$, $^2J(P^3\text{-}P^4) = 12$ Hz (Table 2).

Complex **3** is different from its Pd analogue **7** in that it is not stable in solution and, with the rate depending on the temperature, undergoes an intramolecular oxidative addition of a P−H bond with the rupture of the Pt−Pt bond affording the new hydrido phosphido dinuclear platinum(II) complex *trans*-$[(PHCy_2)(Cl)Pt(\mu\text{-}PCy_2)_2Pt(PHCy_2)(H)]$ (**4**).

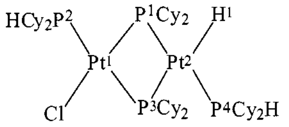


**3** **4**

This complex shows one band at 281 cm$^{-1}$ in the IR spectrum that is due to the Pt−Cl stretching, one broad band at 2301 cm$^{-1}$ attributable to the P−H stretching, and one intense band at 1929 cm$^{-1}$ due to the Pt−H stretching.

The $^{31}P\{^1H\}$ NMR spectrum of **4** consists of four signals, all flanked by $^{195}$Pt satellites, centred at $\delta = 21.3$, $\delta = 12.5$, $\delta = -126.9$ and $\delta = -156.2$ (Table 3). The high-field signals at $\delta = -126.9$ and $\delta = -156.21$ indicate for **4**, as in the case of **2**, a dinuclear structure in which two phosphide groups are bound to two platinum atoms without Pt−Pt linkage.

Table 3. NMR parameters for complex **4** ([D$_6$]benzene, 295 K); chemical shifts (bold) are in ppm; coupling constants (normal) are in Hz



**4**

| | $P^1$ | $P^2$ | $P^3$ | $P^4$ | $H^1$ |
|---|---|---|---|---|---|
| $P^1$ | **−126.9** | 12 | 146 | 328 | 9 |
| $P^2$ | 12 | **12.5** | 318 | | |
| $P^3$ | 146 | 318 | **−156.2** | [a] | 138 |
| $P^4$ | 328 | | [a] | **21.3** | 24 |
| $H^1$ | 9 | | 138 | 24 | −3.19 |

[a] $^2J(P^3-P^4)$ not assessed because less than signal linewidth.

Moreover, proton-coupled $^{31}$P NMR spectra show that, of the two phosphide groups, the phosphorus atom at $\delta = -156.2$ is strongly hydrogen-coupled [$^2J(P\text{-}H) = 138$ Hz]. The signals at $\delta = 21.3$ and $\delta = 12.5$ belong to two inequivalent terminally bound secondary phosphane ligands [$^1J(P\text{-}H) = 320$ and 314 Hz, respectively] with the first appearing as a doublet [$^2J(P\text{-}P) = 328$ Hz], and the second as a doublet of doublets [$^2J(P\text{-}P) = 318$ and 12 Hz]. These findings indicate that both of the terminal phosphane ligands are *trans* to a bridging phosphide group. From the $^{195}$Pt satellites the coupling constants [$^1J(Pt\text{-}P) = 2070$ Hz, $^3J(Pt\text{-}P) = 124$ Hz (phosphorus signal at $\delta = 21.3$), and $^1J(Pt\text{-}P) = 1760$ Hz, $^3J(Pt\text{-}P) = 68$ Hz (phosphorus signal at $\delta = 12.5$)] could be extracted.

The signals of the bridging phosphide groups at $\delta = -126.9$ and $\delta = -156.2$ are both doublets of doublets due to the mutual coupling [$^2J(P\text{-}P) = 146$ Hz] and also to the additional coupling of each of them with the *trans*-phosphane ligand. 2D COSY $^{31}P\{^1H\}$ NMR spectroscopic experiments enable one to clearly distinguish the satellites due to different couplings with Pt$^1$ and Pt$^2$ (such satellites, sixteen lines in total, are not unambiguously assigned in the monodimensional $^{31}$P NMR spectrum) and the following values for the relevant coupling constants can be extracted: $^1J(P^1\text{-}Pt^1) = 2497$, $^1J(P^1\text{-}Pt^2) = 2239$, $^1J(P^2\text{-}Pt^1) = 1729$, $^1J(P^3\text{-}Pt^1) = 1766$, $^1J(P^3\text{-}Pt^2) = 1332$, $^1J(P^4\text{-}Pt^2) = 2070$ Hz.

The $^1$H NMR spectrum shows, beside resonances due to aliphatic protons, two doublets centred at $\delta = 4.79$ and $\delta = 4.35$ as well as a doublet of doublets of doublets centred at $\delta = -3.19$ [$J(H\text{-}P) = 138$, 24, and 9 Hz]. The latter signal, which is flanked by $^{195}$Pt satellites [$^1J(Pt\text{-}H) = 912$ Hz] is due to a terminal hydride ligand *cis* to P$^4$ (see Table 3 for P, H, and Pt numbering for **4**). Among the coupling constants shown by the hydride signal the largest one [$^2J(H\text{-}P) = 138$ Hz] is attributed to the coupling with *trans*-P$^3$, whereas the two smaller ones [$^2J(H\text{-}P) = 24$ and 9 Hz] are due to the couplings with *cis*-P$^4$ and *cis*-P$^1$, respectively.

When the Na reduction of **1** was carried out at room temperature (instead of at 0 °C), the reaction solution showed signals attributed to $[Pt(\mu\text{-}PCy_2)(PHCy_2)]_2$(*Pt−Pt*) (**5**) and [*trans*-$Pt(PHCy_2)_2(PCy_2)Cl$] (**6**) in the $^{31}P\{^1H\}$ NMR spectrum. $^{31}P\{^1H\}$ NMR of **5** consists of two triplets centred at $\delta = 242.0$ and $\delta = 19.6$ [$^2J(P\text{-}P) = 51$ Hz] both with $^{195}$Pt satellites.

The signal at $\delta = 242.0$ (Figure 3) which is flanked by two sets of satellites due to the isotopomers containing one or both NMR-active platinum atoms, does not change substantially in the proton-coupled spectrum, and belongs to the bridging phosphide groups that couple with the Pt nuclei [$^1J(Pt\text{-}P) = 2598$ Hz]. The low-field resonance of this bridging phosphide group indicates the presence of a three-membered Pt$_2$P ring[7a,7b] and, therefore, of a Pt−Pt bond in complex **5**. The triplet at $\delta = 19.6$ can be attributed to the terminal dicyclohexylphosphane ligands. The signal splits into a doublet of badly resolved triplets in the proton-coupled spectrum [$^1J(P\text{-}H) = 318$ Hz] and is flanked by satellites due to $^{195}$Pt couplings [$^1J(Pt\text{-}P) = 4811$ Hz]. Neglecting signals due to the isotopomer containing two $^{195}$Pt atoms, the main satellites each appear as a doublet of triplets due to the coupling with the phosphide groups [$^2J(P\text{-}P) = 51$ Hz] and with the other terminal phosphane ligand [$^3J(P\text{-}P) = 70$ Hz]. The relevant coupling constants found for the related complex $[Pt\{\mu\text{-}P(SiMe_3)_2\}(PEt_3)]_2$(*Pt−Pt*) are: $^1J(Pt\text{-}P) = 4957$, $^2J(P\text{-}P) = 63$, and $^3J(P\text{-}P) = 66$ Hz.[9]

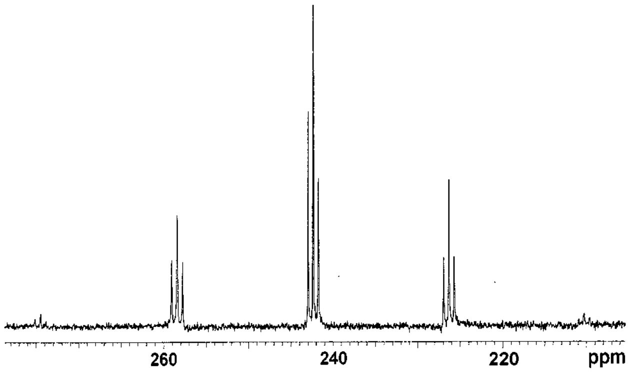


Figure 3. Phosphide region of the $^{31}P\{^1H\}$ NMR spectrum for **5** ([D$_6$]benzene, 81 MHz, 295 K)

The $^1H$ NMR spectrum of **5** shows the resonance of the hydrogen atoms directly bound to phosphorus atoms for the coordinated $PCy_2H$ at low field. This resonance appears as a doublet of triplets [$^1J$(P-H) = 318 Hz and $^3J$(μP-H) = 13 Hz] each broadened at the base due to H−Pt coupling (Figure 4). Moreover, each of the triplet components appears split into three peaks, due to the additional coupling with the cyclohexyl methyne protons, but the value of such coupling constants (< 4 Hz) could not exactly be assessed.

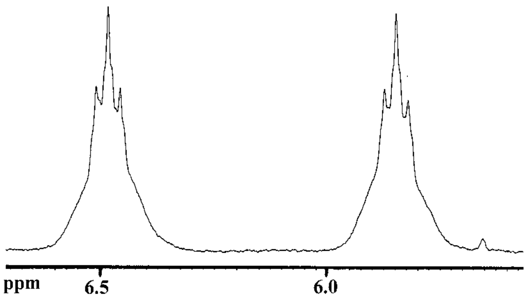
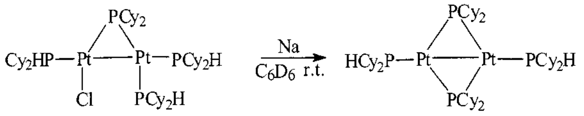


Figure 4. $^1H$ NMR spectrum in the low-field region for **5** ([D$_6$]benzene, 500 MHz, 295 K)

The IR spectrum of **5** shows a strong band at 2238 cm$^{-1}$ attributed to the P−H stretching of the coordinated dicyclohexylphosphane ligand. Spectroscopically pure **5** was directly obtained in an NMR tube by treating **3** in [D$_6$]benzene with sodium at room temperature.



**3** **5**

In the $^{31}P\{^1H\}$ NMR spectrum, complex **6** shows a doublet at δ = 27.6 and a triplet at δ = 20.6, in a 2:1 ratio (as assessed by the integrals in the proton coupled spectrum) with the same coupling constant of 41 Hz. The triplet at δ = 20.6, which does not substantially change in the proton-coupled spectrum, is flanked by satellites from which a coupling constant $^1J$(P-Pt) = 931 Hz could be extracted. Therefore such a triplet can be ascribed to a terminal dicyclohexylphosphide group, coupled with two equivalent phosphorus atoms, directly bound to the platinum atom.

The doublet at δ = 27.6 is flanked by two satellites characterised by $^1J$(P-Pt) = 3006 Hz. The pattern of the central signal (isotopomer without $^{195}$Pt) in the proton-coupled spectrum is typical for the *A* part of a second-order spin system $(AXY_2)_2$[10] which is further coupled with a phosphorus atom [$^2J$(P-P) = 41 Hz]. In the present case *A* is $^{31}$P, *X* is the proton bound to $^{31}$P, and *Y* are the methyne protons of the cyclohexyl rings. In Figure 5 the experimental and simulated *A* part of the spectrum are reported. The spectroscopic features obtained through the analysis developed by Palmer and Whitcomb[10] are collected in Table 4. A similar pattern has been observed for the phosphorus atom of the coordinated secondary phosphane ligands in the palladium complexes [*trans*-Pd(SPh)$_2$-(PCy$_2$H)$_2$][11] and [*trans*-PdCl(CHCl$_2$)(P*t*Bu$_2$H)$_2$].[12]

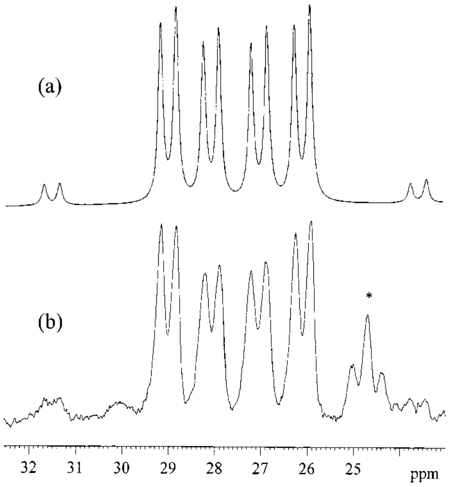
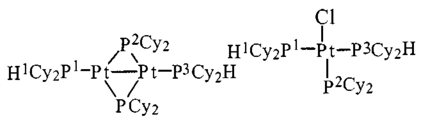


Figure 5. Proton-coupled $^{31}P$ NMR spectrum of complex **6** in the P$^1$ region ([D$_6$]benzene, 121 MHz, 295 K): (a) simulated, (b) experimental; the asterisked triplet belongs to P$^2$ satellites

The IR spectrum of **6** shows a strong band at 2324 cm$^{-1}$ attributed to the P−H stretching of the coordinated dicyclohexylphosphane ligands and a medium 259 cm$^{-1}$ band attributed to the Pt−Cl stretching. According to the above reported spectroscopic data, **6** can be formulated as [*trans*-Pt(PHCy$_2$)$_2$(PCy$_2$)Cl], a neutral terminal phosphido complex of platinum(II).

Due to the exceedingly high *trans*-effect of phosphido ligands, terminal (phosphido)platinum(II) complexes are quite rare, so that the pioneering work of Chatt and Davidson concluded that, at least in the case of diphenylphosphide, it seemed unlikely that such a ligand, terminally bound to platinum(II), could even exist.[13] Nevertheless, starting from the late 1980s, a number of terminal phosphido complexes of platinum(II) have been prepared. The first molecule of this type to be synthesised was the dichloro-

Table 4. Spectroscopic features for complexes **5** and **6** ([D$_6$]benzene, 295 K); chemical shifts are in ppm; coupling constants are in Hz



| | **5**[a] | **6**[b] |
|---|---|---|
| $\delta$ (P$^1$) | 19.6 | 27.6 |
| $\delta$ (P$^2$) | 242.0 | 20.6 |
| $\delta$ (H$^1$) | 6.17 | 4.09 |
| $\delta$ (Pt) | –5514 | –4825 |
| $^2J$(P$^1$–P$^2$) | 51 | 41 |
| $^{2/3}J$(P$^1$–P$^3$) | 70 | 420 |
| $^1J$(P$^1$–H$^1$) | 318 | 352 |
| $^3J$(P$^2$–H$^1$) | 13 | 6 |
| $^2J$(Pt–H$^1$) | ca. 50 | 108 |
| $^1J$(P$^2$–Pt) | 2598 | 931 |
| $^1J$(P$^1$–Pt) | 4811 | 3006 |
| $\nu$(Pt–Cl) | | 259 cm$^{-1}$ |
| $\nu$(P–H) | 2238 cm$^{-1}$ | 2324 cm$^{-1}$ |

[a] $|^2J$(P$^1$-Pt)$|$ = 50 Hz. [b] $^3J$(P$^3$-H$^1$) = 1 Hz.

phosphide complex [PtCl(PEt$_3$)(PCl$_2$)].[14] Other examples are the cations [Pt{PPh(CH$_2$CH$_2$PPh$_2$)$_2$}(PR$_2$)]$^+$ (R = Cy, Ph)[15] and [(xp$_3$)Pt(PEt$_2$)]$^+$ [xp$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$, P(CH$_2$CH$_2$PPh$_2$)$_3$][16] and the neutral [Pt(NCN)PPh$_2$)] [NCN = C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6] complex.[17] More recently, Glueck et al. have described a series of terminal (phosphido)platinum(II) complexes of the type [Pt(dppe)Me(X)]$^{n+}$ (X = primary or secondary phosphide, *n* = 0 or 1).[18]

In all of these terminal (phosphido)platinum complexes, the chemical shifts of the phosphido phosphorus atom fall in the range $\delta = -88.4$ to $\delta = 56.7$ and give scarce information about the character of the phosphorus ligand. On the other hand, the relatively small $^1J$(Pt-P) coupling constant expected between platinum and a terminal phosphido ligand, rationalised in terms of low *s* character of the Pt−P bond,[18b] can be taken as diagnostic of the presence of such a ligand. The value of the relevant $^1J_{\mathrm{Pt,P}}$ for the aforementioned complexes ranges from 767 Hz to 1305 Hz. The $^1J$(Pt-P) = 931 Hz found for **6** supports our assignment as [*trans*-Pt(PCy$_2$H)$_2$(PCy$_2$)Cl].[19]

In order to gain insight into the structure of complex **6**, a crystallographic analysis was undertaken. The X-ray diffraction study revealed that **6** crystallises in the space group $P\bar{1}$ and contains a distorted square-planar platinum(II) centre (Figure 6 and Table 5), the largest angle between ligands being 99.87(11)° [P(3)−Pt−P(2)]. A tetrahedral distortion from planarity is also evident from the 172.46(12)° [P(3)−Pt−P(1) and 171.98(12)° [P(2)−Pt−Cl] angles, significantly differing from the ideal 180°.

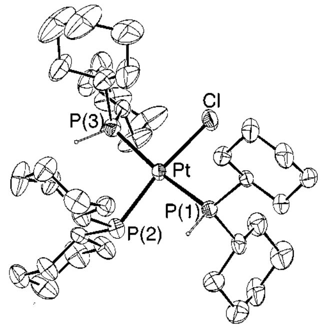


Figure 6. Displacement ellipsoid plot[29] of **6**; ellipsoids are scaled to 30% probability, H atoms are shown with arbitrary radii

Table 5. Selected bond lengths [Å] and angles [°] for **6**

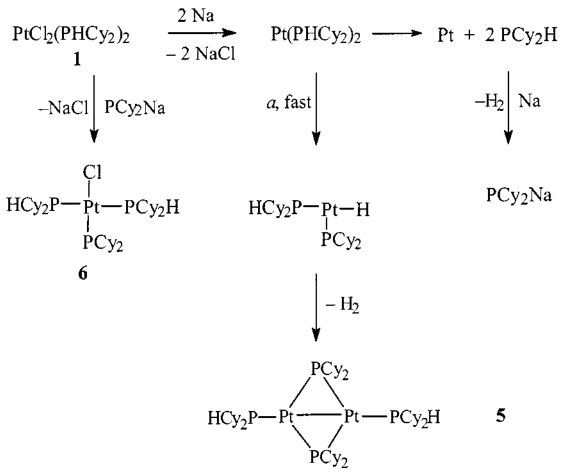
| | |
|---|---|
| Pt−P(3) | 2.272(3) |
| Pt−P(1) | 2.293(3) |
| Pt−P(2) | 2.326(3) |
| Pt−Cl | 2.421(3) |
| P(3)−Pt−P(1) | 172.46(12) |
| P(3)−Pt−P(2) | 99.87(11) |
| P(1)−Pt−P(2) | 85.63(11) |
| P(3)−Pt−Cl(1) | 86.03(11) |
| P(1)−Pt−Cl(1) | 89.01(11) |
| P(2)−Pt−Cl(1) | 171.98(12) |

The phosphide P atom is pyramidal as indicated by the sum of the angles at P(2) of 320.5° (compared to 328.5° for a tetrahedral and 360° for a planar atom). The hydrogen atoms bonded to the phosphorus atom were located in a Fourier difference synthesis. The two P−H bonds of the dicyclohexylphosphane ligands are both oriented toward the phosphido ligand; such orientation minimises the repulsions between the six cyclohexyl groups around the Pt atom. The relatively long[20] Pt−Cl bond [2.421(3) Å] indicates a pronounced *trans* effect of the terminal phosphide group. The P(2)−Pt bond length [2.326(3) Å] is slightly shorter than those reported for related terminal phosphido platinum(II) complexes. The Pt−P(phosphido) bond lengths of Pt(dppe)(Me)(PHMes*),[18b] Pt(dppe)(Me)(PMes$_2$),[18b] and Pt(*S*,*S*-Chiraphos)(Me)(PPhIs)[18d] [Mes* = 2,4,6-(*t*Bu)$_3$C$_6$H$_2$, Mes = 2,4,6-Me$_3$C$_6$H$_2$, Chiraphos = 2,3-bis(diphenylphosphanyl)butane, Is = 2,4,6-(*i*Pr)$_3$C$_6$H$_2$] are, in fact, 2.378(5), 2.351(2), and 2.3622(15) Å, respectively.

A possible pathway for the reaction of **1** with sodium at room temp. could start with the abstraction of two subsequent chloride ions giving the dicoordinated Pt$^0$ complex [Pt(PHCy$_2$)$_2$] (Scheme 2). This intermediate could lead to intramolecular electrophilic attack of one coordinated PHCy$_2$ yielding [Pt(H)(PCy$_2$)(PHCy$_2$)] which, in turn, can dimerise to **5** via reductive elimination of hydrogen.[21]

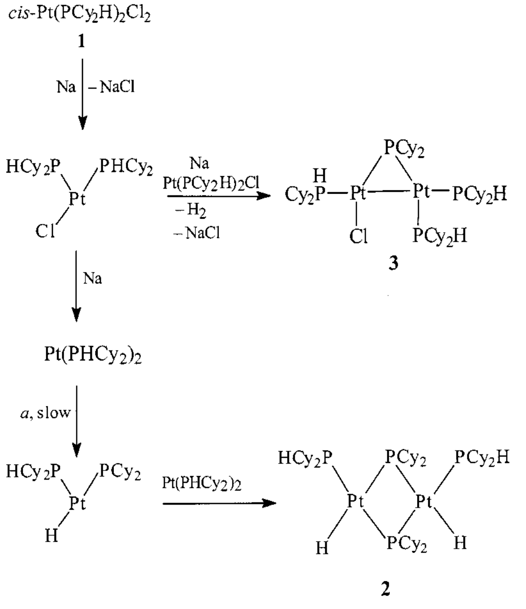
On the other hand, at room temperature, **1** could also react with sodium dicyclohexylphosphide (one of the products formed when **1** decomposes in the presence of sodium metal) giving **6** by substitution of the chloride ion with the dicyclohexylphosphide group (Scheme 2). A confirmation of this proposed mechanism came from the reaction between **1** and LiPCy$_2$ which gave pure **6**.[22]

The lack of formation of both **5** and **6** when the reaction of **1** with sodium metal is carried out at 0 °C can be explained by admitting that both chloride ion abstraction and intramolecular attack of a dicyclohexylphosphane ligand in [Pt(PHCy$_2$)$_2$] leading to [Pt(H)(PCy$_2$)(PHCy$_2$)] (Step *a* in Scheme 2) are temperature-sensitive and slow in the reac-



Scheme 2. Proposed mechanism for the sodium reduction of **1** at room temperature

tion at 0 °C. Under these conditions both intermediate $[PtCl(PHCy_2)_2]$ and $[Pt(PHCy_2)_2]$ could accumulate in the reaction medium (Scheme 3). Therefore $[Pt(PHCy_2)_2]$ may become the preferential target for the attack of $[Pt(H)(PCy_2)(PHCy_2)]$ which results in the formation of **2** (effectively found in the reaction solution at 0 °C as the major product). On the other hand, dimerization of $[PtCl(PHCy_2)_2]$ by HCl evolution (revealed as $H_2$ and NaCl formation in the presence of Na) could also account for the formation of compound **3** as the minor product.



Scheme 3. Proposed mechanism for the sodium reduction of **1** at 0 °C

## Experimental Section

**General Remarks:** All manipulations were carried out under pure dinitrogen, using freshly distilled and oxygen-free solvents. All aromatic deuterated solvents were carefully dehydrated (Na) and deoxygenated (freeze and pump). Dicyclohexylphosphane was purchased from Strem and used as received. $PCy_2Li$[23] and $PtCl_2(PhCN)_2$[24] were prepared by literature methods. Infrared spectra were recorded with a Bruker Vector 22 spectrometer. Elemental analyses (C, H) were carried out using a Carlo Erba model EA 1108 instrument. The Cl and P contents (where reported) were determined by potentiometric titration with AgCl (716DMS Metrohm) and by spectrophotometric methods (Uvikon 942 Kontron, λ = 460 nm), respectively. NMR spectra were recorded with BRUKER Avance DRX500 (CARSO), BRUKER Avance DPX300, and VARIAN XL200 spectrometers; frequencies are referenced to $Me_4Si$ ($^{1}H$ and $^{13}C$), 85% $H_3PO_4$ ($^{31}P$), and $H_2PtCl_6$ ($^{195}Pt$).

***cis*-Dichlorobis(dicyclohexylphosphane)platinum(II) (1):**[25] 1.45 g of dicyclohexylphosphane, dissolved in 10 mL of toluene, was added dropwise to a toluene solution of *trans*-$PtCl_2(PhCN)_2$ (1.7 g in 30 mL) kept at 60 °C. After 1.5 h, the resulting white suspension was cooled at room temp. and the solid filtered off, washed with toluene (5 mL), and dried under vacuum affording pure **1** as a colourless microcrystalline powder (2.03 g, 85% yield). IR (nujol mull): $\tilde{\nu}_{max}$ = 2351 w (P–H), 285 m (Pt–Cl) $cm^{-1}$. $^{1}H$ NMR ($CDCl_3$, 500 MHz): $\delta = 3.60$ [m, $^{1}J$(P-H) = 362, $^{2}J$(Pt-H) = 96, $^{2}J$(*H*P-C*H*) = 6 Hz, PH]. $^{31}P$ NMR ($CDCl_3$, 202 MHz): $\delta = 18.6$ [s, $^{1}J$(P-Pt) = 3402, $^{1}J$(P-H) = 362, $^{2}J$(P-P′) = 19, $^{3}J$(P-H′) = 8 Hz]. $^{195}Pt\{^{1}H\}$ NMR ($CDCl_3$, 64 MHz): $\delta = -4540$ [t, $^{1}J$(P-Pt) = 3402 Hz]. $C_{24}H_{46}Cl_2P_2Pt$ (662.58): calcd. C 43.51, H 7.00, Cl 10.70, P 9.35; found C 43.48, H 7.10, Cl 10.75, P 9.27.

**Reduction of 1 with Sodium at 0 °C:** A suspension of *cis*-$PtCl_2(PHCy_2)_2$ (**1**) (0.98 g, 1.48 mmol) and sodium metal (0.067 g, 2.91 mmol) in toluene (40 mL) was vigorously stirred at 0 °C (ice bath) for 9 h. In the course of the reaction dihydrogen evolved, as revealed by gas chromatographic analysis. The resulting suspension was filtered (to remove 0.243 g of unchanged **1** and 0.104 g of platinum metal) and the solvent was removed at low temperature (0 °C). Treatment of the obtained solid with cold methanol afforded pure **2** (0.12 g, 13.7% yield) as a white powder and a yellow solution from which, after solvent removal and crystallisation of the residue from THF/*n*-hexane (1:1) at −30 °C, pure **3** precipitated as a yellow solid (28 mg, 3.1% yield). $^{1}H$ NMR spectroscopic features of **2** other than those reported in Table 1 ([D$_8$]toluene, 295 K): $\delta = 4.50$ [br. d, $^{1}J$(P-H) = 317 Hz, *H*-P$^{2}$). IR (nujol mull): $\tilde{\nu}_{max}$ = 2299 w (P–H), 1940 s (Pt–H) $cm^{-1}$. $C_{48}H_{92}P_4Pt_2$ (1183.34): C 48.72, H 7.84, P 10.47; found C 47.86, H 7.95, P 10.13. $^{1}H$ NMR spectroscopic features of **3** other than those reported in Table 2 ([D$_8$]toluene, 295 K): $\delta = 4.31$ [d, $^{1}J$(P-H) = 319 Hz, *H*-P$^{4}$], $\delta = 4.45$ [d, $^{1}J$(P-H) = 312 Hz, *H*-P$^{2}$], $\delta = 5.3$ [br. d $^{1}J$(P-H) = 320 Hz, *H*-P$^{3}$]. IR (nujol mull): $\tilde{\nu}_{max}$ = 2295 w and 2255 w (P–H), 301 w (Pt–Cl) $cm^{-1}$. $C_{48}H_{91}ClP_4Pt_2$ (1217.78): calcd. C 47.34, H 7.53, Cl 2.91; found C 46.87, H 7.27, Cl 2.85.

**Isomerisation of 3 To Give 4:** A toluene solution of **3** was stirred at 50 °C for 5 h causing the colour to lighten from yellow-orange to pale yellow. Evaporation of the solvent afforded a solid, which was washed with cold methanol and after crystallisation from toluene/*n*-hexane (2:1), **4** was obtained as white needles. IR (nujol mull): $\tilde{\nu}_{max}$ = 2301 w (P–H), 1929 w (Pt–H), 281 w (Pt–Cl) $cm^{-1}$. $^{1}H$ NMR spectroscopic features of **4** other than those reported in Table 3 ([D$_6$]benzene, 295 K): $\delta = 4.35$ [d, $^{1}J$(P-H) = 314, $^{2}J$(Pt-H) = 98 Hz, *H*-P$^{2}$], $\delta = 4.79$ [d, $^{1}J$(P-H) = 320 Hz, *H*-P$^{4}$]. $C_{48}H_{91}ClP_4Pt_2$ (1217.78): calcd. C 47.34, H 7.53, Cl 2.91, P 10.17; found C 46.38, H 7.68, Cl 2.85, P 10.12.

**Reduction of 1 with Sodium at Room Temperature:** A suspension of *cis*-PtCl$_2$(PHCy$_2$)$_2$ (0.30 g, 0.45 mmol) and sodium metal (0.10 g, 4.3 mmol) in toluene (30 mL) was vigorously stirred at room temperature (25 °C) for 70 min. In the course of the reaction dihydrogen was evolved, as revealed by gas chromatographic analysis. The resulting suspension was filtered and the solvent was removed in vacuo from the yellow-orange filtrate. The residue was redissolved in deuterated benzene and used for NMR spectroscopic analysis, revealing the formation of **5** and **6** in an approximately 1:3 ratio.

**Reduction of 3 with Sodium:** A light yellow solution of complex **3** in [D$_6$]benzene was treated with sodium sand in an NMR tube at room temperature until the hydrogen evolution stopped (about 0.5 h). The resulting dark yellow solution was analysed by NMR spectroscopy giving signals due to **5** alone.

***trans*-Chloro(dicyclohexylphosphido)bis(dicyclohexylphosphane)-platinum(II) [Pt(PHCy$_2$)$_2$(PCy$_2$)Cl] (6):** A suspension of *cis*-[Pt(PHCy$_2$)$_2$Cl$_2$] (0.54 g, 0.82 mmol) and PCy$_2$Li (0.166 g, 0.82 mmol) in toluene (20 mL) was vigorously stirred at 0 °C until a yellow solution was obtained (about 8 h). LiCl was filtered and the solution concentrated in vacuo to ca. 5 mL. By cooling at −20 °C pale yellow crystals of **6** precipitated which were isolated by filtration (0.435 g, 65%). IR (nujol mull): $\tilde{\nu}_{max}$ = 2324 s (P−H), 259 m (Pt−Cl) cm$^{-1}$. C$_{36}$H$_{68}$ClP$_3$Pt (824.40): calcd. C 52.45, H 8.31, Cl 4.30, P 11.27; found C 51.93, H 8.45, Cl 4.37, P 11.32.

**X-ray Data Collection, Structure Solution, and Refinement of 6:**[26] Crystal data and parameters for intensity data collection and structure refinement are compiled in Table 6. A pale yellow rod with the approximate dimensions of 0.15 × 0.11 × 0.03 mm was studied at room temperature with a BRUKER-AXS SMART Apex diffractometer. An empirical absorption correction[27] was applied (max. trans. 1.000, min. trans. 0.797). The structure was solved by direct methods and refined on $F^2$ with the SHELXTL[28] suite of programs.

Table 6. Crystal data and structure refinement for **6**

| | |
|---|---|
| Empirical formula | C$_{36}$H$_{68}$ClP$_3$Pt |
| Formula mass | 824.35 |
| Temperature [K] | 293(2) |
| Wavelength [Å] | 0.71073 |
| Crystal system | triclinic |
| Space group | $P\bar{1}$ (no. 2) |
| Unit cell dimensions | |
| $a$ [Å] | 9.9460(10) |
| $b$ [Å] | 10.7743(11) |
| $c$ [Å] | 18.772(2) |
| $\alpha$ [°] | 80.872(2) |
| $\beta$ [°] | 79.098(2) |
| $\gamma$ [°] | 82.054(3) |
| $V$ [Å$^3$] | 1938.1(3) |
| $Z$ | 2 |
| $D_{calcd.}$ [Mg m$^{-3}$] | 1.413 |
| Absorption coeff. [mm$^{-1}$] | 3.835 |
| $\theta$ range for data coll. [°] | 1.12−28.26 |
| Independent reflections | 9509 |
| Observed reflections | 3665 |
| Refinement method | full-matrix least squares on $F^2$ |
| Data/parameters | 9509/370 |
| Goodness-of-fit on $F^2$ | 0.840 |
| Final $R$[a] [$I > 2\sigma(I)$][a] | 0.0747 |
| $wR2$[b] (all data) | 0.1279 |
| Largest diff. peak/hole [eÅ$^{-3}$] | 1.657, −0.881 (close to Pt) |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

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[19] In this regard it should be noted that the related complex *trans*-Pt(PEt$_3$)(PPhH)Cl proposed as intermediate in the reaction between (PPh)$_5$ and PtCl$_2$(PEt$_3$)$_2$ on the basis of its spectroscopic features (I. P. Parkin, A. M. Z. Slawin, D. J. Williams, D. Woollins, *Inorg. Chim. Acta* **1990**, *172*, 159−163) exhibits a coupling constant $^1J$(P-Pt) of 3460 Hz which seems to be very unusual for a terminal phosphide group.

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[22] Such a type of reaction is unprecedented for Pt species, except in the case of (Et$_3$P)$_2$PtCl$_2$ with LiP(SiMe$_3$)$_2$ reported in ref.[9] where unstable compounds such as (Et$_3$P)$_2$Pt[P(SiMe$_3$)$_2$]Cl and (Et$_3$P)$_2$Pt[P(SiMe$_3$)$_2$]$_2$ form, the latter of which, in turn, affords, by splitting off of the phosphane ligands, a mixture of a (diphosphene)Pt$^0$ complex and a phosphido-bridged Pt$^I$ complex.

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[26] CCDC-172800 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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