Platinum(II) Complexes with 1-Cyclohepta-2,4,6-trienyl-diphenylphosphane, $Ph_2P(C_7H_7)$, and Alkyn-1-yl Ligands

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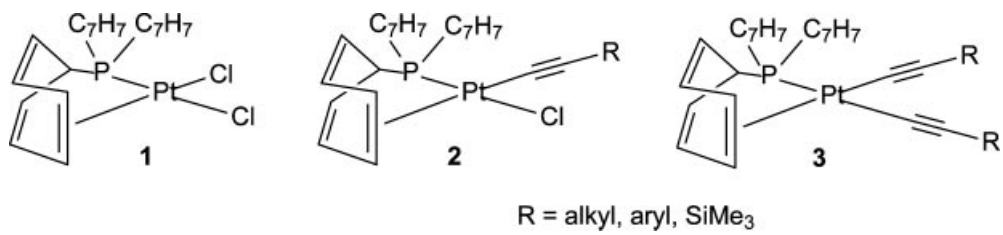
Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. [1-Cyclohepta-2,4,6-trienyl-diphenylphosphane]platinum(II) dichloride (**4**) was prepared by the 1:1 reaction of $(cod)PtCl_2$ (cod = η^4-cycloocta-1,5-diene) with the phosphane. The reaction of **4** with di(alkyn-1-yl)dimethylstannanes, $Me_2Sn(C{\equiv}C\text{-}R)_2$ [R = H (**a**), Me (**b**), Ph (**c**), $SiMe_3$ (**d**)], in boiling THF gave selectively in high yield the monoalkynyl complexes $[Ph_2P(C_7H_7)]Pt(Cl)C{\equiv}C\text{-}R$ (**6b,c,d**), in which the alkyn-1-yl group is arranged in *cis* position with respect to the phosphorus atom, and the C_7H_7 ring is η^2-coordinated to platinum through the central C=C bond. The same reaction at room temperature afforded, again selectively and in high yield, the dialkynyl complexes $[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}R)_2$ (**7a-d**). The new complexes were characterised in solution by ^1H, ^{13}C, ^{29}Si, ^{31}P and ^{195}Pt NMR spectroscopy, and the molecular structures of **4** and **7d** were determined by X-ray crystallography.

Keywords: Platinum; Tin; Alkynes; Phosphanes; NMR spectroscopy; Crystal structures



Introduction

Among chelating phosphanes coordinated to a metal by both the phosphorus atom and a C=C bond [1, 2], 1-cyclohepta-2,4,6-trienylphosphanes [3] deserve special attention. In the case of the complexes **2** and **3**, the nature of the platinum-ligand bonds in *cis*- and *trans*-positions relative to the phosphorus atom is remarkably different. It has been shown, that the complexes **2** are accessible selectively by the reaction of the platinum dichloride **1** [4] with di(alkyn-1-yl)-dimethylstannanes, $Me_2Sn(C{\equiv}C\text{-}R)_2$, in boiling THF [5], whereas the complexes **3** have been prepared [5] from the corresponding dialkyn-1-yl(cod)Pt complexes by the reaction with tri(cyclohepta-2,4,6-trienyl)phosphane, $P(C_7H_7)_3$ [3].

The presence of two pending C_7H_7 rings in the complexes **1** − **3** causes fast intramolecular exchange between the three C_7H_7 rings with respect to their coordination to platinum. This is evident from NMR spectra [4−6] and, therefore, one aim of this work was to replace the $P(C_7H_7)_3$ ligand by 1-cyclohepta-2,4,6-trienyl-diphenylphosphane, $Ph_2P(C_7H_7)$, in order to facilitate NMR spectroscopic studies. Another problem remained to be addressed, considering the current interest in alkyn-1-ylplatinum chemistry [7], namely the selectivity by which the complexes **2** are formed [5] in the exchange reaction of **1** with di(alkyn-1-yl)-dimethylstannanes. Thus, the complex **4**, analogous to **1** [4], was prepared (Scheme 1a) and characterised, and its reactivity towards di(alkyn-1-yl)dimethylstannanes, $Me_2Sn(C{\equiv}C\text{-}R)_2$ [R = H (**a**), Me (**b**), Ph (**c**), $SiMe_3$ (**d**)], was studied.

Results and Discussion

Synthesis of the [1-cyclohepta-2,4,6-trienyl-diphenylphosphane]platinum dichloride (**4**)

The reaction of $(cod)PtCl_2$ with one equivalent of 1-cyclohepta-2,4,6-trienyl-diphenylphosphane proved to be the most straightforward route to the platinum dichloride **4** (Scheme 1a). The complex **4** was formed in essentially quantitative yield as a yellowish solid, crystallised from CH_2Cl_2/hexane, and was characterised in solution by ^1H,

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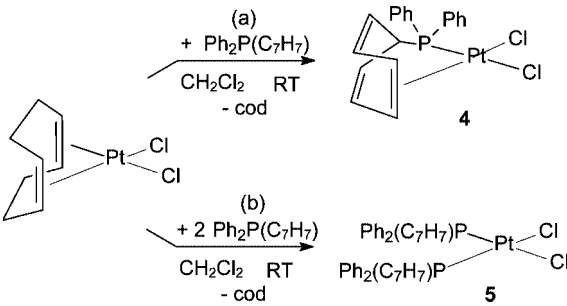
^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy (Table 1) and in the solid state by X-ray structural analysis (vide infra). An excess of the phosphane gave the complex **5**, in which the two phosphane ligands are in *cis*-positions and coordinated to platinum by the phosphorus atoms (Scheme 1b). The proposed structure of **5** is based on a consistent set of ^{1}H, ^{13}C, ^{31}P and ^{195}Pt NMR data (Table 1). Thus, the coupling constant $^{1}J(^{195}Pt,^{31}P)$ = 3666 Hz is observed in the typical range known for the *cis*-arrangement of phosphane ligands in platinum(II) dichlorides [8]. It should be noted that a complex analogous to **5** with the $P(C_7H_7)_3$ ligand is not accessible by this route [4]. The complex *trans*-$[(C_7H_7)_3P]_2PtCl_2$ has been identified in solution when $[PtCl_4]^{2-}$ reacts with two equivalents of $P(C_7H_7)_3$; however, even *trans*-$[(C_7H_7)_3P]_2PtCl_2$ rearranges slowly into **1** by elimination of phosphane [4].



Scheme 1 Synthesis of the complexes **4** and **5**, starting from $(cod)PtCl_2$.

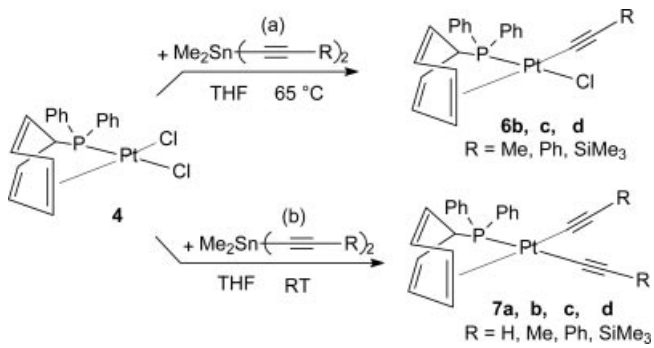
Table 1 ^{13}C, ^{31}P and ^{195}Pt NMR data of the platinum(II) complexes $[Ph_2P(C_7H_7)]PtCl_2$ (**4**) and $[Ph_2P(C_7H_7)]_2PtCl_2$ (**5**).

	4[a),c)]	**5**[b),c)]
^{13}C NMR		
C^{1}	38.3 [31.4]	38.4 [15.9] [40.7]
$C^{2,7}$	130.7 [1.7]	117.5
$C^{3,6}$	130.4 [11.2] {36.7}	125.8 [12.8]
$C^{4,5}$	80.9 {143.7}	130.4
Ph^{i}	125.0 [60.1]	128.4 [52.0]
Ph^{o}	133.8 [9.4]	134.0 [9.3]
Ph^{m}	128.6 [11.1]	128.2 [10.6]
Ph^{p}	132.3 [2.9]	131.3
^{31}P NMR	97.3 {4137}	14.0 {3666}
^{195}Pt NMR	549.4 [4137]	134.2 [3666]

[a)] In CD_2Cl_2 at 25 °C; [b)] in $CDCl_3$ at 25 °C; [c)] Coupling constants [$^{n}J(^{31}P,X)$], {$^{n}J(^{195}Pt,X)$} in Hz.

*Reaction of $[Ph_2P(C_7H_7)]PtCl_2$ (**4**) with di(alkyn-1-yl)dimethylstannanes, $Me_2Sn(C{\equiv}C\text{-}R)_2$*

The reaction of the dichloride **4** with $Me_2Sn(C{\equiv}C\text{-}R)_2$ [R = Me (**b**), Ph (**c**), $SiMe_3$ (**d**)] in boiling THF proceeds in the same way as has been reported for **1** [5], and the monoalkynyl complexes **6**, analogous to **2**, were isolated in high yield (Scheme 2a). However, by monitoring this reaction using ^{31}P NMR spectroscopy it became evident that the dialkynyl complexes **7**, analogues of **3**, are formed. These complexes **7** could be isolated when the reactions were carried out at room temperature (Scheme 2b). Except of the complex **7a** (R = H) which was found to decompose in CD_2Cl_2 solution after several hours at room temperature, all other complexes **6** and **7** could be kept in solution for prolonged periods. The ^{1}H, ^{13}C, ^{29}Si, ^{31}P and ^{195}Pt NMR data of **6** and **7** are listed in Table 2, and the molecular structure of **7d** was determined by X-ray analysis (vide infra).



Scheme 2 Selective synthesis of the complexes **6** and **7**, depending on the reaction conditions.

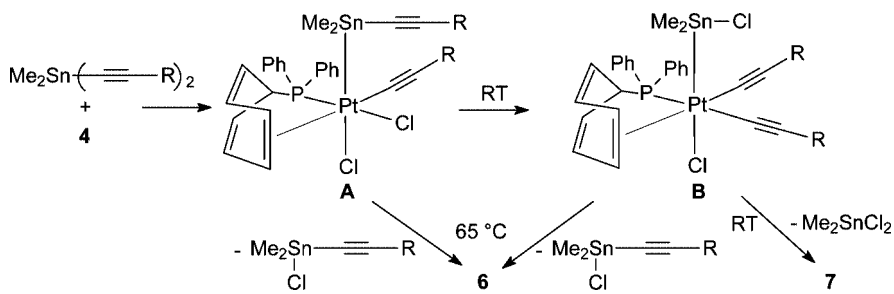
The known reaction of **1** with $Me_2Sn(C{\equiv}C\text{-}R)_2$ (R = Me, Ph, $SiMe_3$) [5] was then reinvestigated, and the same selectivity, depending on the reaction conditions, was observed. Thus, the complexes **3** and **7** can be obtained directly from the dichlorides **1** and **4**, respectively, avoiding the preparation of the intermediates $(cod)Pt(C{\equiv}C\text{-}R)_2$ [5].

In the case of bis(phosphane)palladium dichlorides, it has been found that exchange reactions with alkyn-1-yltin compounds lead to complexes containing Pd-Sn bonds, and this was explained by assuming short-lived Pd(IV) intermediates as a result of oxidative addition of the di(alkyn-1-yl)tin compounds [9]. A similar mechanism is proposed here (Scheme 3) for the alternative formation of **6** or **7**, starting from **4**. Fast reductive elimination of $Me_2Sn(Cl)C{\equiv}C\text{-}R$ in the intermediate **A** at elevated temperatures gives **6** or, at room temperature, **A** has time to rearrange into **B** by intramolecular exchange, followed by elimination of Me_2SnCl_2 to give **7**. It is also conceivable that at elevated temperatures the elimination of $Me_2Sn(Cl)C{\equiv}C\text{-}R$ from **B** to give **6** is preferred over the elimination of Me_2SnCl_2. These assumptions are supported by experimental observations. In equilibrated mixtures containing **7**, $Me_2Sn(Cl)C{\equiv}C\text{-}R$ and an excess of $Me_2Sn(C{\equiv}C\text{-}R)_2$, obtained at room temperature in THF, the formation of **6** at the cost of **7** starts at 40 °C. Addition of Me_2SnCl_2 to the reaction solution at room temperature shifts the equilibria from **7** towards **6**. In this context it is interesting to note that the reaction of $(dppe)PtCl_2$ with $Me_2Sn(C{\equiv}C\text{-}R)_2$ in THF gave selectively the dialkyn-1-yl complexes $(dppe)Pt(C{\equiv}C\text{-}R)_2$ under all experimental conditions studied [10].

Table 2 ^{13}C, ^{31}P, ^{195}Pt and ^{29}Si NMR data [a),b)] of the platinum(II) complexes $[Ph_2P(C_7H_7)]Pt(Cl)C{\equiv}C\text{-}R$ (**6**) and $[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}R)_2$ (**7**).

(R)	6b (Me)	6c (Ph)	6d ($SiMe_3$)[c)]	7a (H)	7b (Me)	7c (Ph)	7d ($SiMe_3$)[d)]
^{13}C NMR[b)]							
C^1	39.6 [30.5] {4.9}	39.4 [30.9] {5.3}	39.2 [30.7] {5.0}	39.4 [26.0] {11.0}	39.1 [24.9] {9.1}	39.8 [25.4] {10.8}	39.6 [25.2] {11.0}
$C^{2,7}$	128.5	127.7	128.5	129.8 [3.3]	128.8 [3.8]	130.2 [3.3]	130.1 [3.6]
$C^{3,6}$	130.3 [10.6]	129.9 [10.6]	130.0 [10.2]	130.0 [11.3]	130.3 [11.3]	130.7 [11.4]	130.4 [11.2]
$C^{4,5}$	95.1 {60.2}	96.4 {58.3}	96.9 {53.6}	91.8 {58.2}	89.5 {59.1}	91.5 {59.0}	92.7 {54.0}
Ph^i	126.5 [62.7]	128.5 [69.9]	126.3 [62.3]	129.2 [36.0]	128.9 [24.8]	128.7 [50.7]	128.4 [50.2]
Ph^o	134.3 [8.7] {25.2}	134.0 [10.0] {25.4}	134.2 [9.3] {27.5}	134.2 [9.8] {18.0}	134.2 [9.9] {18.4}	134.6 [9.8] {18.3}	134.6 [10.0] {18.1}
Ph^m	128.7 [11.7]	128.6 [11.0]	128.4 [11.0]	128.5 [10.4]	128.3 [10.2]	128.9 [10.5]	128.7 [10.4]
Ph^p	132.0	131.8 [2.8]	131.7 [2.9]	131.4 [2.5]	130.9 [2.5]	131.6 [2.6]	131.5 [2.5]
Pt-***C***≡C-*cis*; *trans* [e)]	76.8 [18.3] {1523.8}	92.1 [16.7] {1543.5}	107.1 [15.9] {1468.4}	96.8 [29.2] {n.o.} 104.2 [162.1] {n.o.}	76.7 [15.3] {1457.0} 97.6 [167.8] {1140.6}	90.6 [15.5] {1562.2} 111.5 [166.2] {1142.9}	108.1 [14.4] {1433.2} 131.6 [152.8] {1086.4}
-C≡***C***-R *cis*; *trans* [e)]	107.4 {402.0}	110.6 {424.5}	117.1 {336.5}	99.1 [2.2] {425.1} 89.9 [33.7] {296.5}	108.4 [1.9] {427.7} 98.1 [34.7] {301.4}	113.9 [2.3] {421.6} 105.1 [34.0] {295.5}	119.1 [1.7] {409.5} 108.4 [27.2] {259.8}
R	6.5 {26.3}	126.2, 126.4 129.0, 131.1	0.2	–	6.0 [3.2] {24.1} 6.1 [1.5] {26.7}	126.3, 126.5, 127.2 [1.5], 127.7 [3.6], 128.3, 128.5, 131.5, 132.1	0.4 [0.6] {3.4} 1.2 {2.8}
^{31}P NMR	85.6 {4210}	87.3 {4156}	86.5 s {4192}	99.7 {2745}	99.0 {2745}	100.1 {2727}	99.6 {2688}
^{195}Pt NMR	92.1 [4210]	92.4 [4156]	97.7 d [4192]	−51.3 [2745]	−18.9[2745]	−25.5 [2727]	−3.9 [2688]

[a)] In CD_2Cl_2 at 25 °C; n.o. means not observed. [b)] Coupling constants [$^nJ(^{31}P,X)$], {$^nJ(^{195}Pt,X)$} in Hz. [c)] ^{29}Si NMR: δ = −20.7 [0.7], {33.9}. [d)] ^{29}Si NMR: δ = −22.1 [3.5] {24.4} (*trans*); −21.3 [1.4] {37.1} (*cis*). [e)] Relative to the phosphorus atom (cf. Figure 1).



Scheme 3 Proposed mechanism for the selective formation of the complexes **6** and **7**.

The NMR data of the complexes **6** and **7** (Table 2) correspond closely to those obtained for the comparable complexes **2** and **3** [5]. This indicates that the influence of the phosphane ligands $Ph_2P(C_7H_7)$ and $P(C_7H_7)_3$ on the electronic structure of the platinum(II) complexes is very similar. Clearly, any fluxional character associated with the C_7H_7 groups in **2** and **3** is absent in **6** and **7**. Therefore, the assignments of the NMR data for the C_7H_7 ring in **4**, **6** and **7** are straightforward. As for **3**, the different ^{13}C NMR data for the alkyny-1-yl groups in *cis*- and *trans*-positions relative to the phosphorus atom in **7** are noteworthy. The ^{29}Si NMR spectrum of **7d** (Figure 1) shows the sensitivity of the ^{29}Si NMR parameters to the influence exerted by the other ligands in *trans*-positions although they are removed by four bonds from the ^{29}Si nuclei. The fast nuclear spin relaxation of ^{195}Pt is also evident from the significantly broadened ^{195}Pt satellites. The relaxation times $T_{1,2}(^{195}Pt)$ become short in Pt(II) complexes because of the efficient relaxation mechanism due to chemical shift anisotropy, depending on B_0^2 [11].

X-Ray structure determinations of **4** *and* **7d**

The molecular structures of the platinum dichloride $[Ph_2P(C_7H_7)]PtCl_2$ (**4**) and of the dialkynyl complex $[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}SiMe_3)_2$ (**7d**) were determined by X-ray analysis (Figures 2 and 3). Selected bond lengths and angles are listed in the Tables 3 and 4. Both complexes are typical 16e platinum(II) complexes with "square-planar" coordination geometry. The phosphane is a chelating ligand with the lone pair of electrons and the central C=C bond of the C_7H_7 ring. The C=C bond axis of the η^2-coordinated double bond is arranged almost exactly perpendicular to the coordination plane (dihedral angles are 88.7° in **4** and 84.6° in **7d**). Expectedly, this C=C bond with 138.9(11) pm in **4** and 140.8(9) pm in **7d** is found to be shorter than a typical single (154 pm) and longer than a typical double bond (134 pm). The data compare well with the data for the η^2-coordinated C=C bonds in numerous platinum com-

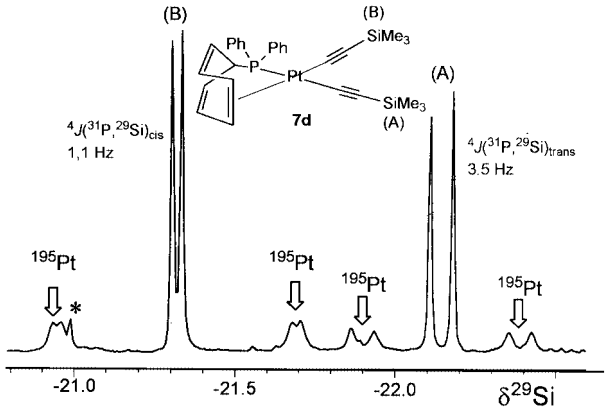


Figure 1 49.7 MHz $^{29}Si\{^1H\}$ NMR spectrum (INEPT [18]) of $[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}SiMe_3)_2$ (**7d**) dissolved in CD_2Cl_2 (saturated solution at 23 °C). Note the broadening of the ^{195}Pt satellites (marked by arrows) as a result of short ^{195}Pt nuclear spin relaxation caused by the chemical shift anisotropy mechanism. A weak signal belonging to an impurity is marked by an asterisk.

plexes containing the $P(C_7H_7)_3$ ligand [4−6] and also with data for(cod)$PtCl_2$ (137.5(8)/138.7(8) pm [12]).

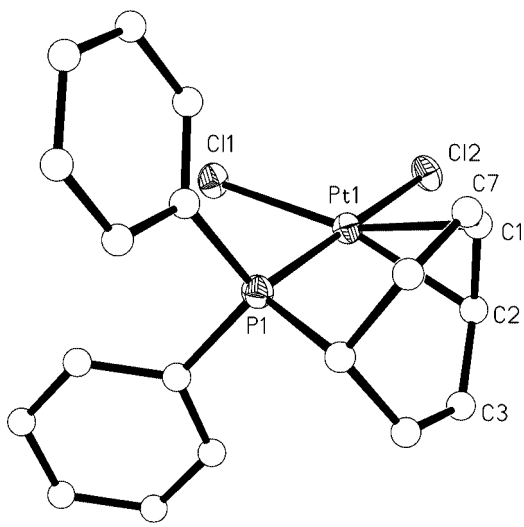


Figure 2 Molecular structure of $[Ph_2P(C_7H_7)]PtCl_2$ (**4**) (ellipsoids correspond to the 50 % probability level).

In the complex **4**, the Pt-Cl distances are significantly different, the one for the chloro ligand *trans* to the coordinated C=C bond (232.40(17) pm) being shorter than the other one in *trans*-position to the phosphorus atom (239.38(16)pm). This effect is comparable to that found for the Pt-I distances in $[P(C_7H_7)_3]PtI_2$ [4].

The Pt-C≡ distance *trans* to the coordinated C=C bond (and *cis* to the phosphorus atom) in **7d** (196.8(7) pm) is observed in the normal range of 193-198 pm, expected for such compounds [13]. However, the Pt-C≡ bond *trans* to phosphorus is significantly enlarged to 201.4(7) pm. This appears to be compensated to some extent by opposite changes in the C≡C bond lengths with 118.90(10) pm for the alkynyl group trans to phosphorus, and 120.5 (9) pm for the alkynyl group trans to the C=C bond.

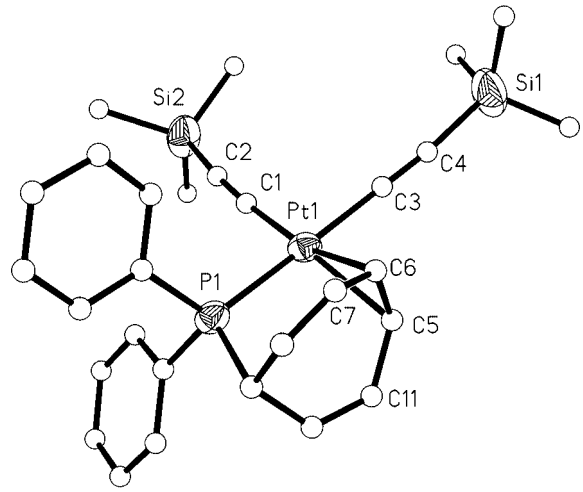


Figure 3 Molecular structure of $[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}SiMe_3)_2$ (**7d**) (ellipsoids correspond to the 50 % probability level).

Table 3 Selected bond lengths/pm and angles/° for $[Ph_2P(C_7H_7)]PtCl_2$ (**4**) (see Figure 2).

Pt(1)-C(1)	218.6(6)	C(1)-Pt(1)-P(1)	91.94(19)
Pt(1)-C(2)	219.4(7)	C(2)-Pt(1)-P(1)	93.0(2)
Pt(1)-P(1)	221.35(17)	C(1)-Pt(1)-Cl(1)	158.0(2)
Pt(1)-Cl(1)	232.40(17)	C(2)-Pt(1)-Cl(1)	165.0(2)
Pt(1)-Cl(2)	239.38(16)	P(1)-Pt(1)-Cl(1)	86.21(7)
C(1)-C(2)	138.9(11)	C(1)-Pt(1)-Cl(2)	91.64(19)
C(1)-C(7)	146.6(10)	C(2)-Pt(1)-Cl(2)	88.5(2)
C(2)-C(3)	144.7(11)	P(1)-Pt(1)-Cl(2)	175.81(6)
		Cl(1)-Pt(1)-Cl(2)	91.28(6)

Table 4 Selected bond lengths/pm and angles/° for $[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}SiMe_3)_2$ (**7d**) (see Figure 3).

C(1)-C(2)	120.5(9)	C(2)-C(1)-Pt(1)	175.1(6)
C(1)-Pt(1)	196.8(7)	C(1)-C(2)-Si(2)	174.1(7)
C(2)-Si(2)	181.6(7)	C(4)-C(3)-Pt(1)	178.6(6)
C(3)-C(4)	118.9(10)	C(3)-C(4)-Si(1)	174.1(7)
C(3)-Pt(1)	201.4(7)	C(6)-C(5)-C(11)	125.5(6)
C(4)-Si(1)	181.3(8)	C(6)-C(5)-Pt(1)	73.1(4)
C(5)-C(6)	140.8(9)	C(11)-C(5)-Pt(1)	112.5(4)
C(5)-C(11)	145.1(8)	C(5)-C(6)-C(7)	125.0(6)
C(5)-Pt(1)	226.5(6)	C(5)-C(6)-Pt(1)	70.9(3)
C(6)-C(7)	145.2(10)	C(7)-C(6)-Pt(1)	115.8(5)
C(6)-Pt(1)	229.4(6)		

By comparing Pt-P distances [13], the Pt-P bond length (221.35(17) pm) in **4** (chloro ligand *trans* to phosphorus) appears to be short, and also Pt-P = 229.60(17) pm in **7d** (alkynyl ligand *trans* to phosphorus) is more on the short side of the known range. In the case of **7d**, there may be a relation between shortening of the Pt-P bond and elongation of the Pt-C≡ bond in *trans*-position to phosphorus.

Conclusions

1-Cyclohepta-2,4,6-trienyl-diphenylphosphane, $Ph_2P(C_7H_7)$, is a useful chelating ligand for complexes of platinum(II) bearing chloro and/or alkyn-1-yl ligands. As already shown

in previous studies [5, 9, 10], di(alkyn-1-yl)dimethylstannanes serve as versatile alkynyl transfer reagents in reactions with platinum(II) dichlorides. The unique dependence on reaction conditions, opening selective routes to the transfer of one or two alkyn-1-yl groups, indicates that short-lived intermediates formed by oxidative addition are involved.

Experimental Section

General and starting materials

Preparation and handling of all compounds were carried out in an atmosphere of dry argon, and carefully dried solvents were used throughout. Starting materials were prepared according to literature procedures, e.g. (cod)$PtCl_2$ [14], $Ph_2P(C_7H_7)$ [15], $Me_2Sn(C{\equiv}C\text{-}H)_2$ [16], $Me_2Sn(C{\equiv}C\text{-}R)_2$ (R = Me, Ph, $SiMe_3$) [17], or were used as commercial products without further purification, e.g. Me-C≡C-H, Ph-C≡C-H, Me_3Si-C≡C-H. NMR spectroscopy: Bruker ARX 250 or DRX 500 (^1H, ^{13}C, ^{29}Si, ^{31}P, ^{195}Pt NMR); direct single pulse measurements were used, or in the case of some ^{13}C and ^{29}Si NMR spectra, the refocused INEPT pulse sequence with ^1H decoupling [18], based on $^nJ(^{13}C,^1H) \approx 3 - 5$ Hz, and $^2J(^{29}Si,^1H) \approx 7$ Hz) was applied. Chemical shifts are given relative to Me_4Si [δ ^1H ($CD(H)Cl_2$) = 5.33; δ ^{13}C (CD_2Cl_2) = 53.8; δ ^{29}Si = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz]; external aqueous H_3PO_4 (85 %) with δ ^{31}P = 0 for $\Xi(^{31}P)$ = 40.480747 MHz, and δ ^{195}Pt = 0 for $\Xi(^{195}Pt)$ = 21.400000 MHz. IR spectra: Perkin Elmer Spectrum 2000 FTIR.

*Synthesis of [$Ph_2P(C_7H_7)$]$PtCl_2$ (**4**)*

The phosphane $Ph_2P(C_7H_7)$ (187 mg; 0.5 mmol), dissolved in CH_2Cl_2 (10 ml), was added dropwise to a solution of (cod)$PtCl_2$ (0.5 mmol) in CH_2Cl_2 (25 ml). The reaction mixture was stirred at room temperature for 2h, and then brought to dryness in a high vacuum. The remaining solid was washed with hexane (30 ml). Recrystallisation from CH_2Cl_2/hexane and drying under high vacuum gave pure **4** [m. p. 279 °C (dec.); 255 mg; 94 %], as a yellow powder.

^1H NMR (CD_2Cl_2, 25 °C): δ = 4.73 (dt, 1H, H^1, $^2J(^{31}P,^1H)$ = 13.6 Hz, $^3J(^1H,^1H)$ = 8.4 Hz), 5.83 (m, 2H, $H^{2,7}$), 5.95 (m, 2H, $H^{4,5}$, ^2J(195Pt,1H) = 18.6 Hz), 6.53 (m, 2H, $H^{3,6}$), 7.47 (m, 4H, Ph), 7.78−7.86 (m, 6H, Ph).

*Synthesis of [$Ph_2P(C_7H_7)$]$_2PtCl_2$ (**5**)*

The phosphane $Ph_2P(C_7H_7)$ (276 mg; 1.0 mmol), dissolved in CH_2Cl_2 (10 ml), was added dropwise to a solution of [(cod)$PtCl_2$] (0.5 mmol) in CH_2Cl_2 (25 ml). The reaction mixture was stirred at room temperature for 2 h, and then all volatiles were removed in a high vacuum. The remaining solid was washed with hexane (30 ml). Recrystallisation from CH_2Cl_2/hexane and drying under high vacuum gave pure **5** (368 mg; 91 %) as a yellow powder.

^1H NMR (CD_2Cl_2, 25 °C): δ = 2.23 (m, 2H, H^1), 5.27 (m, 4H, $H^{2,7}$), 6.13 (m, 4H, $H^{3,6}$), 6.44 (m, 4H, $H^{4,5}$), 7.36 (m, 8H, Ph), 7.46 (m, 12H, Ph).

*General procedure for the synthesis of [$Ph_2P(C_7H_7)$]Pt(Cl)C=C-R (**6**)*

A suspension of the complex [$Ph_2P(C_7H_7)$]$PtCl_2$ (**4**) (271 mg; 0.50 mmol) in THF (20 ml) was prepared, then $Me_2Sn(C{\equiv}C\text{-}R)_2$ (R = Me, Ph, $SiMe_3$) (0.28 mmol) was added, and the mixture was heated at reflux for 30 min. During this time a clear yellow solution was formed. The volume of the solution was reduced under vacuum to 5 ml, and hexane (50 ml) was added. The precipitate was separated, recrystallised from CH_2Cl_2/hexane, and dried in a high vacuum to give the products **6** as yellow powders.

6b: 254 mg (93 %).

^1H NMR (CD_2Cl_2, 25 °C): δ = 1.70 (s, 3H, $^4J(^{195}Pt,^1H)$ = 19.1 Hz, Me), 4.83 (dt, 1H, H^1 $^2J(^{31}P,^1H)$ = 13.3 Hz, $^3J(^1H,^1H)$ = 8.5 Hz), 5.60 (m, 2H, $H^{2,7}$), 5.99 (m, 2H, $H^{4,5}$ $^2J(^{195}Pt,^1H)$ = 40.3 Hz), 6.45 (m, 2H, $H^{3,6}$), 7.38−7.46 (m, 4H, Ph), 7.82−7.87 (m, 6H, Ph).

6c: m. p. 172 °C (dec.), 258 mg (85 %).

^1H NMR (CD_2Cl_2, 25 °C): δ = 4.97 (dt, 1H, H^1, $^2J(^{31}P,^1H)$ = 13.2 Hz, $^3J(^1H,^1H)$ = 8.8 Hz), 5.70 (m, 2H, $H^{2,7}$), 6.11 (m, 2H, $H^{4,5}$, $^2J(^{195}Pt,^1H)$ = 42.5 Hz), 6.54 (m, 2H, $H^{3,6}$), 6.81−7.07, 7.42-7.55, 7.87-7.94 (m, m, m,15H, Ph).
IR: ν(C≡C) = 2092 cm^{-1}.

6d: 224 mg (74 %).

^1H NMR (CD_2Cl_2, 25 °C): δ = −0.29 (s, 9H, $SiMe_3$), 4.85 (dt, 1H, H^1, $^2J(^{31}P,^1H)$ = 13.3 Hz, $^3J(^1H,^1H)$ = 8.6 Hz), 5.62 (m, 2H, $H^{2,7}$), 6.11 (m, 2H, $H^{4,5}$, $^2J(^{195}Pt,^1H)$ = 36.5 Hz), 6.48 (m, 2H, $H^{3,6}$), 7.36−7.52 (m, 4H, Ph), 7.84−7.92 (m, 6H, Ph).

*General procedure for the synthesis of [$Ph_2P(C_7H_7)$]Pt($C{\equiv}C\text{-}R)_2$ (**7**)*

The complex [$Ph_2P(C_7H_7)$]$PtCl_2$ (**4**) (271 mg; 0.50 mmol) was suspended in THF (20 ml), and then $Me_2Sn(C{\equiv}C\text{-}R)_2$ (R = H, Me, Ph, $SiMe_3$) (0.55 mmol) was added. When the mixture had been kept stirring at room temperature for 1 h, a clear yellow solution was formed. After removing all volatile materials in a high vacuum, hexane (30 ml) was added. The insoluble precipitate was separated, recrystallised from CH_2Cl_2/hexane, and dried in a high vacuum to give the products as yellow powders.

7a: m. p. 140 °C (dec.), 235 mg (90 %).

^1H NMR (CD_2Cl_2, 25 °C): δ = 2.32 (d, 1H, ≡C-H^{trans}, $^3J(^{195}Pt,^1H)$ = 43.8 Hz, $^4J(^{31}P,^1H)$ = 7.0 Hz), 2.60 (d, 1H, ≡C-H^{cis}, $^3J(^{195}Pt,^1H)$ = 67.3 Hz, $^4J(^{31}P,^1H)$ = 2.3 Hz), 4.98 (dt, 1H, H^1, $^2J(^{31}P,^1H)$ = 13.7 Hz, $^3J(^1H,^1H)$ = 8.6 Hz), 5.63 (m, 2H, $H^{2,7}$), 6.29 (m, 2H, $H^{4,5}$, $^2J(^{195}Pt,^1H)$ = 44.4 Hz), 6.45 (m, 2H, $H^{3,6}$), 7.42−7.51 (m, 4H, Ph), 7.85−7.93 (m, 6H, Ph). **IR**: ν(C≡C) = 2057 cm^{-1}.

7b: 236 mg (86 %).

^1H NMR (CD_2Cl_2, 25 °C): δ = 1.80 (d, 3H, Me^{trans}, $^4J(^{195}Pt,^1H)$ = 21.5 Hz, $^5J(^{31}P,^1H)$ = 2.1 Hz), 2.01 (d, 3H, Me^{cis}, $^4J(^{195}Pt,^1H)$ = 13.3 Hz, $^5J(^{31}P,^1H)$ = 2.1 Hz), 4.85 (dt, 1H, H^1, $^2J(^{31}P,^1H)$ = 13.2 Hz, $^3J(^1H,^1H)$ = 8.5 Hz), 5.51 (m, 2H, $H^{2,7}$), 6.11 (m, 2H, $H^{4,5}$, $^2J(^{195}Pt,^1H)$ = 42.2 Hz), 6.32 (m, 2H, $H^{3,6}$), 7.30−7.44 (m, 4H, Ph), 7.86−7.94 (m, 6H, Ph). **IR** ν(C≡C) = 2146 cm^{-1}.

7c: m. p. 105 °C (dec.), 246 mg (73 %).

^1H NMR (CD_2Cl_2, 25 °C): δ = 4.96 (dt, 1H, H^1, $^2J(^{31}P,^1H)$ = 13.7 Hz, $^3J(^1H,^1H)$ = 8.7 Hz), 5.62 (m, 2H, $H^{2,7}$), 6.37 (m, 2H, $H^{4,5}$, $^2J(^{195}Pt,^1H)$ = 45.2 Hz), 6.45 (m, 2H, $H^{3,6}$), 6.95−7.05, 7.13-7.21, 7.32-7.51, 7.89-7.97 (m, m, m, m, 20H,Ph). **IR** ν(C≡C) = 2118 cm^{-1}.

7d: 296 mg (89 %).

^1H NMR (CD_2Cl_2, 25 °C): δ = − 0.21, 0.15 (s, s, 9H, 9H, $SiMe_3$), 4.92 (dt, 1H, H^1 $^2J(^{31}P,^1H)$ = 13.3 Hz, $^3J(^1H,^1H)$ = 8.6 Hz), 5.55 (m, 2H, $H^{2,7}$), 6.22 (m, 2H, $H^{4,5}$, $^2J(^{195}Pt,^1H)$ = 43.8 Hz), 6.36 (m, 2H, $H^{3,6}$), 7.30−7.45 (m, 4H, Ph), 7.85−7.93 (m, 6H, Ph). **IR** ν(C≡C) = 2060 cm^{-1}.

X-ray structural analyses of the complexes **4** *and* **7d**

Single crystals of **4** and **7d** were mounted directly out of the mother liquid under N_2 atmosphere at low temperature. Relevant experimental details of the crystal structure analyses [19] are given in Table 5.

The intensity data were collected on a STOE IPDS II diffractometer with MoK_α-radiation (λ=71.073 pm, graphite monochromator) at 193(2) K. The hydrogen atoms are in calculated posi-

Table 5 Crystal structure data (at 193(2) K) for the complexes $[Ph_2P(C_7H_7)]PtCl_2$ (**4**), and $[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}SiMe_3)_2$ (**7d**).

	$[Ph_2P(C_7H_7)]PtCl_2$ (**4**)	$[Ph_2P(C_7H_7)]Pt(C{\equiv}C\text{-}SiMe_3)_2$ (**7d**)
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Unit cell dimensions	a = 1040.7(1) pm, α = 90.000°. b = 1220.3(1) pm, β = 90.000°. c = 1401.5(2) pm, γ = 90.000°.	a = 1284.1(1) pm, α = 90.000°. b = 2334.0(1) pm, β = 94.276(5)°. c = 3284.3(1) pm, γ = 90.000°.
Volume	1.7799(3) nm^3	9.82(1) nm^3
Z	4	12
Density (calculated)	2.024 Mg/m^3	1.460 Mg/m^3
Absorption coefficient	8.269 mm^{-1}	4.535 mm^{-1}
F(000)	1032	4260
Crystal size	0.32 x 0.23 x 0.19 mm^3	0.79 x 0.47 x 0.17 mm^3
Theta range for data collection	2.21 to 26.18°.	1.07 to 24.01°.
Index ranges	−12<=h<=12, −15<=k<=14, −17<=l<=17	14<=h<=14, −26<=k<=26, 0<=l<=37
Reflections collected	24338	29126
Independent reflections	3501 [R(int) = 0.0669]	15313 [R(int) = 0.0227]
Absorption correction	Numerical	Numerical
Max. and min. transmission	0.26 and 0.13	0.58 and 0.16
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3501 / 0 / 208	15313 / 0 / 920
Goodness-of-fit on F^2	1.340	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0187, wR2 = 0.0620	R1 = 0.0355, wR2 = 0.0926
R indices (all data)	R1 = 0.0199, wR2 = 0.0756	R1 = 0.0448, wR2 = 0.0956
Largest diff. peak and hole	0.879 and −1.603 e·$Å^{-3}$	2.129 and −1.817 e·$Å^{-3}$

tions. All non-hydrogen atoms were refined with anisotropic temperature factors.

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References

[1] (a) M. A. Bennett, H. W. Kouwenhoven, J. Lewis, R. S. Nyholm, *J. Chem. Soc.* **1964**, 4570. (b) M. A. Bennett, J. Chatt, G. J. Erskine, R. F. Long, R. S. Nyholm, *J. Chem. Soc.* **1967**, 501. (c) D. I. Hall, R. S. Nyholm, *J. Chem. Soc.* **1971**, 1491. (d) M. A. Bennett, W. R. Kneen, R. S. Nyholm, *J. Organomet. Chem*. **1971**, *26*, 293. (e) B. L. Simms, J. A. Ibers, *J. Organomet. Chem*. **1987**, *327*, 125.

[2] (a) K. Issleib, M. Haftendorn, *Z. Anorg. Allg. Chem*. **1967**, *351*, 9. (b) R. N. Haszeldine, R. J. Lunt, R. V. Parish, *J. Chem. Soc.* **1971**, 3705.

[3] (a) M. Herberhold, K. Bauer, W. Milius, *Z. Anorg. Allg. Chem*. **1994**, *620*, 2108. (b) M. Herberhold, K. Bauer, W. Milius, *J. Organomet. Chem*. **1995**, *502*, C1. (c) M. Herberhold, W. Milius, St. Eibl, *Z. Anorg. Allg. Chem*. **1999**, *625*, 341.

[4] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Z. Anorg. Allg. Chem.* **2002**, *628*, 437.

[5] M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *J. Organomet. Chem*. **2002**, *641*, 173,

[6] (a) M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Z. Naturforsch*. **2002**, *57b*, 53. (b) M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Z. Anorg. Allg. Chem.* **2002**, *628*, 979. (c) M. Herberhold, T. Schmalz, W. Milius, B. Wrackmeyer, *Inorg. Chim. Acta* **2003**, *352*, 51.

[7] (a) K. Osakada, T. Yamamoto, *Coord. Chem. Rev.* **2000**, *198*, 379. (b) N. J. Long, C. K. Williams, *Angew. Chem.* **2003**, *115*, 2690; *Angew. Chem. Int. Ed.* **2003**, *42*, 2586. (c) A. J. Canty, T. Rodemann, B. W. Skelton, A. H. White, *Inorg. Chem. Commun.* **2003**, *8*, 55.

[8] P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*. In Diehl, P., Fluck, E., Kosfeld, R. (eds.), *NMR − Basic Principles and Progress*, Vol. 16, Springer, Berlin, 1979.

[9] (a) C. Stader, B. Wrackmeyer, *J. Organomet. Chem*. **1985**, *295*, C11. (b) A. Sebald, C. Stader, B. Wrackmeyer, W. Bensch, *J. Organomet. Chem*. **1986**, *311*, 233.

[10] A. Sebald, B. Wrackmeyer, *Z. Naturforsch*. **1983**, *38b*, 1156.

[11] A. Syed, E. D. Stevens, S. G. Cruz, *Inorg. Chem.* **1984**, *23*, 3673.

[12] P. S. Pregosin, in P. S. Pregosin (ed.), *Transition Metal Nuclear Magnetic Resonance*, Elsevier, Amsterdam, 1991, pp. 216−263.

[13] (a) A. Sebald, B. Wrackmeyer, C. R. Theocharis, W. Jones, *J. Chem. Soc., Dalton Trans.* **1984**, 747. (b) U. Behrens, K. Hoffmann, J. Kopf, J. Moritz, *J. Organomet. Chem*. **1976**, *117*, 91. (c) P. J. Stang, M. H. Kowalski, *J. Am. Chem. Soc*. **1989**, *111*, 3356. (d) H. Ogawa, K. Onitsuka, T. Joh, S. Takahashi, *Organometallics* **1988**, *11*, 2257. (e) C. J. Cardin, D. J. Cardin, M. F. Lappert, K. W. Muir, *J. Chem. Soc. Dalton Trans.* **1978**, 46. (f) U. Croatto, L. Toniolo, A. Immirzi, G. Bombieri, *J. Organomet. Chem*. **1975**, *102*, C31. (g) H. Lang, A. del Villar, G. Rheinwald, *J. Organomet. Chem*. **1999**, *587*, 284.

[14] J. X. McDermott, J. F. White, G. M. Whitesides, *J. Am. Chem. Soc*. **1976**, *98*, 6521.

[15] M. Herberhold, B. Ullmann, B. Wrackmeyer, manuscript in preparation.

[16] B. Wrackmeyer, in R. B. King, J. J. Eisch (eds.) *Organometallic Syntheses*, Vol. 3, p. 572, Elsevier, New York, 1986.

[17] W. E. Davidsohn, M. C. Henry, *Chem. Rev.* **1967**, *67*, 73.

[18] (a) G. A. Morris, R. Freeman, *J. Am. Chem. Soc*. **1979**, *101*, 760. (b) G. A. Morris, *J. Am. Chem. Soc*. **1980**, *102*, 428. (c) D. P. Burum, R. R. Ernst, *J. Magn. Reson*. **1980**, *39*, 163.

[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-263004 (**4**) and CCDC-263006 (**7d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (internat.): +44 (0)1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

