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ALKYNYL/CHLORIDE EXCHANGE BETWEEN *trans*-PLATINUM(II) AND -PALLADIUM(II) CHLORIDES AND ALKYNYLSTANNANES. CRYSTAL STRUCTURE OF *trans*-[BIS(1-PROPYNYL)-BIS(TRIETHYLPHOSPHINE)PLATINUM(II)]

ANGELIKA SEBALD, CARIN STADER, BERND WRACKMEYER*,

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-8000 München 2 (F.R.G.)

and WOLFGANG BENSCH

Anorganisch Chemisches Institut der Universität Zürich, Winterthurer Strasse 190, CH-8057 Zürich (Switzerland)

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Summary

The reaction between alkynylstannanes (**3,4**) and *trans*-[$(Et_3P)_2PtCl_2$] (**1**) gives *trans*-[$(Et_3P)_2Pt(Cl)C{\equiv}CR$] (**5**) or *trans*-[$(Et_3P)_2Pt(C{\equiv}CR^1)_2$ (**6**) in high yield (R^1 = H, Me, Ph). Complexes **5** react with alkynylstannanes to give the unsymmetrical bis(alkynyl) complexes **7**, *trans*-[$(Et_3P)_2Pt(C{\equiv}CR^2)C{\equiv}CR^1$] ($R^1$ = Me, Ph; R^2 = H). Although the palladium(II) dichloride **2**, *trans*-[$(Bu_3P)_2PdCl_2$], reacts much faster with alkynylstannanes than **1**, the compounds *trans*-[$(Bu_3P)_2Pd(C{\equiv}CR^1)_2$] (**9**) are always obtained as mixtures with *trans*-[$(Bu_3P)_2Pt(Cl)C{\equiv}CR^1$] (**8**), except for R^1 = H. Compounds **8** can be obtained pure for R^1 = Me or t-Bu if the reaction between **2** and **3** is carefully controlled. The dependence of the product distribution under experimental conditions in the case of the palladium(II) acetylides indicates that oxidative addition-reductive elimination reactions are involved. The crystal structure of *trans*-[$(Et_3P)_2Pt(C{\equiv}CMe)_2$] (**6b**) has been determined. All the products have been characterized by ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy.

The M–C≡C– unit in transition metal acetylides [1] can be regarded as a truly multifunctional system. Reactions in the ligand sphere may be controlled by the presence of alkynyl groups [2,3], exchange reactions (cleavage of the M–C≡ bond) are frequently carried out [4], various types of additions to the C≡C triple bond are known [5,6] and, recently, 1,1-additions, in particular 1,1-organoboration [7,8], have further increased the synthetic potential of transition metal acetylides. In that context, with this work, we thought it of interest to develop new convenient high yield syntheses of platinum(II) and palladium(II) acetylides.

There are various literature methods available for the synthesis of *trans*- and *cis*-platinum(II) and -palladium(II) acetylides containing phosphine ligands [9–13].

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We have been successful, following the work of Lappert et al. [14], in synthesizing *cis*-platinum(II) acetylides via exchange reactions between alkynylstannanes and $dppePtCl_2$ [15] or $dppmPtCl_2$ [16]. However, attempts to use these methods for the synthesis of the analogous *cis*-palladium(II) acetylides led to competely different results which were reported in a preliminary communication [17]. The strikingly different behaviour of platinum(II) and palladium(II) compounds towards alkynylstannanes under the same experimental conditions prompted us to carry out a comparative study of the reactions of the *trans* compounds, *trans*-$[(Et_3P)_2PtCl_2]$ (**1**), and *trans*-$[(Bu_3P)_2PdCl_2]$ (**2**), towards alkynylstannanes of the type $Me_3SnC{\equiv}CR^1$ (**3**) and $Me_2Sn(C{\equiv}CR^1)_2$ (**4**).

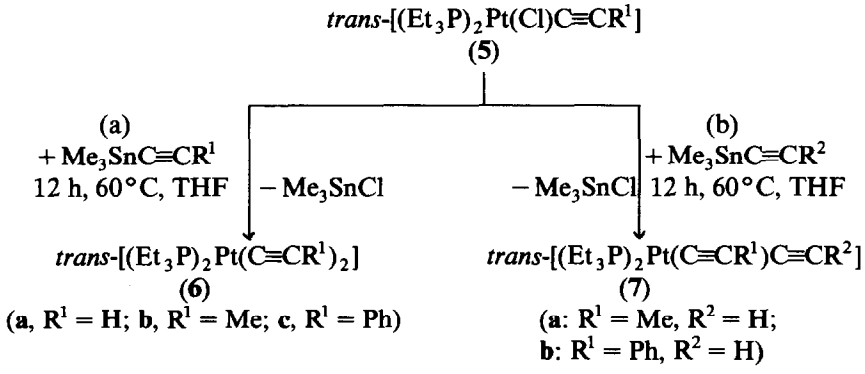
Results and discussion

Reactions of trans-$[(Et_3P)_2PtCl_2]$ (1) with alkynylstannanes 3, 4

In agreement with previous results for *cis*-$[(MePh_2P)_2PtCl_2]$ and *cis*-$[(Et_2PhP)_2PtCl_2]$ [14] the reaction between **1** and alkynylstannanes (**3**,**4**) was found to lead to compounds **5** in high yield (> 95%) (eq. 1). The bis(alkynyl)stannanes, **4**, are more reactive than the monoalkynylstannanes, **3**.

$$\underset{(\mathbf{1})}{trans\text{-}[(Et_3P)_2PtCl_2]} + \underset{(\mathbf{3})}{Me_3SnC{\equiv}CR^1} \xrightarrow[-\,Me_3SnCl]{2\text{ d, THF, }60\,^\circ C} \underset{(\mathbf{5})}{trans\text{-}[(Et_3P)_2Pt(Cl)C{\equiv}CR^1]} \quad (1)$$

Compounds **5** react with a second equivalent of **3** to give compounds **6** ($R^1 = R^2$). This stepwise procedure enables compounds **7** with $R^1 \neq R^2$ (eq. 2) to be obtained for the first time.



(2)

Since compounds **6** are readily available by other methods [9] we studied the reaction between **6** and **1** as a possible way to compounds **5**. This is a very slow reaction which is significantly accelerated by adding a small amount of Me_3SnCl to the reaction solution (eq. 3).

$$\underset{(\mathbf{1})}{trans\text{-}[(Et_3P)_2PtCl_2]} + \underset{(\mathbf{6})}{trans\text{-}[(Et_3P)_2Pt(C{\equiv}CR^1)_2]} \xrightarrow[5\text{ d, THF, }60\,^\circ C]{+[Me_3SnCl]} 2\ \underset{(\mathbf{5})}{trans\text{-}[(Et_3P)_2Pt(Cl)C{\equiv}CR^1]} \quad (3)$$

All reactions were monitored by ^{31}P NMR. These measurements show that the overall reaction represented by eq. 1 initially yields a mixture containing the platinum compounds **1**, **5**, **6**. Heating to 60°C for 2 d (or ca. 8 h if the dialkynyl-

TABLE 1

NMR DATA[a] (^{13}C, ^{31}P, ^{195}Pt) FOR PLATINUM(II) AND PALLADIUM(II) ACETYLIDES

Nr	Compound	$\delta(^{13}C^{\alpha})$	$\delta(^{13}C^{\beta})$	$\delta(^{13}C(R^1))$	$\delta(^{31}P)$	$\delta(^{195}Pt)$	Solvent
trans-[$(Et_3P)_2Pt(Cl)C^{\alpha}\equiv C^{\beta}R^1$]							
5b	R^1 = Me	65.7	93.4	6.4	15.4	+42.1	C_6D_6
		[1384.2]	[400.6]	[31.8]	[2455]		
		(14.6)	(2.5)	(<1.2)			
5c	R^1 = Ph	84.3	102.4	129.9(i), 131.2(o)	15.6	+67.7	C_6D_6
		[1402.8]	[398.0]	[36.6] [14.5]	[2410]		
		(14.3)	(2.3)	128.4(m), 125.4(p)			
trans-[$(Et_3P)_2Pt(C^{\alpha}\equiv C^{\beta}R^1)_2$]							
6a	R^1 = H	100.0	94.4	–	11.3	−279.9	C_6D_6
		[945.0]	[268.0]		[2405]		
		(14.8)	(<1.0)				
6b	R^1 = Me	91.5	100.4	6.7	12.2	−274.9	C_6D_6
		[942.0]	[267.5]	[21.4]	[2460]		
		(14.8)	(<1.5)				
6c	R^1 = Ph	108.3	110.0	130.1(i), 131.2(o)	12.1	−245.0	C_6D_6
		[961.0]	[269.0]	[25.0] [9.5]	[2392]		
		(15.0)	(1.2)	128.0(m), 125.2(p)			
trans-[$(Et_3P)_2Pt(C^{\alpha}\equiv C^{\beta}R^1)C^{\alpha}\equiv C^{\beta}R^2$]							
7a	R^1 = Me	91.0	101.0	6.6	11.9	−277.5	C_6D_6
		[943.0]	[269.4]	[21.7]	[2443]		
		(15.0)	(1.8)	(1.1)			
	R^2 = H	100.7	93.9	–			
		[943.0]	[267.1]				
		(14.6)	(1.8)				
7b	R^1 = Ph	108.2	109.5	130.1(i), 131.2(o)	11.8	−262.5	C_6D_6
		[956.0]	[257.0]	[24.5] [9.8]	[2396]		
		(14.7)	(<1.5)	128.3(m), 125.1(p)			
	R^2 = H	100.0	94.9	–			
		[948.2]	[269.2]				
		(15.0)	(1.2)				
trans-[$(Bu_3P)_2Pd(Cl)C^{\alpha}\equiv C^{\beta}R^1$]							
8a	R^1 = H	94.8	91.0	–	6.9	–	C_6D_6
		(14.6)	(5.5)				
8b	R^1 = Me	78.0	99.1	5.6	10.8	–	$CDCl_3$
		(15.8)	(5.0)				
8c	R^1 = t-Bu	92.7	113.3	29.1, 32.0	9.1	–	$CDCl_3$
		(17.4)	(5.5)				
trans-[$(Bu_3P)_2Pd(C^{\alpha}\equiv C^{\beta}R^1)_2$]							
9a	R^1 = H	104.2	95.4	–	10.8	–	C_6D_6
		(16.9)	(3.2)				
9b	R^1 = Me	95.0	101.5	6.2	12.1	–	$CDCl_3$
		(16.8)	(3.0)				
9c	R^1 = t-Bu	n.o.	117.4	28.9, 32.4	9.1	–	$CDCl_3$
			(3.3)				

[a] Values $J(^{195}Pt^{13}C)$, $J(^{195}Pt^{31}P)$ are given in brackets and values of $J(^{31}P^{13}C)$ in parentheses.

TABLE 2

ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	x	y	z	U_{eq} [a]
Pt	0.5000(0)	0.0000(0)	0.0000(0)	0.041(1)
P	0.3308(2)	−0.1078(2)	0.1044(2)	0.047(1)
C(2)	0.3563(10)	0.0200(5)	−0.1597(8)	0.053(7)
C(21)	0.2864(8)	0.0380(7)	−0.2400(9)	0.053(7)
C(22)	0.1893(12)	0.0521(11)	−0.3654(10)	0.088(11)
C(11)	0.2734(11)	−0.0412(9)	0.2533(8)	0.064(8)
C(12)	0.1559(9)	−0.1450(7)	0.0166(8)	0.067(9)
C(13)	0.4086(10)	−0.2385(6)	0.1607(7)	0.063(8)
C(111)	0.1960(12)	0.0731(9)	0.2278(10)	0.085(12)
C(121)	0.0407(10)	−0.2114(9)	0.0834(11)	0.095(13)
C(131)	0.4701(13)	−0.3083(8)	0.0517(10)	0.086(11)

[a] $U_{eq} = 1/3\ (U_{11} + U_{22} + U_{33})$.

sannanes **4** are used) is necessary for > 95% conversion into **5**. As shown in eq. 3, Me_3SnCl plays an important role in these reactions. Consequently, the reaction conditions for the synthesis of **7** (eq. 2b) are critical, since equilibration with **6** may occur in the presence of Me_3SnCl. The reactivity of the alkynylstannanes **3** and **4** increases in the order R = Me < Ph < H and so it is advisable to prepare first compound **5** from the less reactive alkynylstannane before treating compound **5** with the more reactive alkynylstannane to give the reaction shown in eq. 2b. In any case in solution some disproportionation of **7** into **6** takes place during several days. This process is faster for **7b** than for **7a**.

NMR data (^{13}C, ^{31}P, ^{195}Pt NMR) for compounds **5**, **6**, **7** are given in Table 1 together with ^{13}C and ^{31}P NMR data for the corresponding palladium(II) complexes. All the data are in accord with those reported previously [18] for similar compounds. They confirm convincingly the proposed *trans*-conformation.

Compound **6b** gave suitable crystals for X-ray diffraction studies. Positional and thermal parameters and bond distances and angles are given in Tables 2 and 3, respectively. Figure 1 shows the coordination around the platinum, which is in a square-planar environment with a P–Pt–C(2) angle of 93.5(2)°. The distances Pt–P of 2.284(2) Å and Pt–C(2) of 2.062(8) Å are in the range observed for many platinum complexes [19]. The shortest Pt–Pt separation is 6.677(1) Å.

In the acetylenic group a very short C≡C bond (1.039(11) Å) was found during the structure refinement. This short distance may be caused by some disorder in the acetylenic group and by strong anisotropic thermal motion of C(2) and C(21). The assumption of disorder is supported by the observation that peaks of about 1.1 e/Å^3 are found near the C(21) atom in the difference Fourier map. The refinement with two C(21) positions and site occupation factors in accordance with the two different positions gave no better results. Furthermore, attempts to refine the C≡CCH_3 group with a C≡C distance fixed at 1.15 Å did not improve the situation. The angle C(2)–C(21)–C(22) of 173.5(9)° indicates that the acetylenic carbons are not in the ideal *sp* geometry. The P–C distances, ranging from 1.800(8) to 1.836(9) Å, are in the region as found in other complexes containing phosphorous carbon bonds [19]. The angles C–P–C are between 102.6(4) and 106.0(4)° and the angles P–C–C range from 112.0(6) to 118.5(7)°.

TABLE 3

BOND DISTANCES (Å) AND ANGLES ( ) IN **6b** [a]

Pt–P	2.284(2)
Pt–C(2)	2.062(8)
P–C(11)	1.836(9)
P–C(12)	1.813(8)
P–C(13)	1.800(8)
C(2)–C(21)	1.039(11)
C(21)–C(22)	1.541(13)
C(11)–C(111)	1.548(15)
C(12)–C(121)	1.487(13)
C(13)–C(131)	1.528(13)
P–Pt–C(2)	93.5(2)
Pt–C(2)–C(21)	174.7(7)
Pt–P–C(11)	111.5(3)
Pt–P–C(12)	117.0(3)
Pt–P–C(13)	113.7(3)
C(11)–P–C(13)	102.6(4)
C(11)–P–C(12)	106.0(4)
C(12)–P–C(13)	104.7(3)
C(2)–C(21)–C(22)	173.5(9)
P–C(11)–C(111)	112.0(6)
P–C(12)–C(121)	118.5(7)
P–C(13)–C(131)	112.1(6)

[a] C–H distances were fixed at 1.08 Å during structure refinement (details see text).

The C(12)–C(121) bond is clearly shorter than the other C–C bonds. This artificial shortening may be caused by relatively strong anisotropically thermal motion of C(121). A riding motion correction leads to 1.511(13) Å for C(12)–C(121).

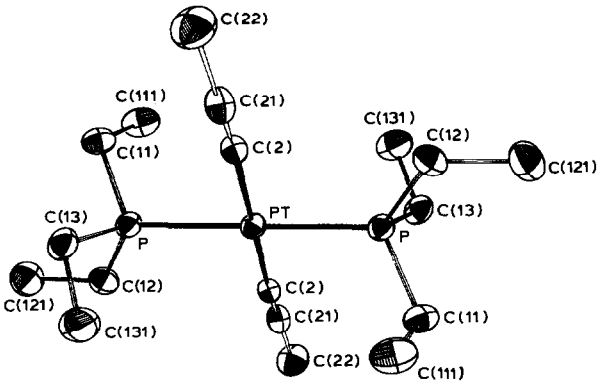


Fig. 1. Perspective view of the molecule **6b** with the atom-numbering scheme; ellipsoids are 50% probability surfaces.

Reactions of trans-[$(Bu_3P)_2PdCl_2$] (2) with alkynylstannanes (3,4)

The reaction between **2** and excess of diethynyldimethylstannane (**4a**) leads to **9a** in quantitative yield. Monitoring of this reaction by ^{31}P NMR spectroscopy shows that, in addition to **2**, **9a** is present even in the beginning of the reaction whereas there is only a small amount of **8a**. In contrast it was not possible to convert **2** completely into **9b** (R^1 = Me) or into **9c** (R^1 = t-Bu) even after prolonged reaction times in the presence of a larger excess of **3** or **4**. Pure compounds **8b**,**8c** can be obtained in high yield (> 95%) if a dilute solution of **3b** (R^1 = Me) or **4c** (R^1 = t-Bu) in benzene is added slowly to a concentrated solution of **2** in benzene at room temperature. Although the compounds **8b**,**8c** do not react with an excess of **3** or **4** to give **9b**,**9c**,

trans-$[(Bu_3P)_2Pd(Cl)C{\equiv}CR^1]$ *trans*-$[(Bu_3P)_2Pd(C{\equiv}CR^1)_2]$
(8) **(9)**

(**a**: R^1 = H; **b**, R^1 = Me; **c**, R^1 = t-Bu)

variable amounts of **9b**,**9c** are formed (up to a 1/1 ratio in the case of **8b**,**9b**, and a 3/1 ratio in the case of **8c**,**9c**) if the correct conditions for the preparation of **8** are not observed. If a dilute solution of **2** in benzene is added at ambient temperature or at 60°C to a concentrated solution of **3b** or **4c** (large excess) in benzene, again mixtures of **8** and **9** are obtained. Clearly these apparently contradictory findings call for a mechanistic explanation.

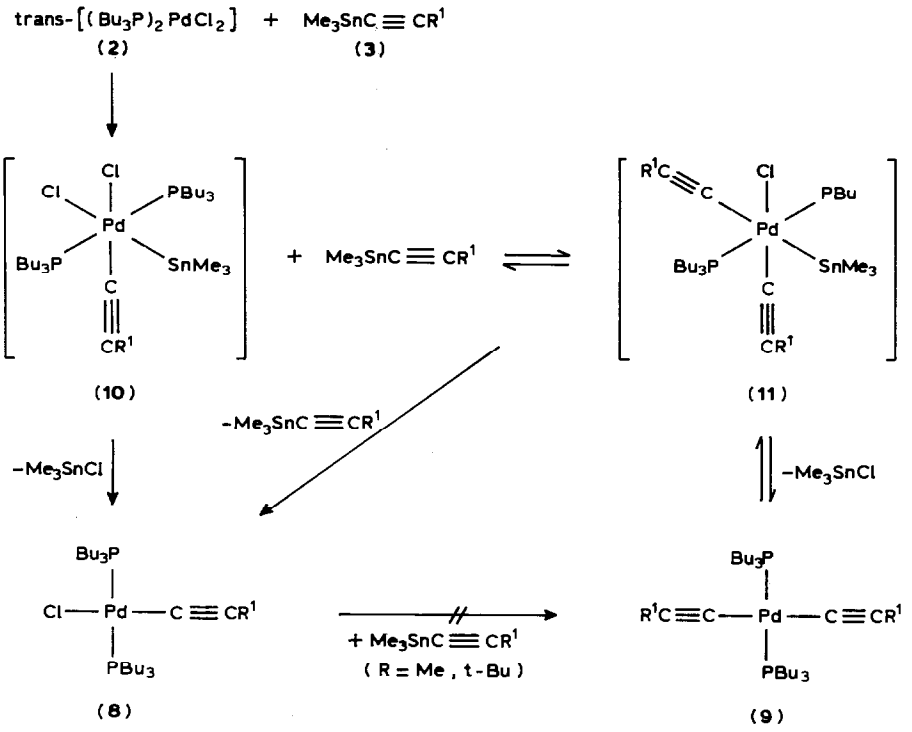
It appears that an S_E2 (cyclic) mechanism of the alkynyl/chloride exchange does not account for the failure of **8b** or **8c** to react with **3b** or **4c** to give **9b** or **9c** . There remains the puzzling finding that **9b** or **9c** are formed even in the early stages of the same reaction which leads preferably to **8b** or **8c**. An alternative explanation involves oxidative addition as the first step in the reaction between **2** and **3** or **4**. The intermediate **10** (Scheme 1) thus formed may undergo reductive elimination of Me_3SnCl, leading to **8**. The exchange of one chloride for an alkynyl group in **10** would lead to **11**. The latter intermediate may undergo reductive elimination to give either **8** ($-Me_3SnC{\equiv}CR^1$) or **9** ($-Me_3SnCl$) (Scheme 1). This explains why the experimental conditions for the selective synthesis of **8** are critical. Scheme 1 also accounts for the fact that formation of **9** is always accompanied by the formation of **8** if a short lifetime is assumed for the octahedral intermediates.

It is interesting to note that the CuI-catalysed reaction of **2** with terminal alkynes in Et_2NH [9] (which works very well with **1**) leads to mixtures of **8** and **9** (3 to 25% **8**), at least in our hands. In the case of **8a**,**9a** and **8b**,**9b** we did not succeed in converting **8a** or **8b** into **9a** or **9b** using an excess of ethyne or propyne. On the other hand a clean reaction between **9** and **2** (in Et_2NH with CuI as catalyst) has been reported to give **8** [10].

The comparison of the reactions of **1** and **2** with alkynylstannanes (**3**,**4**) leads to the following conclusions: (i) The platinum complex **1** reacts much more slowly with alkynylstannanes than the palladium complex **2**.

(ii) Although the octahedral complexes of platinum(II) should be more stable than those of palladium(II), neither the initial nor the final product distribution in the case of the reaction of the platinum compounds permit firm mechanistic conclusions.

(iii) The product distribution (**8**,**9**) in the case of the palladium compounds and its



SCHEME 1. Proposed mechanism of the reaction between **1** and **3** (or **4**). Other arrangements of the ligands are possible in the octahedral intermediates **10** and **11**.

strong dependence on the conditions strongly suggests that an oxidative addition-reductive elimination sequence is involved.

(iv) The conversion of **5** into **6** or **7** is in strong contrast to the lack of reaction of **8b** or **8c** under comparable conditions. This finding is of particular importance in view of the fact that **2** is much more reactive than **1** towards alkynnylstannanes.

Experimental

NMR spectra were recorded with a Bruker WP 200 spectrometer. Chemical shifts are referred to internal Me_4Si (δ^1H, $\delta^{13}C$), external H_3PO_4 (85%) ($\delta(^{31}P)$), and to $J(^{195}Pt)$ 21.4 MHz ($\delta(^{195}Pt)$). IR spectra were obtained with a Perkin–Elmer 325 spectrometer.

All syntheses and handling of the compounds were performed under a N_2-atmosphere in dry, oxygen-free solvents. The starting materials **1** [20], **2** [21], **3**,**4** [22] were prepared by literature methods. Compounds **6** have been synthesized by a literature method [9] and by alkynyl/Cl-exchange between **1** and **3** or **4** as described below. This was also attempted in the case of **9**, but the literature method [9] always gave mixtures containing 3 to 25% of **8** in addition to **9**.

*trans-(Alkynyl)chloro-bis(triethylphosphine)platinum(II) (**5b**,**5c**)*

A solution of 2.23 g (4.43 mmol) *trans*-[$(Et_3P)_2PtCl_2$] (**1**) in 40 ml of THF was

added at room temperature to a solution of 0.90 g (4.44 mmol) $Me_3SnC{\equiv}CMe$ (**3b**) in 5 ml of THF. The mixture was heated under reflux for 48 h. The solvent and Me_3SnCl were removed in vacuo (6 h, 40°C). The yellow solid residue was dissolved in benzene and chromatography on Al_2O_3 (neutral, 15 cm column) with benzene yielded pure **5b** (1.78 g, 80%) as a colourless solid (m.p. 46°C). IR (Nujol): ν(C≡C) 2150 cm^{-1}. ^1H NMR (in C_6D_6): $\delta(^1H)$ 2.02 (t) ≡C–Me, $^4J(^{195}Pt^1H)$ 22.6 Hz, $^5J(^{31}P^1H)$ 2.0 Hz; 1.94(m), 1.10(m) PEt_3. Found: C, 36.2; H, 6.6. $C_{15}H_{33}ClP_2Pt$ calcd.: C, 35.6; H. 6.6%.

Compound **5c** was prepared in the same way or by reaction between **6c** and **1**, and was purified as described for **5b**. It is obtained as a pale-yellow solid, m.p. 67°C IR (Nujol): ν(C≡C) 2120 cm^{-1}. Found: C, 42.3; H, 6.3. $C_{20}H_{35}ClP_2Pt$ calcd.: C, 42.9; H, 6.2%.

trans-Bis(alkynyl)bis(triethylphosphine)platinum(II) (6a–6c)

The reaction between **1** and the alkynylstannanes **3** or **4** was conducted as described for the synthesis of **5**. In the presence of a small excess of **3** or **4** complexes **6** were formed quantitatively. Purification by chromatography as described gave **6** in > 90% yield with properties as reported previously [9,18].

trans-(Ethynyl)(1-propynyl)bis(triethylphosphine)platinum(II) (7a) and trans-(ethynyl)-(phenylethynyl)bis(triethylphosphine)platinum(II) (7b)

A solution of **5b** (or **5c**) (2 mmol) in 20 ml of THF was added to a solution of $Me_3SnC{\equiv}CH$ in 5 ml of THF (0.7 *M*). The mixture was heated under reflux for 12 h. Chromatography (vide supra) then gave **7a** as a colourless oil and **7b** as a pale-yellow solid (both in > 80% yield). Both compounds were characterized from their NMR spectra. The appearance of ^{13}C resonances of compounds **6** after several days in solution proves that **7a,7b** are distinct compounds and not equimolar mixtures of **6a/6b** and **6a/6c**, respectively.

trans-(Alkynyl)chlorobis(tributylphosphine)palladium(II) (8b,8c)

A solution of 0.22 g (1 mmol) $Me_3SnC{\equiv}CMe$ (**3b**) in 20 ml of benzene was added during 2 h to a solution of 0.58 g (1 mmol) *trans*-$[(Bu_3P)_2PdCl_2]$ (**2**), in 2 ml of benzene at room temperature. After removal of volatile materials, pure **8b** was left as a colourless oil. The same method gave pure **8c**.

trans-Diethynylbis(tributylphosphine)palladium(II) (9a)

A solution of 0.5 g (2.5 mmol) of diethynyldimethylstannane (**4a**), in 5 ml of benzene was added during 10 min to a solution of 0.58 g (1 mmol) of *trans*-$[Bu_3P)_2PdCl_2]$ (**2**), in 5 ml of benzene at room temperature. the reaction was complete after 12 h. After removal of the volatile materials in vacuo, chromatography (vide supra) gave pure **9a** [9].

Crystal structure determination of 6b

A colourless rod-like single crystal with dimensions $0.7 \times 0.26 \times 0.15$ mm^3 was mounted under dry argon and sealed in a glass capillary. Reflection intensities were recorded on a CAD 4 diffractometer (Enraf–Nonius, Delft, NL) with graphite monochromated Mo-K_α radiations (λ 0.7107 Å) with the θ–2θ scan technique. The cell parameters were refined with 25 automatically centered reflections within the

range $20.6 < 2\theta < 34.5°$ by a least-squares routine. In the range $1 < \theta < 30°$ a total of 3547 intensities (including standards) was collected with Miller indices running from $0 \rightarrow 12$ for h, $0 \rightarrow 16$ for k and $-14 \rightarrow 14$ for l. Five orientation control reflections were measured after each 250 data and 5 intensity control reflections after each 10000 sec of measurement gave evidence for no significant decay (< 2%).

Lorentz, polarization, numerical absorption, and isotropic extinction corrections were made. Calculations were performed using SHELX-76 [23], PARST7 [24], and ORTEP [25] (for the figures) programs on an IBM 3033 computer (University of Zürich). Scattering factors for the neutral atoms were obtained from ref. 26.

Crystal data: $C_{18}H_{36}P_2Pt$, $M = 509.52$, space group $P2_1/c$, monoclinic, a 8.780(2), b 11.993(1), c 10.430(2) Å; β 92.45(2)°, V 1099.6 Å^3, D_c 1.539 g/cm^3, $F(000) = 504$, μ 62.54 cm^{-1}, $Z = 2$, 3203 unique data.

The structure was determined by conventional Patterson technique and subsequent difference Fourier syntheses. All non-hydrogen atoms could be refined anisotropically with a full-matrix least-squares procedure using 1870 data with $I > 3\sigma(I)$. Only one hydrogen atom could not be located in the difference Fourier maps. Nevertheless, the positions and distances of the H atoms were idealized (C–H distance kept at 1.08 Å). The CH_3/CH_2 groups were then refined with the H atoms riding free on the corresponding C atom. The isotropic temperature factors of the H atoms attached to the same C atom were refined with a common temperature factor. Refinements with freely varying temperature factors and unfixed C–H distances did not give better results.

The function minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$ such that $w = k/(\sigma^2(F) + 0.0071F^2)$ (k refined to 0.81). The weighting scheme showed no significant dependence of the minimized function upon the magnitude of F_o and $(\sin\theta)/\lambda$. The final R and R_w values were 0.034 and 0.038, respectively. At convergence the largest parameter shift (Δ/τ) was $\leqslant 0.005$. The final difference Fourier map exhibited a maximum at 2.1 e/Å^3 near Pt, and the lowest minimum was 1.1 e/Å^3. Two reflections were suppressed ((011) and (102)) owing to strong extinction effects.

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