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Synthesis and characterisation of the platinum complexes $[PtCl(CCl{=}PAr)(PPh_3)_2]$ and $[PtCl(CCl{=}PAr')(PPh_3)_2]$ as potential intermediates in the preparation of phosphaalkynes

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Abstract

Oxidative addition reactions of $Cl_2C{=}PR$ (R = 2,4,6-tris(trifluoromethyl)phenyl (Ar) or 2,6-bis(trifluoromethyl)phenyl (Ar′) with $Pt(PPh_3)_4$ yield the *cis* and *trans* (at platinum) complexes $[PtCl(ClC{=}PAr)(PPh_3)_2]$ and $[PtCl(ClC{=}PAr')(PPh_3)_2]$. All starting materials and intermediates have been characterised by NMR spectroscopy. The crystal and molecular structures of the *trans*-platinum complexes have been determined by single-crystal X-ray diffraction at low temperature.

Keywords: Platinum complexes; Crystal structures; NMR

1. Introduction

As the field of low-coordinate phosphorus chemistry grows, research on multiply bonded phosphaalkenes (P=C bond) and phosphaalkynes (P≡C bond) is of considerable interest, as many applications can be envisaged [1,2]. For example, phosphaalkenes have been employed as ligands in transition-metal-catalysed organic reactions [3–7] and for the synthesis of new inorganic polymers [8–10]. The use of bulky substituents on phosphorus has facilitated the development of several synthetic routes to phosphaalkenes [2].

The chemistry of the bulky and electron-withdrawing $2,4,6\text{-}(CF_3)_3C_6H_2$ (fluoromes = Ar) and $2,6\text{-}(CF_3)_2C_6H_3$ (fluoroxyl = Ar′) substituents and their ability to stabilise low-coordinate main group elements or transition metals is now well documented [11–16]. We recently reported the synthesis and characterisation of several group 13 [17], group 14 [18] and group 15 [19] compounds containing either one or two Ar/Ar′/Ar″ (Ar″ = $2,4\text{-}(CF_3)_2C_6H_3$) ligands, and several other phosphorus compounds containing these bulky substituents have been described in the literature [2,11b,20–28].

In low-coordinate phosphorus chemistry, the fluoromesityl and fluoroxyl groups have been employed in the synthesis of stable diphosphenes (ArP=PAr) [12,20–23], iminophosphines ArP=NAr [24], phosphenium salts ($ArPNR_2^+$) [25] and phosphides $ArPR^-$ [26]. Surprisingly, only a few phosphaalkenes containing the $2,4,6\text{-}(CF_3)C_6H_2$ group have been described: $ArP{=}CCl_2$, $ArP{=}C(SiMe_3)H$, ArP=C(H)Ph [27] and $ArP{=}CMe_2$ [28]. The only phosphaalkenes with the $2,6\text{-}(CF_3)_2C_6H_3$ substituent, $Ar'P{=}CMe_2$ and Ar′P=C-MePh, have been reported very recently by Gates et al. [28].

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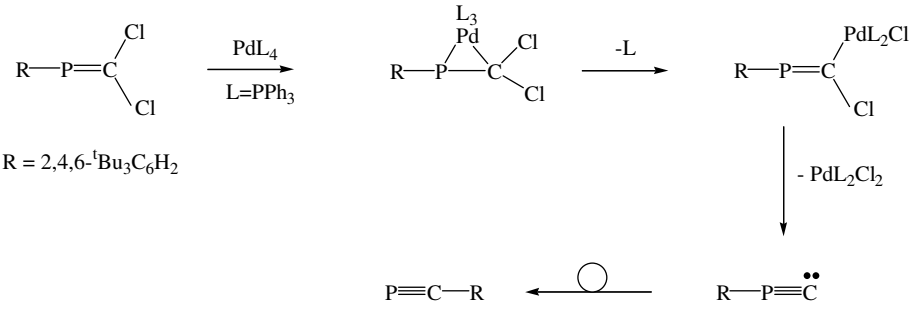


Scheme 1. Proposed mechanism for the synthesis of a phosphaalkyne using PdL_4 and $RP{=}CCl_2$.

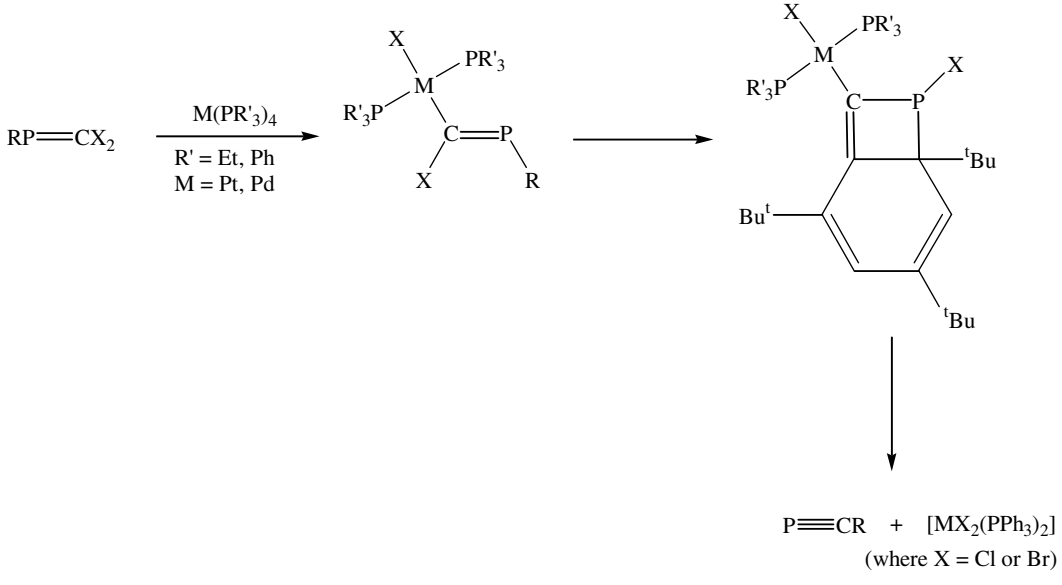
Phosphorus–carbon double bonds can be seen as the starting point for the formation of phosphaalkynes with the ligands Ar or Ar′. Among the numerous routes known to prepare phosphaalkynes [2], the synthesis of Mes*C≡P (Mes* = super-mes = 2,4,6-tris-$^t Bu_3C_6H_2$) by the reaction of the phosphaalkene Mes*P=CCl_2 with $Pd(PPh_3)_4$ was described by Romanenko et al. [29], with a mechanism involving the rearrangement of the intermediate species [RP≡C:] (Scheme 1). It involves the dechlorination of $Cl_2C{=}PR$ and the migration of the ligand R from phosphorus to carbon. Similar products were observed by Angelici and coworkers from reactions of phosphaalkenes with Pd(0) or Pt(0) complexes of phosphanes [30], although in this case they described the intermediate formation of a four-membered ring between a C=C bond in the aryl ring and the P=C phosphaalkene bond (Scheme 2).

The chemistry of phosphaalkynes is diverse and work has mainly been performed with aryl and alkyl substituents on the carbon atom. The alkyl groups used, such as ^{t}Bu, tend to be electron-donating ligands and increase the electron density at the C≡P triple bond. So far, to our knowledge, no phosphaalkynes containing fluoromes or fluoroxyl ligands have been reported. However, some unsuccessful attempts at their synthesis have been reported by Goodwin [31].

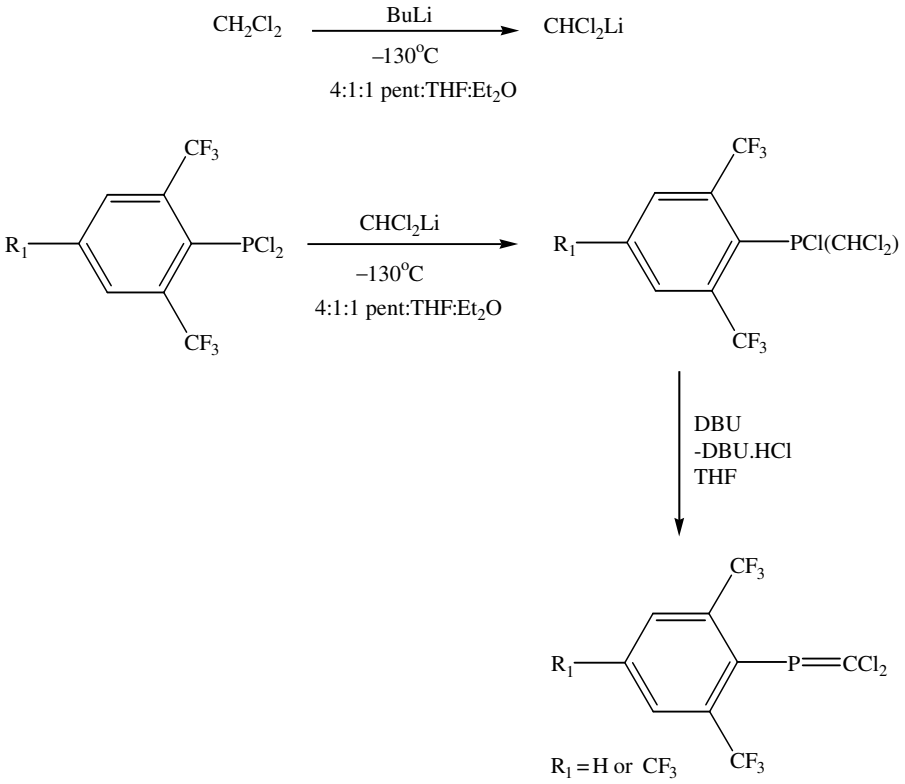
Using ''Angelici's method'' in an attempt to prepare phosphaalkynes containing either Ar or Ar′ ligands, we report here the reaction between $RP{=}CCl_2$ (R = Ar or Ar′) and $Pt(PPh_3)_4$ to form the stable complexes $[PtCl(C(Cl){=}PR)(PPh_3)_2]$, the *trans*-isomers of which have been structurally characterised by single crystal X-ray diffraction.

2. Results and discussion

The phosphaalkenes were prepared via reaction of the phosphane $ArPCl_2$ or a mixture of $Ar'PCl_2$ and $Ar''PCl_2$ with a solution of $CHCl_2Li$ at −130 °C to give $ArP(Cl)CHCl_2$ (**1**) and $Ar'P(Cl)CHCl_2$ (**2**). $Ar''PCl_2$ did not produce the intermediate compound $Ar''P(Cl)CHCl_2$, since the signals from the starting material $Ar''PCl_2$ were still visible in both ^{31}P and



Scheme 2. Mechanism demonstrated by Angelici et al.



Scheme 3. Synthesis of a phosphaalkene.

^{19}F NMR spectra after reaction. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was then added to $RP(Cl)CHCl_2$ (R = Ar (**1**) or Ar′ (**2**)) solution at −78 °C (Scheme 3) to give the phosphaalkenes $ArP{=}CCl_2$ (**3**) or $Ar'P{=}CCl_2$ (**4**), respectively. Purification by distillation under reduced pressure led to a colourless oil in both cases. NMR data for the products $ArPCl_2$ [12,21], $Ar'PCl_2$ [20], $ArP(Cl)CHCl_2$ (**1**), $Ar'P(Cl)CHCl_2$ (**2**), $ArP{=}CCl_2$ (**3**) and $Ar'P{=}CCl_2$ (**4**) are listed in Table 1.

Comparison of the chemical shifts with those of the starting material $ArPCl_2$ (or $Ar'PCl_2$) shows that $\delta^{19}F$ values are at lower frequency for the phosphaalkene than for the phosphane, and that $\delta^{31}P$ moves to a higher frequency. This implies more shielding and electron density on the CF_3 groups. The electron-withdrawing effect is facilitated by the formation of the phosphorus–carbon double bond. The creation of this P=C bond decreases the *p*-character of the phosphorus hybrid orbital. The phosphorus becomes more positive and the chemical shifts move to higher frequency. Simultaneously the electron density in the trifluoromethyl groups increases, moving the fluorine shifts to a lower frequency.

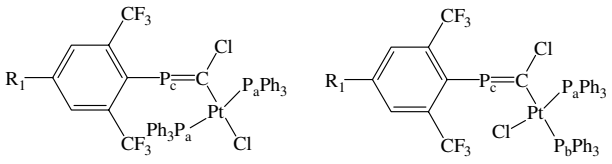
According to Angelici et al. [30], reaction of phosphaalkenes having two Cl substituents on carbon with Pt(0) or Pd(0) compounds leads to an intermediate Pt or Pd complex, which can undergo rearrangement to give a phosphaalkyne (Scheme 2). In the present work, addition of the phosphaalkene $RP{=}CCl_2$ (R = Ar or Ar′) to a $Pt(PPh_3)_4$ solution in toluene (or benzene) at room temperature gave rise to a mixture of *trans*- and *cis*-$[PtCl(ClC{=}PR)(PPh_3)_2]$ (R = Ar for **5a** (*trans*) or **5b** (*cis*): R = Ar′ for **6a** (*trans*) or **6b** (*cis*)) (Fig. 1),

Table 1
^{31}P and ^{19}F NMR data for $RPCl_2$, $RP(Cl)CHCl_2$ and $RP{=}CCl_2$ (R = Ar (2,4,6-$(CF_3)_3C_6H_2$) or Ar′ (2,6-$(CF_3)_2C_6H_3$))

	$\delta^{31}P$	$\delta^{19}F$	
		o-CF_3	*p*-CF_3
$ArPCl_2$	145.6 (septet, $^4J_{P-F}$ 61.3)	−53.3 (d, $^4J_{P-F}$ 61.3)	−64.2
$ArP(Cl)CHCl_2$ (**1**)	63.1 (septet, $^4J_{P-F}$ 49.3)	−55.3 (d, $^4J_{P-F}$ 49.3)	−64.5
$ArP{=}CCl_2$ (**3**)	202.4 (septet, $^4J_{P-F}$ 20.6)	−60.0 (d, $^4J_{P-F}$ 21.1)	−63.9
$Ar'PCl_2$	148.4 (septet, $^4J_{P-F}$ 61.3)	−53.2 (d, $^4J_{P-F}$ 61.3)	
$Ar'P(Cl)CHCl_2$ (**2**)	65.3 (septet, $^4J_{P-F}$ 48.8)	−53.9 (d, $^4J_{P-F}$ 48.9)	
$Ar'P{=}CCl_2$ (**4**)	207.6 (septet, $^4J_{P-F}$ 20.7)	−59.6 (d, $^4J_{P-F}$ 21.1)	

Chemical shifts are given in ppm and coupling constants in Hz.

Trans and *cis* [Pt(Cl)(RP=CCl)(PPh_3)$_2$]



trans-isomer

5a R_1=CF_3
6a R_1=H

cis-isomer

5b R_1=CF_3
6b R_1=H

Fig. 1. *trans*- and *cis*-[Pt(Cl)(RP=CCl)(PPh_3)$_2$].

identified from their ^{31}P and ^{19}F NMR data (Tables 2 and 3, respectively). It should be emphasised that some of the values for coupling constants in Table 2 are approximate, because of the low intensity and complexity of the satellite signals. Resonances in the ^{19}F NMR spectra were assigned according to their relative intensities when compared with the ^{31}P NMR spectra. A signal for free PPh_3 was also observed at −6 ppm in the ^{31}P spectra.

The multiplet in the phosphaalkene region for complex **5b** should, in fact, be a doublet of doublets of septets, due to coupling with the fluorines of the two *o*-CF_3 groups (7 lines) and the phosphorus from the PPh_3 groups. It was not possible to extract $^3J_{P-P}$ between P_a and P_c, expected to be the smallest value, from the complex spectrum observed for P_c, although an approximate value was derived from the P_a resonance. Similar behaviour was found for *cis*-isomer **6b** (Table 2). The *trans*-isomer **5a** should exhibit a triplet of septets. The resonance at 14.1 ppm for P_a in **5b** appeared as a triplet but should be a doublet of doublets. The coupling constants $^2J_{P-P}$ (from P_b) and $^3J_{P-P}$ (from P_c) are very similar in this instance, and separate couplings could not be distinguished.

The initial ^{31}P NMR of the platinum complex containing the Ar′ ligand exhibited signals assigned to the *cis*-isomer **6b**. Removing half of the solvent afforded a white solid, which was isolated and displayed a resonance with platinum satellites at 15.3 ppm ($^1J_{Pt-P}$ 3673 Hz), probably from *cis*-[Pt(PPh_3)$_2$Cl$_2$] (δ 13.5 ppm, $^1J_{Pt-P}$ 3680 Hz [30]). Spectra were recorded regularly for the filtrate, and resonances corresponding to the *trans*-complex **6a** were observed after two weeks. Solvent was removed in vacuo, leaving a yellow/brown oil which was dissolved in toluene. The ^{31}P NMR spectrum of this solution did not show the presence of the *cis*- and *trans*-isomers, but new signals of low intensity were observed: a multiplet at 131.5 and a peak at 26.4 ppm. No platinum satellites were found, probably due to the low intensity of the signals. The ^{19}F NMR spectrum displayed a doublet at −58.6 ppm ($^4J_{P-F}$ 8.1 Hz) and a singlet at −63.2 ppm. These could arise from an intermediate compound in the synthesis of a phosphaalkyne; a cyclic species such as the one characterised by Angelici et al. [30] (Scheme 2) would require three ^{31}P signals, however, since all three P atoms are inequivalent.

Table 2
^{31}P NMR data for the platinum complexes (chemical shifts are given in ppm and coupling constants in Hz)

	cis **5b**						*trans* **5a**			
		δ	J_{Pt-P}[a]	$^3J_{P-P}$	$^2J_{P-P}$	$^4J_{P-F}$	δ	J_{Pt-P}[a]	$^3J_{P-P}$	$^4J_{P-F}$
[PtCl(ClC=PAr)(PPh_3)$_2$]	P_a	14.1 (t[b])	4064	15.3[c]	15.3[c]		24.1(d)	2963	29.0	
	P_b	17.3 (dd)	1897	46.5	16.8					
	P_c	198.1 (m)	376	45.4		24.4	203.7	512	NR	22.6
	cis **6b**						*trans* **6a**			
[PtCl(ClC=PAr′)(PPh_3)$_2$]	P_a	13.5 (t[b])	4118	18.7[c]	18.7[c]		24.3(d)	2992	29.8	
	P_b	17.1 (dd)	1935	46.6	16.7					
	P_c	202.4 (m)	412	46.1		22.3	208.6	507	NR	24.1

NR = not resolved.
[a] $^1J_{Pt-Pa/b}$ and $^2J_{Pt-Pc}$.
[b] Pseudo-triplet.
[c] See text re coupling constants.

Table 3
^{19}F NMR data for the platinum complexes (chemical shifts are given in ppm and coupling constants in Hz)

		cis **5b** and **6b**		*trans* **5a** and **6a**	
		δ	$^4J_{P-F}$	δ	$^4J_{P-F}$
[PtCl(ClC=PAr)(PPh_3)$_2$]	*o*-CF_3	−57.9	23.7	−58.3	23.0
	p-CF_3	−63.0		−63.7	
[PtCl(ClC=PAr′)(PPh_3)$_2$]	*o*-CF_3	−57.5	23.0	−58.0	23.7

The rate of isomerisation of the *cis*- to the *trans*-complex was faster for compound **5**, where both *cis*- and *trans*-isomers could be observed in the solution NMR spectra in the first instance, with possibly a slight excess of the *cis*-complex. Chemical shifts for compounds **5a** and **6a**, or **5b** and **6b**, are very similar. The $^{1}J_{Pt-P}$ coupling constants for **5a** (2963 Hz) and **6a** (2992 Hz), and for **5b** (4064 Hz) and **6b** (4118 Hz), are typical of *trans*- and *cis*-isomers, respectively. They may be compared with the data of Angelici et al. [30] for *trans*-[PtCl(CCl=PR)(PEt_3)$_2$] (2753 Hz) and its bromo-analogue (2712 Hz), and for *cis*-[PtCl(ClC=PR)(PPh_3)$_2$], observed as an intermediate (4203 Hz), where R = 2,4,6-$^{t}Bu_3C_6H_2$. Both *trans*-complexes **5a** and **6a** were isolated (Section 3), and characterised by single crystal X-ray diffraction at 120 and 150 K, respectively. Their molecular structures are displayed in Figs. 2 and 3, while selected bond distances and angles are listed in Table 4.

Both **5a** and **6a** crystallise in the triclinic space group $P\bar{1}$, with $Z = 2$. In both cases there is also one molecule of solvent of crystallisation present in the unit cell (toluene and dichloromethane for **5a** and **6a**, respectively). The platinum adopts a square planar environment, which is defined by the two PPh_3 (in a *trans*-arrangement), Cl and [ClC=PR] ligands. The atoms Pt, P(2), P(3), Cl(1) and C(10) are nearly coplanar. The C(10)–P(1) distances (1.688(2) Å in **5a**, 1.688(4) Å in **6a**) are the same within experimental error as those of the C=P bonds in *trans*-[PtCl(ClC=PMes*)(PEt_3)$_2$] (1.678(5) Å) [30], Ph(Me_3Si)C=PMes* (1.676(6) Å) [32] and Ph_2C=PMes (1.692(3) Å) [32]. Three short contacts between the fluorine atoms of the *o*-CF_3 groups and the phosphorus atom were found in both structures: P(1)···F(11) 3.039(2), P(1)···F(12) 3.159(2), P(1)···F(17) 2.911(1) Å in **5a**, 3.088(3), 3.126(3) and 2.893(3) Å for the corresponding distances in **6a**. They are all shorter than the expected sum of the van der Waals radii for P and F (1.91 and 1.40 Å, respectively [33]). In both structures, the plane formed by the carbon atoms C(11)–C(16) of the Ar or Ar′ ring is twisted with respect to the plane of the Pt(1), P(1), C(10) and Cl(11)

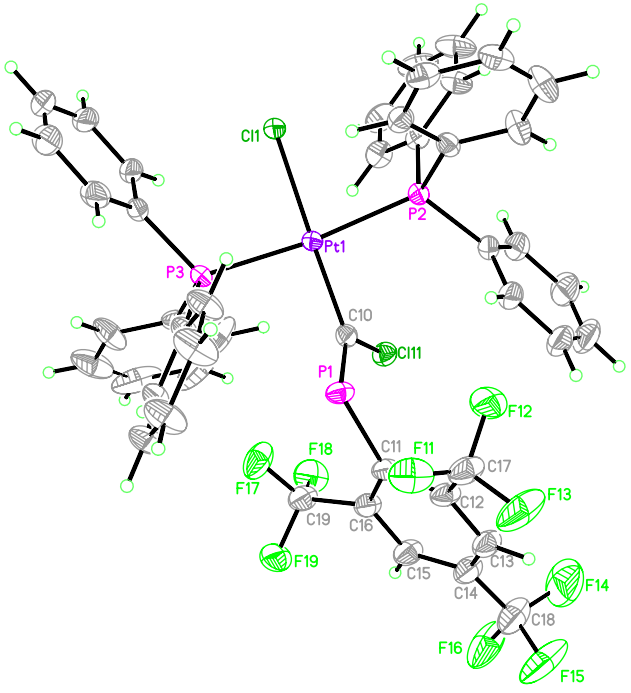


Fig. 2. The crystal structure of *trans*-[Pt(Cl)(ClC=PAr)(PPh_3)$_2$] (**5a**) with selected atoms labelled. Displacement ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

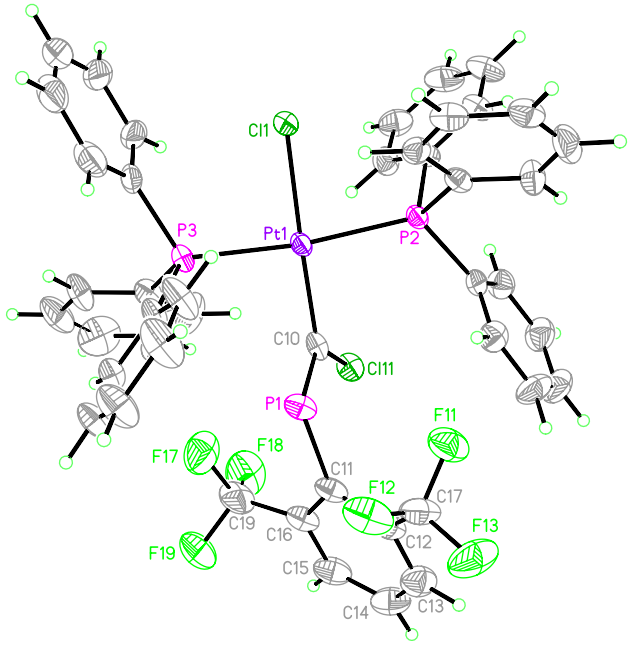


Fig. 3. The crystal structure of [Pt(Cl)(ClC=PAr′)(PPh_3)$_2$] (**6a**) with selected atoms labelled. Displacement ellipsoids for the non-hydrogen atoms are drawn at the 50% probability level.

Table 4
Bond distances (Å) and angles (°) for the two platinum complexes **5a** and **6a**

	5a	**6a**
Bond distances (Å)		
Pt(1)–C(10)	2.014(2)	2.022(4)
Pt(1)–P(3)	2.3203(4)	2.323(1)
Pt(1)–P(2)	2.3286(4)	2.334(1)
Pt(1)–Cl(1)	2.3629(5)	2.368(2)
P(1)–C(10)	1.688(2)	1.688(4)
P(1)–C(11)	1.873(2)	1.882(5)
Cl(11)–C(10)	1.766(2)	1.773(4)
Bond angles (°)		
C(10)–Pt(1)–P(3)	92.42(5)	92.6(1)
C(10)–Pt(1)–P(2)	93.94(5)	94.0(1)
P(3)–Pt(1)–P(2)	173.64(2)	173.38(4)
C(10)–Pt(1)–Cl(1)	177.65(5)	177.8(1)
P(3)–Pt(1)–Cl(1)	89.04(2)	89.27(5)
P(2)–Pt(1)–Cl(1)	84.61(2)	84.12(5)
P(1)–C(10)–Cl(11)	123.0(1)	122.1(3)

atoms, with interplanar angles of 63.02(4)° in **5a** and 66.35(9)° in **6a**, in order to minimise steric interactions.

3. Experimental

All manipulations, including NMR sample preparation, were carried out under an inert atmosphere of dry nitrogen or in vacuo, using standard Schlenk procedures or a glovebox. All solvents employed were reagent grade and dried by refluxing under appropriate drying agents.

The ^{31}P NMR spectra of phosphorus-containing starting materials were checked to confirm the absence of any major impurities. ^{19}F NMR spectra were recorded on a Varian Mercury 200, Varian VXR 400 or Varian Inova 500 Fourier transform spectrometer at 188.18, 376.35 and 470.26 MHz, respectively. ^{31}P NMR spectra were recorded on the same instruments at 80.96, 161.91 or 202.32 MHz. Chemical shifts were measured relative to external $CFCl_3$ (^{19}F) or 85% H_3PO_4 (^{31}P), with the higher frequency direction taken as positive. Elemental analyses were performed by the Microanalytical Services of the Chemistry Department, University of Durham.

Compounds $Pt(PPh_3)_4$ [34], $ArPCl_2$ [12,21], $ArP(Cl)CHCl_2$ (**1**) [27], $ArP{=}CCl_2$ (**3**) [27] and $Ar'PCl_2/Ar''PCl_2$ [19,20] were prepared according to the literature procedures. $ArP(Cl)CHCl_2$ was synthesised via the direct reaction of $CHCl_2Li$ with $ArPCl_2$ at −130 °C, rather than via the $CdCl_2$ route [27].

3.1. Synthesis of $Ar'P(Cl)CHCl_2$ (2)

BuLi (15.6 ml, 25 mmol, 1.6 M in hexanes) was added dropwise to a solution of CH_2Cl_2 (1.6 ml, 25 mmol) in a 4:1:1 mixture of pentane:THF:Et_2O at −130 °C with vigorous stirring. The mixture was allowed to stir for 1 h and was then added rapidly through a pre-cooled cannula to a solution of $Ar'PCl_2/Ar''PCl_2$ (6 g, 20 mmol) in diethyl ether at −130 °C. The solution was allowed to warm up and stirred for 4 h. A precipitate of LiCl formed. The solution was filtered and the solvent removed under vacuum. The product was purified by distillation under reduced pressure, giving a colourless oil, b.p. 65 °C (0.03 Torr). ^{31}P NMR ($CDCl_3$): δ 65.3 (septet, $^4J_{P-F}$ 48.8 Hz) ppm; ^{19}F NMR ($CDCl_3$): δ −53.9 (d, $^4J_{P-F}$ 48.9 Hz, 6F, *o*-CF_3) ppm.

3.2. Synthesis of $Ar'P{=}CCl_2$ (4)

DBU (2.85 g, 2.8 ml, 18.8 mmol) was added dropwise to a solution of $ArP(Cl)CHCl_2$ (6.8 g, 18 mmol) in THF. The solution was stirred for 2 h, giving an orange solution. The solvent was removed under vacuum and the product purified by distillation under reduced pressure, b.p. 57 °C (0.02 Torr). ^{31}P NMR ($CDCl_3$): δ 207.6 (septet, $^4J_{P-F}$ 20.7 Hz); ^{19}F NMR ($CDCl_3$): δ −59.6 (d, $^4J_{P-F}$ 21.1 Hz, 6F, *o*-CF_3) ppm.

3.3. Synthesis of $[PtCl(ClC{=}PAr)(PPh_3)_2]$ (5a/5b)

A solution of $ArP{=}CCl_2$ (0.24 g, 0.6 mmol) in toluene was added to a solution of $Pt(PPh_3)_4$ (0.75 g, 0.6 mmol) in toluene. The resulting yellow solution was allowed to stir. A sample was removed for NMR spectroscopy. ^{31}P NMR (C_7D_8): *cis*-[PtCl(CCl=PAr)(PPh_3)$_2$] (**5b**): δ 198.1 (multiplet with Pt satellites, $^2J_{Pt-P}$ 376 Hz, $^3J_{P-P}$ 45.4, $^4J_{P-F}$ 24.4 Hz), 17.3 (dd with Pt satellites, $^1J_{Pt-P}$ 1897, $^3J_{P-P}$ 46.5, $^2J_{P-P}$ 16.8 Hz), 14.1 (t with Pt satellites, $^1J_{Pt-P}$ 4064, $^3J_{P-P}$ 15.3 Hz); *trans*-[PtCl(CCl=PAr)(PPh_3)$_2$] (**5a**): δ 203.7 (multiplet with Pt satellites, $^2J_{Pt-P}$ 512, $^4J_{P-F}$ 22.6 Hz), 24.1 (d with Pt satellites, $^1J_{Pt-P}$ 2963, $^3J_{P-P}$ 29.0 Hz) ppm; ^{19}F NMR ($CDCl_3$): *cis*-[PtCl(CCl=PAr)(PPh_3)$_2$] (**5b**): δ −57.9 (d, $^4J_{P-F}$ 23.7 Hz, 6F, *o*-CF_3), −63.0 (s, *p*-CF_3) ppm; *trans*-[PtCl(CCl=PAr)(PPh_3)$_2$] (**5a**): δ −58.3 (d, $^4J_{P-F}$ 23.0 Hz, 6F, *o*-CF_3), −63.7 (s, *p*-CF_3) ppm. The solution turned dark orange and an orange precipitate was formed. This was separated (0.3 g, 0.26 mmol, 43%) and recrystallised from toluene, to give the *trans*-complex **5a** (Anal. Found: C, 52.78; H, 3.36%; $C_{49.5}H_{36}Cl_2F_9P_3Pt$ requires C, 51.22; H, 3.13%; $C_{53}H_{40}Cl_2F_9P_3Pt$, i.e., with one toluene molecule per molecule of complex, requires C, 52.75; H, 3.34%).

3.4. Synthesis of $[PtCl(CCl{=}PAr')(PPh_3)_2]$ (6a/6b)

A solution of $Ar'P{=}CCl_2$ (0.51 g, 1.6 mmol) in benzene was added to a solution of $Pt(PPh_3)_4$ (1.9 g, 1.5 mmol). The resulting yellow solution was left to stir, and a sample was removed for NMR spectroscopy. ^{31}P NMR (C_7D_8): *cis*-[PtCl(CCl=PAr')(PPh_3)$_2$] (**6b**): δ 202.4 (septet with Pt satellites, $^2J_{Pt-P}$ 412, $^3J_{P-P}$ 46.1, $^4J_{P-F}$ 22.3 Hz), 17.1 (dd with Pt satellites, $^1J_{Pt-P}$ 1935, $^3J_{P-P}$ 46.6, $^3J_{P-P}$ 16.7 Hz), 13.5 (t with Pt satellites, $^1J_{Pt-P}$ 4118, $^3J_{P-P}$ 18.7 Hz); *trans*-[PtCl(CCl=PAr')(PPh_3)$_2$] (**6a**): δ 208.6 (m with Pt satellites, $^2J_{Pt-P}$ 507, $^4J_{P-F}$ 24.1 Hz), 24.3 (d with Pt satellites, $^1J_{Pt-P}$ 2992, $^3J_{P-P}$ 29.8 Hz) ppm; ^{19}F NMR ($CDCl_3$): *cis*-[PtCl(CCl=PAr')(PPh_3)$_2$] (**6b**): δ −57.5 (d, $^4J_{P-F}$ 23.0 Hz, 6F, *o*-CF_3) ppm; *trans*-[PtCl(CCl=PAr')(PPh_3)$_2$] (**6a**): δ −58.0 (d, $^4J_{P-F}$ 23.7 Hz, 6F, *o*-CF_3) ppm. The solution turned dark orange and an orange precipitate was formed. The product was isolated (1.2 g, 1.1 mmol, 73%) and recrystallised from toluene to yield the *trans*-isomer **6a.**

3.5. X-ray crystallography

Single crystal structure determinations were carried out from data collected using graphite monochromated

Table 5
Crystal data and structure refinement parameters for **5a** and **6a**

	5a	**6a**
Empirical formula	$C_{46}H_{32}Cl_2F_9P_3Pt$, $0.5(C_7H_8)$	$C_{45}H_{33}Cl_2F_6P_3Pt$, $0.5(CH_2Cl_2)$
Formula weight	1160.68	1089.08
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size (mm)	$0.30 \times 0.30 \times 0.30$	$0.40 \times 0.20 \times 0.20$
Unit cell dimensions		
a (Å)	9.3490(2)	9.471(2)
b (Å)	11.6028(2)	11.653(2)
c (Å)	22.6978(4)	21.394(4)
α (°)	88.8750(10)	75.24(3)
β (°)	83.8450(10)	91.85(3)
γ (°)	75.3280(10)	74.64(3)
Volume (Å)	2368.05(8)	2189.0(8)
Z	2	2
Temperature (K)	120	150
Density (g cm^{-3})	1.628	1.652
μ (mm^{-1})	3.247	3.556
Data/restraints/parameters	14436/0/560	11486/1/533
R_{int}	0.0205	0.0288
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0218$, $wR_2 = 0.0529$	$R_1 = 0.0397$, $wR_2 = 0.0726$
R indices (all data)	$R_1 = 0.0250$, $wR_2 = 0.0538$	$R_1 = 0.0658$, $wR_2 = 0.0791$
Goodness-of-fit (S)	1.040	0.916
Residual electron density	$\Delta\rho_{max} = +1.21$, $\Delta\rho_{min} = -0.64$	$\Delta\rho_{max} = 1.80$, $\Delta\rho_{min} = -1.48$

Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART-CCD 1K diffractometer. The data were recorded at 120 and 150 K for **5a** and **6a**, respectively, and the temperature was controlled using a Cryostream N_2 flow cooling device [35]. In each case, series of narrow ω-scans (0.3°) were performed at several φ-settings in such a way as to cover a sphere of data to a maximum resolution of 0.70 Å. Cell parameters were determined and refined using the SMART software [36], and raw frame data were integrated using the SAINT program [37]. The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using SHELXTL [38]. Relevant parameters for data collection and structure solution are given in Table 5.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 258132 and 258133. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336 033; e-mail: deposit@ccdc. cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.04.029.

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