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Preparation and reactivity of mononuclear platinum(0) complexes containing a η^2-coordinated alkynylphosphine

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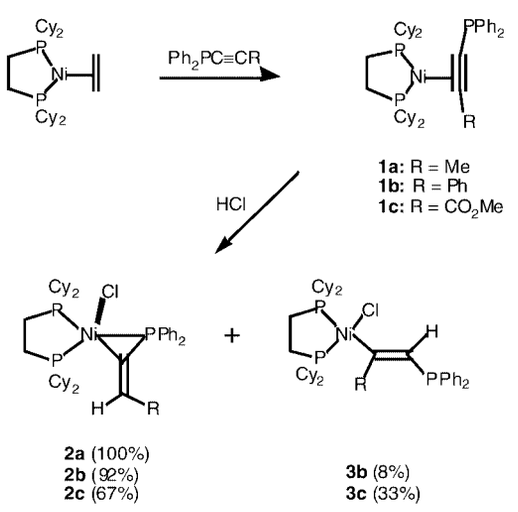
Displacement of ethene from [Pt(η^2-C_2H_4)(dcpe)] by $Ph_2PC{\equiv}CMe$ gives the monomeric η^2-alkynylphosphine complex [Pt(η^2-$Ph_2PC{\equiv}CMe$)(dcpe)] (**5**). Reaction of **5** with one equivalent of HCl forms, in benzene, the four-coordinate η^1-vinyl–platinum(II) complex [PtCl{C(=CHMe)PPh_2}(dcpe)] (**6**) by regiospecific addition of the proton to the alkyne carbon atom bearing the methyl group. In dichloromethane, reversible dissociation of the chloride ion from **6** takes place and the cation [Pt{C(=CHMe)PPh_2-κ*P*,*C*^{1}}(dcpe)]$^+$ (**6′**) that contains a three-membered methylenephosphaplatinacycle fragment can be observed. Treatment of complex **5** with methyl iodide results in the formation of a phosphonium salt [Pt{η^2-C(=CH_2)=CHPPh_2Me}(dcpe)]$^+$I$^-$, [**8**]I, in which the alkynylphosphine has rearranged to the corresponding allene. The alkynylphosphine complex **5** is cleanly oxidised at phosphorus in the presence of sulfur or air to give the corresponding sulfide or oxide [Pt(η^2-Ph_2P(X)C≡CMe)(dcpe)] (X = S (**9**), O (**10**)). Complexes **5**, **6**, **8**, **9** and **10** have been structurally characterised by single-crystal X-ray diffraction analysis.

Introduction

Although (alkynyl)diphenylphosphines, $Ph_2PC{\equiv}CR$, commonly behave as simple P-donor ligands,[1] they can also bridge a pair of metal atoms *via* phosphorus and the triple bond, as in the complexes [$Ni_2(CO)_2$(μ-η^1 : η^2-$Ph_2PC{\equiv}C$–^{t}Bu)],[2] or [M(PPh_3)-(μ-η^1 : η^2-$Ph_2PC{\equiv}CCF_3$)]$_2$ (M = Pd, Pt).[3] There are only a few examples in which alkyne coordination is favoured, *e.g.* [$Co_2(CO)_6${μ-η^2-$(C_6F_5)_2PC{\equiv}CR$}] (R = Me, Ph),[4] [$(CpNi)_2$(μ-η^2-$Ph_2PC{\equiv}C$–^{t}Bu)][5] and [$W(CO)(\eta^2$-$Ph_2PC{\equiv}CPPh_2)(S_2CNEt_2)_2$].[6] We have recently characterised the complexes [Ni(η^2-$Ph_2PC{\equiv}$CR)(dcpe)] [R = Me, Ph, CO_2Me (**1a**–**c**); [dcpe = 1,2-bis(dicyclohexylphosphino)ethane, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$], which represent the first examples of this behaviour with nickel(0) (3d[10]), and have shown that they react with HCl to form five-coordinated nickel(II) complexes (**2a**–**c**) that contain a three-membered methylenephosphanickelacycle (Scheme 1).[7,8]

In the cases of complexes **1b** and **1c**, small amounts of isomeric four-coordinate nickel(II) complexes **3b** and **3c** are also formed as a result of proton addition to the carbon bearing the PPh_2 group instead of that carrying the substituent R. Since five-coordination is less favoured for platinum(II) than nickel(II), and platinum(0) is larger and more basic than nickel(0), we thought it worthwhile for purposes of comparison to examine the chemistry of an (alkynyl)diphenylphosphine with platinum(0). The results are reported here.



Scheme 1

Results

Reaction of the ethene complex [Pt(η^2-C_2H_4)(dcpe)] with one mole equivalent of $Ph_2PC{\equiv}CMe$ in diethyl ether at 0 °C gives initially a yellow–green solution, which is believed to contain a platinum(0) complex of the P-coordinated alkynylphosphine, [Pt(η^1-$Ph_2PC{\equiv}CMe)_2$(dcpe)] (**4**). The ^{31}P-{^{1}H} NMR spectrum of the solution exhibits two broad triplets assigned to **4** at δ_P −22.9 and 36.2 [J(PP) = 53.1 Hz] with J(PtP) of 4190 and 3400 Hz, respectively, together with a singlet with ^{195}Pt satellites at δ_P 72.4 [J(PtP) = 3151 Hz] due to unreacted ethene complex. The multiplicity of the signal at δ_P 36.2, corresponding to coordinated dcpe, suggests the presence of two coordinated alkynylphosphines in **4**.

When the solution is allowed to warm to room temperature, the colour changes to yellow. The signals due to **4** disappear and are replaced by a doublet of doublets at δ_P −11.5 and two sets of doublets of doublets in the region δ_P 67–70, which are assigned to the uncoordinated phosphorus atom and the dcpe ligand, respectively, of the η^2-coordinated species [Pt(η^2-Ph_2-PC≡CMe)(dcpe)] (**5**) (Scheme 2). Complex **5** can be isolated as a colourless solid that, in contrast to its nickel(0) analogue **1a**, is stable almost indefinitely at room temperature in the absence of air; its structure has been determined by single-crystal X-ray crystallography (see below).

The ^{31}P-{^{1}H} NMR spectrum of **5** corresponds to a tightly coupled ABMX spin system, and is similar to that of the nickel analogue [Ni(η^2-$Ph_2PC{\equiv}CMe$)(dcpe)].[8] The more deshielded phosphorus atom of dcpe (δ_P 69.8) is probably that *trans* to the alkyne carbon atom C^1 bearing the PPh_2 group since it shows the larger of the two couplings with PPh_2 (44.6 *vs.* 22.1 Hz) and also with Pt (3281 *vs.* 2968 Hz); the latter values are typical of ^1J(PtP) couplings in platinum(0)-alkyne complexes.[9,10]

† Single crystal X-ray diffraction unit.

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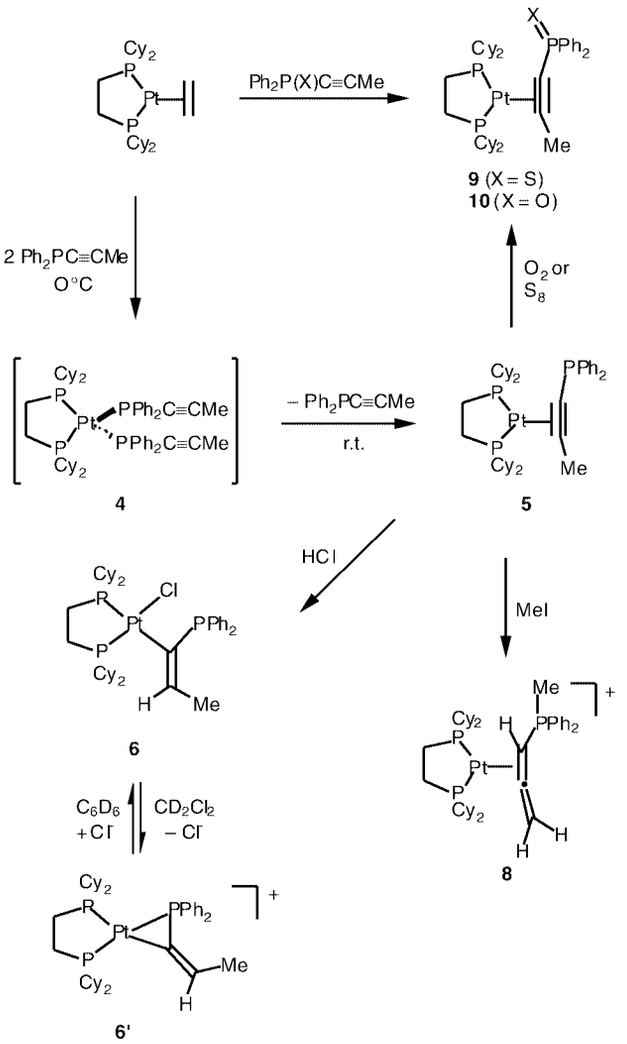


Scheme 2

The ^{13}C NMR chemical shifts assigned to the quaternary carbons of the coordinated triple bond of $Ph_2PC^1{\equiv}C^2C^3H_3$, δ_C 117.60 and 145.55, are deshielded by about 40 ppm compared with those of the free alkynylphosphine,[7,11,12] as expected for alkyne coordination to a zerovalent Group 10 metal.[13] The electron-withdrawing character of PPh_2 causes C^2 to be less shielded than C^1 in the free alkyne and this order of chemical shifts is maintained on coordination to platinum. The J(PC) values are, in general, larger than those found in η^2-alkyne–nickel(0) complexes.[8,14] The IR band due to ν(C≡C) is observed at 1700 cm^{-1}, which is lower than that of the nickel analogue, in accord with the trend noted for other alkyne complexes of nickel(0) and platinum(0).[15–17]

Complex **5** is unaffected by MeOH, even at 50 °C, but addition of one mole equivalent of HCl in diethyl ether precipitates a colourless 1 : 1 adduct whose ^{31}P-{^{1}H} NMR spectrum in C_6D_6 shows a broad signal at δ_P 7.9 due to PPh_2 and two broad signals, with ^{195}Pt satellites, due to coordinated dcpe: a singlet at δ_P 49.0 and a doublet at δ_P 61.8. The corresponding Pt–P coupling constants are 4095 and 1821 Hz, which are characteristic of phosphorus *trans* to Cl and σ-bonded carbon, respectively.[18] The ^{13}C NMR spectrum shows a multiplet at δ_C 143.89 assigned to the metal-bonded carbon and a doublet of doublets at δ_C 22.33 for the methyl group [J(PC) = 20.8, 9.7 Hz]; a multiplet at δ_H 6.72 in the ^{1}H NMR spectrum is assigned to a vinylic CH group and a ν(C=C) band at 1580 cm^{-1} in the IR spectrum also indicates the presence of a vinyl group. The spectroscopic data, therefore, suggest that the compound is a planar chloroplatinum(II) complex bearing a σ-C-bonded vinylphosphine but do not distinguish between the possibilities [PtCl{η^1-C(PPh$_2$)=CH(Me)}(dcpe)] (**6**) and [PtCl{η^1-CMe=CH(PPh$_2$)}(dcpe)] (**7**) arising from proton addition to C^2 or C^1, respectively. A single crystal X-ray diffraction study has confirmed that the compound has structure **6** (see below); several other observations discussed below point to the same conclusion.

First, the ^{31}P-{^{1}H} NMR signal of the PPh_2 group in **6** is significantly less shielded than those in free alkenyldiphenylphosphines[19,20] or in the nickel(II)–vinyl complexes **3b** (δ_P −13.3) or **3c** (δ_P −28.7), in which the PPh_2 group is on the β-carbon atom relative to the metal.[8] In free alkenyldiphenylphosphines, methyl group substitution on the carbon atom bearing the PPh_2 group causes a 10–20 ppm deshielding in δ_P,[19] possibly as a consequence of a decrease in the P–C^1–C^2 angle, and a bulky platinum-containing substituent would probably have a similar effect. Second, the ^{31}P-{^{1}H} spectrum of **6** in CD_2Cl_2 is quite different from that in C_6D_6. The broad signal at δ_P 7.9 is absent and is replaced by a doublet with ^{195}Pt satellites at δ_P −88.3 [J(PP) = 306.5 Hz, J(PtP) = 1136 Hz]. The high shielding of this PPh_2 resonance indicates the presence of a three-membered methylenephosphametallacycle similar to that in the nickel compound **2a**, which can only arise if the PPh_2 group is on the carbon atom bonded to platinum, as in **6**. Thus, in CD_2Cl_2, complex **6** presumably exists as a salt-like species [Pt{C(=CHMe)PPh$_2$-κ*C,P*}(dcpe)]$^+$Cl$^-$, [**6′**]Cl, formed by partial or complete dissociation of chloride ion from the coordination sphere and its replacement by the PPh_2 group. The magnitude of ^2J(PP) is consistent with the presence of mutually *trans* P-donors in a planar platinum(II) species, though it is somewhat less than the values of 400–500 Hz usually found when both ligands are tertiary phosphines.[21] A similar comment applies to the magnitude of ^1J(PtP).

Treatment of **5** with one mole equivalent of methyl iodide in ether at 0 °C gives initially a brown precipitate, which redissolves at room temperature. The ^{31}P-{^{1}H} NMR spectrum of the solution shows the presence of one main constituent having doublets of doublets at δ_P 20.3, 68.9 and 73.7; the last two, due to dcpe, have Pt–P couplings of 2472 and 3542 Hz, respectively. The small values of J(PP) (12.9 and 2.0 Hz) and J(PtP) (110 Hz) associated with the signal at δ_P 20.3 suggest that this phosphorus atom is not coordinated to platinum and its chemical shift is consistent with the presence of a quaternary phosphonium ion, [R$_3$PMe]$^+$.[22] In agreement, the ^{1}H NMR spectrum contains a 3H-doublet at δ_H 2.13 [J(PH) = 22.0 Hz] due to P–Me but, surprisingly, no resonance due to the expected methyl group bonded to C^2. Instead, there are three 1H-resonances assignable to an allene fragment –CH=C=CH$_2$: a triplet of doublets at δ_H 2.85 with a P–H coupling of 4.5 Hz that is characteristic of a geminal coupling in such compounds,[23,24] a doublet of doublets of doublets at δ_H 6.08, and a doublet of quintets at δ_H 6.70, the last two being due to the =CH$_2$ group. We were unable to obtain a satisfactory ^{13}C NMR spectrum because of the limited quantity of material available, but the IR spectrum of the colourless solid isolated from the reaction mixture shows a band at 1647 cm^{-1}, which is similar to the value reported for metal–allene complexes such as [Pt(η^2-CH$_2$=C=CH$_2$)(PPh$_3$)$_2$];[25,26] the FAB mass spectrum shows a parent ion at *m*/*z* 856 consistent with the formulation [Pt{η^2-C(=CH$_2$)=CHPPh$_2$Me}(dcpe)]$^+$ (**8**). This structure has been confirmed by single-crystal X-ray diffraction (see below), the allenyl fragment being coordinated to the metal through carbon atoms C^1 and C^2.

The observed quaternisation of the free phosphorus atom in **5** by methyl iodide prompted us to examine briefly other oxidation reactions. Addition of sulfur to **5** gives the η^2-coordinated alkynylphosphine sulfide complex [Pt{η^2-Ph$_2$P(S)C≡CMe}(dcpe)] (**9**), whose structure has been determined by X-ray crystallography (see below). Complex **9** can be prepared independently by reaction of the phosphine sulfide with

[Pt(η^2-C_2H_4)(dcpe)]. The NMR and IR spectroscopic properties of **9** generally resemble those of **5**; the ^{31}P chemical shift of the phosphorus atom of P(S)Ph_2 group, δ_P 29.1, is almost identical to that of *Z*-Ph_2P(S)CH=CHMe.[20]

Solutions of **5** in benzene or diethyl ether are oxidised in air over a period of hours to give the corresponding phosphine oxide complex [Pt{η^2-Ph_2P(O)C≡CMe}(dcpe)] (**10**), which also has been characterised by X-ray diffraction (see below). The compound can also be prepared by reaction of Ph_2P(O)C≡CMe with [Pt(η^2-C_2H_4)(dcpe)] in diethyl ether. Although its spectroscopic data are generally as expected, the ^{31}P NMR chemical shift of the P(O)Ph_2 group (δ_P 12.3) is surprisingly shielded in comparison with the values for *Z*-Ph_2P(O)CH=CHMe and Ph_2P(O)CH=CH_2,[20,27] which are in the region of δ_P 21–22. This may be a consequence of the apparent hydrogen bond between the P=O group of compound **10** and the α-CH bond of one of the cyclohexyl groups (see below). This attraction would lead to an increase in the P–C^1–C^2 angle, resulting in a shielding of the phosphorus atom as seen for the free alkenyldiphenylphosphines discussed above.[19]

Molecular structures of [Pt(η^2-Ph_2PC≡CMe)(dcpe)] (5), [PtCl{η^1-C(=CHMe)PPh_2}(dcpe)] (6), [Pt{η^2-C(=CH_2)=CHPPh_2Me}(dcpe)]I ([8]I) and [Pt(η^2-Ph_2P(X)C≡CMe)(dcpe)] [X = S (9), O (10)]

The molecular geometries of **5**, **6**, **8**, **9** and **10** are shown, together with the atom labelling, in Figs. 1 to 5, respectively; selected values of bond lengths and angles are listed in Table 1. ‡

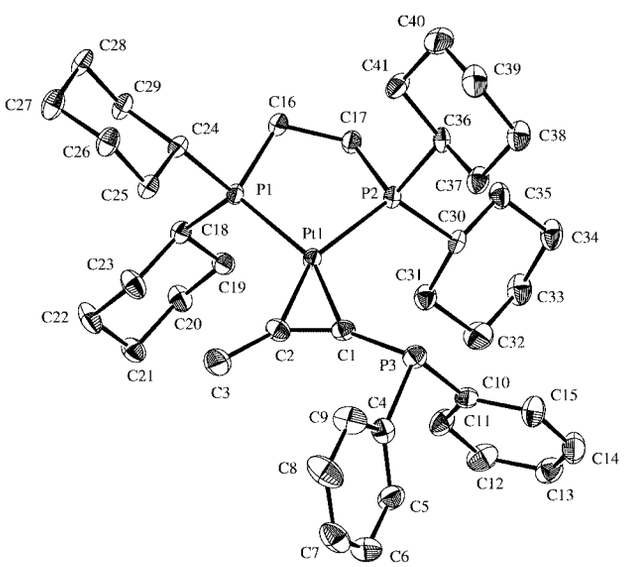


Fig. 1 An ORTEP diagram of [Pt(η^2-Ph_2PC≡CMe)(dcpe)] **5** with selected atom labelling and 30% probability ellipsoids; hydrogen atoms have been omitted for clarity.

The structures of complexes **5**, **9** and **10** display trigonal planar coordination typical of metal(d^{10})–alkyne complexes,[28] the coordinated carbon atoms being displaced slightly (0.07–0.20 Å) above the PtP_2 plane. The Pt–C distances fall in the range 2.01–2.05 Å, *ca.* 0.13 Å greater than the Ni–C bond lengths in the nickel compound **1a**.[8] The coordinated C≡C bond lengths are equal within experimental error [1.295(4)–1.300(6) Å]; these distances are slightly greater than that in **1a** [1.280(4) Å] and significantly greater than those in free Ph_2PC≡CMe

‡ The numbering scheme of the bonded carbon atoms in the structures of complexes **5**, **8**, **9** and **10** is identical to that used in the NMR discussion, *viz.* Ph_2P–C^1≡C^2–Me or Ph_2P–C^1H=C^2=C^3H_2. However, it should be noted that this numbering is reversed from that used in the deposited CCDC structures or in the reported molecular structures of the nickel(0) analogues,[8] *viz.* Ph_2P–C^3≡C^2–C^1H_3 or Ph_2P–C^3H=C^2=C^1H_2.

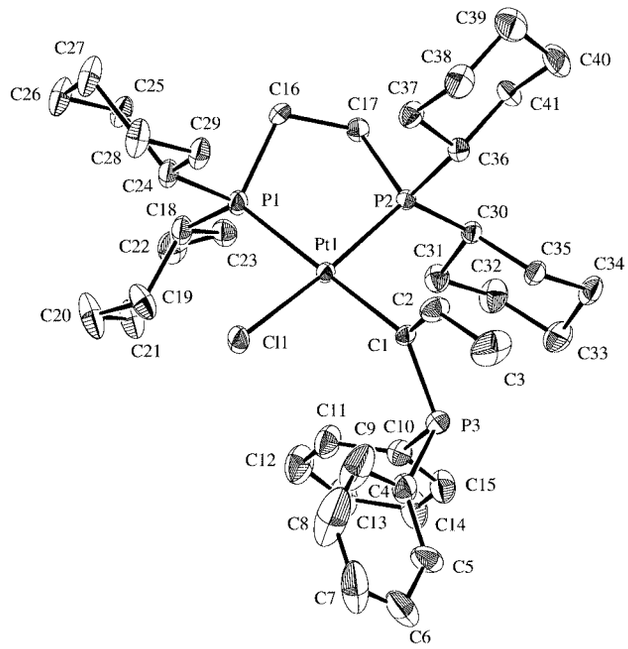


Fig. 2 An ORTEP diagram of one conformer of [PtCl{η^1-C(=CHMe)PPh_2}(dcpe)] **6** with selected atom labelling and 30% probability ellipsoids; hydrogen atoms have been omitted for clarity.

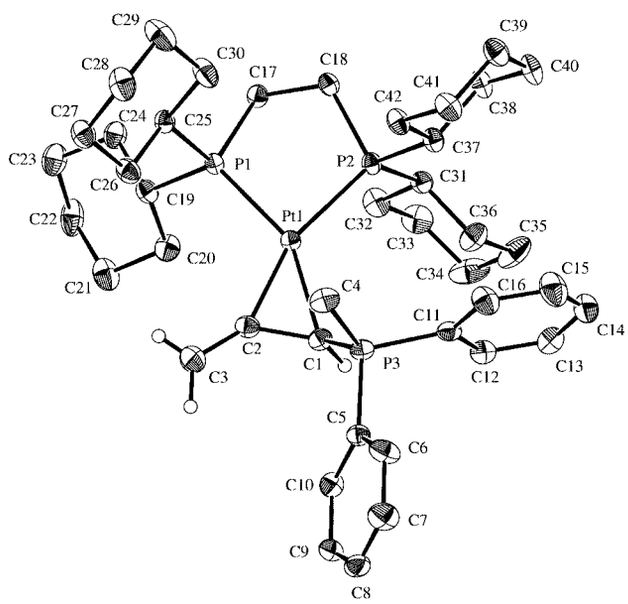


Fig. 3 An ORTEP diagram of [Pt(η^2-$MePh_2$PCH=C=CH_2}(dcpe)]$^+$ **8** with selected atom labelling and 30% probability ellipsoids; only hydrogen atoms on C(1) and C(3) are shown.

[1.206(2) Å]§ and Ph_2PC≡CPPh_2 [1.207(5) Å],[29] or in P-coordinated phosphinoalkynes.[12] The bend-back angles of the alkyne substituents are generally in the usual range (140–145°) and are slightly smaller than those in [Ni(η^2-Ph_2PC≡CMe)(dcpe)] (**1a**) (see Table 1). The exceptionally large C(2)–C(1)–P(3) angle of 151.1(2)° in complex **10** may be associated with the surprisingly short distance of 3.288(3) Å between the oxygen atom O(1) of the phosphine oxide and one of the P-bonded cyclohexyl carbon atoms, C(30), which is within the range quoted for electrostatic C–H ··· O hydrogen bonds[30] (the H ··· O distance using a calculated position for the hydrogen atom is *ca* 2.45 Å, see Fig. 6).

§ This work; this structure is not discussed in this paper but has been deposited with the Cambridge Crystallographic Data Centre as CCDC reference number 168392.

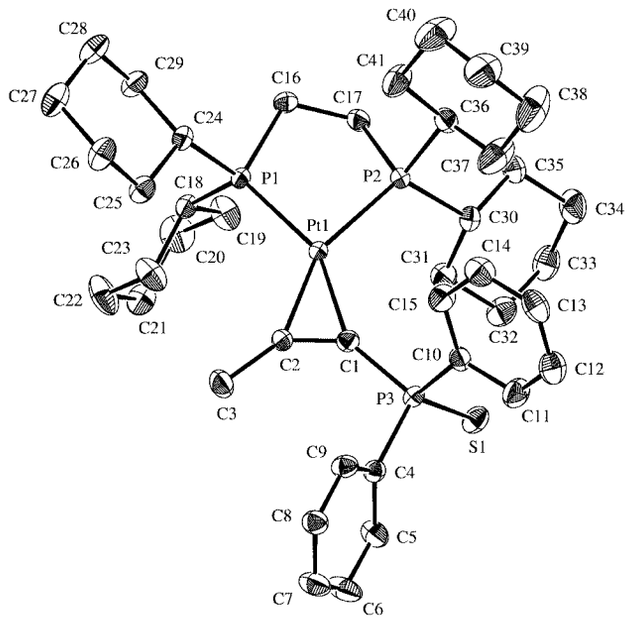


Fig. 4 An ORTEP diagram of [Pt{η²-Ph_2P(S)C≡CMe}(dcpe)] **9** with selected atom labelling and 30% probability ellipsoids; hydrogen atoms have been omitted for clarity.

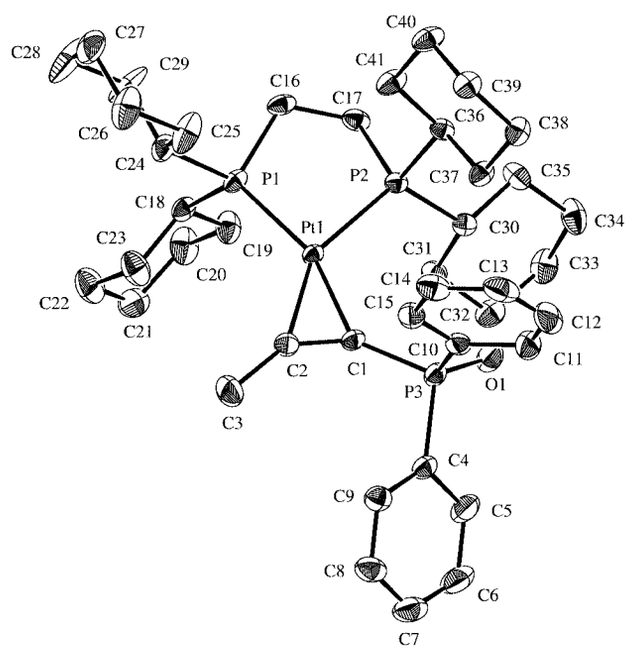


Fig. 5 An ORTEP diagram of the major conformer of [Pt{η²-Ph_2P(O)-C≡CMe}(dcpe)] **10** with selected atom labelling and 30% probability ellipsoids; hydrogen atoms have been omitted for clarity.

In complex **6**, platinum(II) is coordinated in a planar array by the phosphorus atoms of dcpe, chloride, and a η¹-C(PPh_2)=CHMe group in which the PPh_2 and methyl groups are mutually *cis*. The chlorine atom Cl(1) and the carbon atom C(1) are, respectively, *ca.* 0.29 and 0.05 Å out of the plane defined by Pt(1), P(1) and P(2). The Pt–C(1) distance [2.108(5) Å] is typical of a Pt–C(sp^2) interaction and the C–C distances within the vinyl group are unexceptional. The vinylphosphine unit is almost planar, the dihedral angle C(3)–C(2)–C(1)–P(3) being only −4.0°, and is almost perpendicular to the PtP_2 plane as shown by a dihedral angle P(2)–Pt(1)–C(1)–C(2) of 78.7°.

In complex **8**, an allenylphosphine unit is coordinated to trigonal-planar platinum(0) through carbon atoms C(1) and C(2), these two atoms lying *ca.* 0.08 and 0.20 Å from the PtP_2 plane. The Pt–C distance to the carbon atom bearing the $[PMePh_2]^+$ group [Pt–C(1) = 2.133(4) Å] is significantly greater

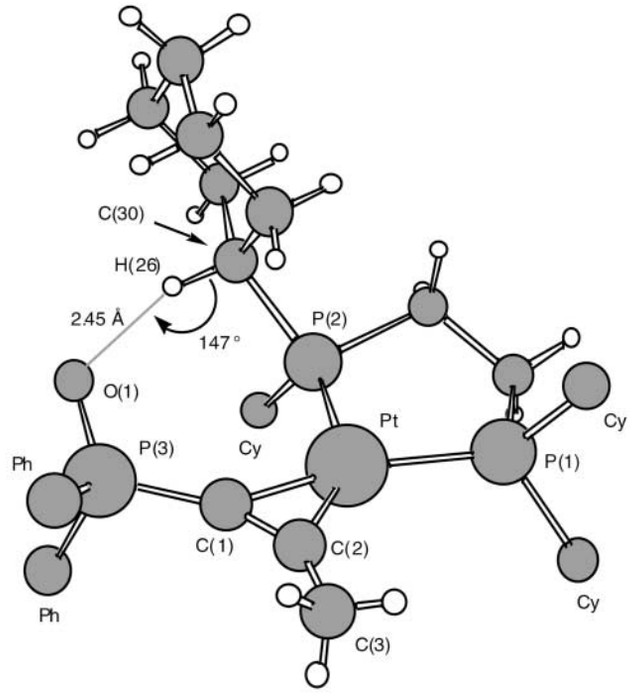


Fig. 6 Simplified view of the X-ray structure of [Pt{η²-Ph_2P(O)-C≡CMe}(dcpe)] **10** showing the postulated C–H ··· O hydrogen bond; the phenyl and cyclohexyl rings not involved in the interaction have been omitted for clarity.

than that to the one bearing the =CH_2 group [Pt–C(2) = 2.004(4) Å]. A similar effect occurs in the allene complex [Pt(η²-C_3H_4)(PPh_3)$_2$] (**11**), in which the Pt–CH_2 and Pt–C(=CH_2) distances are 2.13(3) and 2.03(3) Å, respectively.[31] The coordinated C=C bond length [C(1)–C(2) = 1.477(5) Å], is greater than the uncoordinated C=C distance [C(2)–C(3) = 1.303(6) Å], these values being similar to those found in complex **11**. Coordination causes the usually linear allene to bend away from the metal centre [C(1)–C(2)–C(3) = 137.9(4)°, *cf.* 142(5)° in **11**]. Finally, as expected for an allene, the plane of the two protons on C(3) is almost perpendicular to that containing the atoms on C(1) [the proton H(3) and P(3)], as illustrated by the dihedral angle C(3)–C(2)–C(1)–P(3) of 69.5°.

Discussion

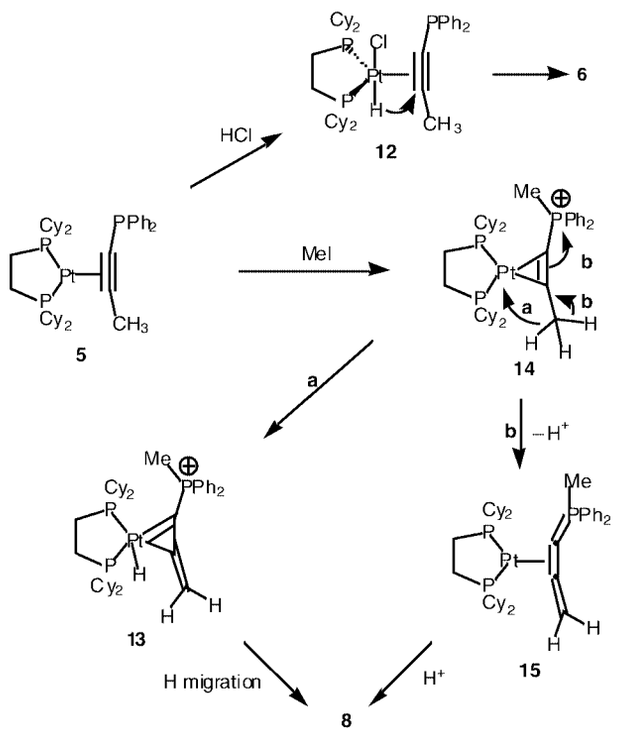
The Pt(dcpe) fragment resembles its nickel(0) analogue in stabilising η²-alkyne coordination of $Ph_2PC{\equiv}CMe$ although in both cases a P-coordinated species is the kinetic product. It is not yet known whether the driving force for the rearrangement is the electron-donating ability or the steric bulk of the M(dcpe) unit. The only comparable reported reaction of an alkynylphosphine is that of $Ph_2PC{\equiv}CCF_3$ with [M(PPh_3)$_4$] (M = Pd, Pt), which gives dinuclear products in which both C≡C and PPh_2 are coordinated[3] (see Introduction).

The first step in the protonation of platinum(0)–alkyne complexes [Pt(η²-RC≡CR)(PPh_3)$_2$] by HCl is probably oxidative addition to the metal atom,[32] and the same is likely to hold for complex **5** as shown in Scheme 3. The hydride in the resulting adduct **12** then migrates from platinum to the more electron-deficient carbon atom of the coordinated $Ph_2PC{\equiv}CMe$, forming a vinyl group in which the PPh_2 and Me groups have a *Z*-configuration. Related vinyl–platinum(II) complexes have been obtained from the addition of alkynylphosphine oxides and alkynylphosphonium salts to $[PtH(PEt_3)_2(THF)]^+$.[33,34] As in the case of **1a**,[8] there is no evidence for migration of hydride to the β-carbon atom to give a complex [PtCl{η¹-C(Me)=CH(PPh_2)}-(dcpe)]. Although the regioselectivity is the same for nickel and platinum, the resulting vinyl-phosphine group is, in the solid state, κ-*P,C*-bonded in the case of nickel and η¹-C-bonded in

Table 1 Selected bond lengths (Å) and bond angles (°) for the molecular structures of **5**, **6**, **8**–**10**, and for the nickel analogue **1a**[a]

	5 (M = Pt)	**6** (M = Pt)	**8** (M = Pt)	**9** (M = Pt)	**10** (M = Pt)	**1a** (M = Ni)[a]
M(1)–P(1)	2.253(1)	2.300(2)	2.2541(8)	2.256(1)	2.2511(7)	2.1478(8)
M(1)–P(2)	2.265(1)	2.216(1)	2.3057(9)	2.280(1)	2.2666(7)	2.1613(9)
M(1)–C(1)	2.047(5)	2.108(5)	2.133(4)	2.053(4)	2.037(3)	1.913(3)
M(1)–C(2)	2.029(5)	—	2.004(4)	2.016(4)	2.032(3)	1.869(3)
C(1)–C(2)	1.296(7)	1.304(8)	1.477(5)	1.300(6)	1.295(4)	1.280(4)
C(2)–C(3)	1.498(8)	1.565(10)	1.303(6)	1.483(7)	1.489(5)	1.489(5)
P(3)–C(1)	1.779(6)	1.804(6)	1.742(4)	1.747(5)	1.760(3)	1.763(3)
P(3)–X[b]	—	—	1.793(4)	1.960(2)	1.484(2)	—
Pt(1)–Cl(1)	—	2.370(2)	—	—	—	—
P(1)–M(1)–P(2)	87.36(5)	87.5(1)	87.11(3)	87.54(4)	87.49(3)	91.46(3)
P(1)–M(1)–C(2)	117.8(2)	—	111.6(1)	116.4(1)	123.17(9)	110.2(1)
P(2)–M(1)–C(1)	117.7(2)	92.7(1)	119.4(1)	118.6(1)	112.13(8)	118.8(1)
C(1)–C(2)–C(3)	141.8(6)	128.0(6)	137.9(4)	140.9(5)	141.8(3)	147.6(3)
P(3)–C(1)–C(2)	145.2(4)	116.1(4)	119.1(3)	140.8(4)	151.1(2)	154.9(3)
M(1)–C(1)–C(2)	70.7(3)	117.3(4)	64.5(2)	69.8(3)	71.2(2)	68.4(2)
P(1)–Pt(1)–Cl(1)	—	91.7(1)	—	—	—	—
C(1)–P(3)–X[b]	—	—	111.4(2)	115.2(2)	116.0(1)	—

[a] Data taken from ref. 8. [b] X = C(4) for **8**, S(1) for **9**, and O(1) for **10**.



Scheme 3

the case of platinum, reflecting the greater tendency of the divalent 3d-element to achieve five-coordination. The balance is evidently delicate in solution, since ionisation of Cl^- from **6** allows the vinyl phosphine to become κ-*P,C*-bonded, and the rather broad ^{31}P resonances of **6** in benzene at room temperature may be caused by reversible loss of Cl^-. As in the nickel(II) complex **2a**,[8] and in several complexes of molybdenum and tungsten,[35–38] the resulting three-membered ring shows a characteristic ^{31}P-NMR shielding that is *ca.* 70 ppm greater than those of known phosphaplatinacyclopropane complexes, $PtCR_2PPh_2$-κ*P,C*.[39,40] This phenomenon has been attributed to decrease in the C–P–M angle resulting from the presence of the sp^2 hybridised methylene carbon atom in the metallacycle.[8]

Methyl iodide quaternises the free phosphorus atom of **5** rather than undergoing oxidative addition to the platinum centre, the reaction being accompanied by an alkyne to allene rearrangement that yields an η^2-allenyl–platinum(0) complex. Although η^2-allenylphosphonium complexes of the type $[(\eta^6$-arene)$M(CO)_2(\eta^2$-$Ph_3PCH{=}C{=}CH_2)]^+$ (M = Cr,[41] Mo[42]) and $[(\eta^5$-$C_5H_5)Mn(CO)_2(\eta^2$-$Ph_3PCH{=}C{=}CH_2)]^+$ [41] are known, complex **8** appears to be the first structurally characterised example. Moreover, the alkynylphosphine to allenylphosphine rearrangement in the coordination sphere of a transition metal atom has not been observed previously, although the base-catalysed rearrangement of the free ligand is well established.[43] There are several examples of the formation of η^2-coordinated allene complexes from alkyne precursors, *e.g.* $[ReCl(\eta^2$-$CH_2{=}C{=}CHPh)(dppe)_2]$ from $[ReCl(N_2)(dppe)_2]$ and $PhC{\equiv}CMe$,[44] $[Rh(\eta^5$-$C_5H_5)(P^iPr_3)(\eta^2$-$CH_2{=}C{=}CHMe)]$ by isomerisation of the corresponding but-2-yne complex on an alumina column,[45] $[Mn(\eta^5$-$C_5H_5)(CO)_2(\eta^2$-1,2-cyclooctadiene)] from the corresponding cyclooctyne complex,[46] and $[Re(\eta^5$-$C_5R_5)(CO)_2(\eta^2$-$CH_2{=}C{=}CHMe)]$ (R = H, Me) by an alumina- or acid-catalysed process from its but-2-yne precursor.[47,48] A detailed study has shown that the acid-catalysed rearrangement of $[Re(\eta^5$-$C_5Me_5)(CO)_2(\eta^2$-$MeC{\equiv}CMe)]$ proceeds *via* a rhenacyclopropene intermediate. On this basis, we suggest an intramolecular transfer of the proton *via* a platinacyclopropene intermediate **13** (pathway **a** in Scheme 3). Alternatively, the strongly electron-withdrawing $[PMePh_2]^+$ substituent could induce a prototropic rearrangement *via* a neutral η^2-allenylylide–platinum(0) complex (**14** ⟶ **15** ⟶ **8**, pathway **b**), the proton lost from C^3 re-adding at C^1.

In conclusion, we have shown that the platinum(0)–dcpe fragment can stabilise η^2-alkyne coordination of the ligand $Ph_2PC{\equiv}CMe$, the product being similar to, but more stable than, its nickel(0) analogue. It is also possible to induce an alkyne to allene rearrangement by quaternisation of the uncoordinated phosphorus atom. The resulting complexes may be capable of insertion reactions leading to functionalisation of the unsaturated centre.

Experimental

General

All experiments, unless otherwise specified, were carried out under nitrogen with use of standard Schlenk techniques. All solvents were dried and degassed before use. NMR spectra were recorded on a Varian XL-200E (^1H at 200 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81.0 MHz), a Varian Gemini 300BB or Inova-300 (^1H at 300 MHz, ^{13}C at 75.4 MHz, ^{31}P at 121.4 MHz), or a Varian Inova-500 instrument (^1H at 500 MHz, ^{13}C at 125.7 MHz) at 298K unless otherwise specified. The chemical shift (δ) for ^1H and ^{13}C are given in ppm relative to residual signals of the solvent, and to external 85% H_3PO_4 for ^{31}P. The spectra of

all nuclei (except ^{1}H) were ^{1}H-decoupled. The coupling constants (J) are given in Hz with an estimated error for the values measured from ^{31}P and ^{13}C NMR spectra of ±0.2 Hz unless otherwise stated. The numbering scheme used in the description of the ^{13}C NMR data of the alkynylphosphine complex **5** is $Ph_2PC^1{\equiv}C^2C^3H_3$ and the same numbering order has been used for its derivatives. Infrared spectra were measured on Perkin–Elmer FT-1800 or Spectrum One instruments. Mass spectra were obtained on a ZAB-2SEQ spectrometer by fast-atom bombardment (FAB).

All the new complexes were isolated as sticky, crystalline solids that tenaciously retained organic solvents. This property, together with the limited amounts of sample, frustrated attempts to obtain satisfactory elemental analyses. However, the compounds have been characterised unambiguously by spectroscopic measurements and single-crystal X-ray diffraction analyses.

Starting materials

(Prop-1-ynyl)diphenylphosphine, $Ph_2PC{\equiv}CMe$, and its chalcogenide derivatives, $Ph_2P(X)C{\equiv}CMe$ (X = O, S), were prepared by published procedures.[49–51] The complex [Pt(η^2-C_2H_4)(dcpe)] has been made previously by treating [Pt(cod)$_2$] with dcpe in ethene-saturated hexane.[52] We prepared it by reducing a THF solution of [$PtCl_2$(dcpe)] with 1% sodium amalgam in an atmosphere of ethene; a similar procedure employing dihydrogen in place of ethene gives [PtH(dcpe)]$_2$.[53]

Preparations

[Pt(η^2-$Ph_2PC{\equiv}CMe$)(dcpe)], 5. $Ph_2PC{\equiv}CMe$ (112 mg, 0.5 mmol) was added at 0 °C to a stirred suspension of [Pt(η^2-C_2H_4)(dcpe)] (320 mg, 0.496 mmol) in diethyl ether (20 cm^3). After 30 min, ^{31}P NMR monitoring of the yellow solution indicated that the reaction was complete, and the solution was evaporated to dryness *in vacuo*. The residue was rinsed with hexane and, after drying, [Pt(η^2-$Ph_2PC{\equiv}CMe$)(dcpe)] (**5**) (359 mg, 85%) was obtained as a white solid. Colorless crystals suitable for X-ray analysis were obtained from a toluene solution layered with hexane at 0 °C. The compound is stable indefinitely in the absence of air. IR (THF) 1700 (m, C≡C), 742 (s), 695 (s) cm^{-1}. δ_H (300 MHz, C_6D_6) 1.05–2.15 (m, 48H, CH_2 and CH of dcpe), 2.94 (d, 3H, J(PH) 7.7, J(PtH) 39.8, Me), 7.03–7.25 (m, 6H), 7.94 (br t, 4H, J(HH) 7.1, Ph). δ_C (125.7 MHz, C_6D_6) 19.56 (t, J(PC) 10.3, Me), 24.01 (dd, J(PC) 25.9, 15.4, PCH_2), 25.4 (dd, J(PC) 27.0, 16.3, PCH_2), 26.25–30.20 (m, CH_2 of C_6H_{11}), 34.86 (ddd, J(PC) 21.1, 3.7, 1.8, CH of C_6H_{11}), 35.89 (dd, J(PC) 22.9, 4.1, CH of C_6H_{11}), 117.61 (ddd, J(PC) 71.5, 42.4, 7.1, C^1), 127.77 (s, aromatic CH), 128.21 (d, J(PC) 21.5, aromatic CH) 134.02 (d, J(PC) 20.2, aromatic CH), 142.89 (dd, J(PC) 14.4, 5.0, aromatic C), 145.55 (ddd, J(PC) 69.9, 11.0, 6.9, C^2). δ_P (80.96 MHz, C_6D_6) −11.5 (dd, ^3J(PP) 44.7, 22.1, J(PtP) 35.3), 67.8 (dd, ^2J(PP) 49.4, ^3J(PP) 22.1, J(PtP) 2968), 69.8 (dd, ^2J(PP) 49.5, ^3J(PP) 44.6, J(PtP) 3281). FAB-MS (tetraglyme, $C_{41}H_{61}PtP_3$) m/z 842 [MH]$^+$.

[PtCl{C(=CHMe)PPh_2}(dcpe)], 6. A solution of **5**, freshly prepared from [Pt(η^2-C_2H_4)(dcpe)] (250 mg, 0.39 mmol) and $Ph_2PC{\equiv}CMe$ (90 mg, 0.4 mmol) in diethyl ether (20 cm^3), was cooled to 0 °C, and treated dropwise with a solution of HCl in diethyl ether (0.39 mmol). A white precipitate formed as the reaction mixture was allowed to warm to room temperature. The solvent was removed and the residue was washed with hexane. The ^{31}P NMR spectrum of the solid indicated complete disappearance of **5**. Complex **6** was obtained in quantitative yield and colourless, air-stable crystals suitable for X-ray crystallography were obtained from diffusion of hexane into a solution in CH_2Cl_2 at 0 °C. IR (KBr) 3048(w), 2920(s), 2848(s), 1580(w, C=C), 1445(m), 746(m), 694(m) cm^{-1}. δ_H (300 MHz, C_6D_6) 1.05–2.90 (m, 51H, CH_2, CH of dcpe and Me), 6.72 (m, 1H, =CH), 6.98–7.28 (m, 6H), 8.51 (t, 4H, J(HH) 7.3, Ph). δ_C (125.7 MHz, C_6D_6) 20.12 (dd, J(PC) 24.7, 11.5, PCH_2), 22.33 (dd, J(PC) 20.8, 9.7, Me), 25.28 (dd, J(PC) 34.4, 16.5, PCH_2), 26.20–29.30 (m, CH_2 of C_6H_{11}), 33.78 (d, J(PC) 24.5, CH of C_6H_{11}), 35.01 (d, J(PC) 33.2, CH of C_6H_{11}), 127.41 (s, aromatic CH), 127.87 (d, J(PC) 8.0, aromatic CH), 136.10 (d, J(PC) 20.2, aromatic CH), 137.73 (m, aromatic C), 143.89 (m, C^1), C^{2}H could not be located. δ_P (80.96 MHz, C_6D_6) 7.9 (br s), 49.1 (br s, J(PtP) 4096), 61.8 (d, J(PP) 10.5, J(PtP) 1822). δ_P (80.96 MHz, CD_2Cl_2) −88.3 (br d, J(PtP) 307, J(PtP) 1136), 72.0 (d, J(PP) 307, J(PtP) 2518), 73.2 (br s, J(PtP) 2416). FAB-MS (tetraglyme, $C_{41}H_{62}ClPtP_3$): m/z 843 [M − Cl]$^+$.

[Pt{η^2-C(=CH_2)=$CHPPh_2Me$}(dcpe)]I, [8]I. A solution of **5**, freshly prepared from [Pt(η^2-C_2H_4)(dcpe)] (150 mg, 0.23 mmol) and $Ph_2PC{\equiv}CMe$ (53 mg, 0.24 mmol) in diethyl ether (10 cm^3), was cooled to 0 °C. A solution of methyl iodide in diethyl ether (0.23 mmol) was added dropwise, initially forming a brown precipitate and a green solution. After 30 min at room temperature, the solid had redissolved and the solution had turned purple. The solvent volume was reduced by evaporation *in vacuo*, and the salt [**8**]I was obtained as colorless, air-stable crystals by diffusion of hexane into the concentrated reaction mixture at 0 °C. IR (KBr) 2923 (s), 2850 (m), 1647 (w, C=C), 1436 (m), 744 (m) cm^{-1}. δ_H (500 MHz, CD_2Cl_2) 1.00–2.05 (m, 48H, CH_2 and CH of dcpe), 2.13 (d, 3H, J(PH) 22.0, PMe), 2.85 (td, 1H, J 13.5, 4.5, J(PtH) 78.0, C^{1}H), 6.08 (ddd, 1H, J 19.5, 10.5, 5.5, J(PtH) 73.0, Z–C^{3}H), 6.70 (app. d of qnt, 1H, J 38.0, 4.5, J(PtH) 133.0, E–C^{3}H), 7.58–7.93 (m, 10H, Ph). δ_P (80.96 MHz, CD_2Cl_2) 20.3 (dd, ^3J(PP) 12.9, 2.0, J(PtP) 110.1), 68.9 (dd, ^2J(PP) 32.6, ^3J(PP) 12.7, J(PtP) 2472), 73.7 (dd, ^2J(PP) 32.6, ^3J(PP) 2.0, J(PtP) 3542). FAB-MS (NOPE, $C_{42}H_{65}IP_3Pt$): m/z 856 [**8**]$^+$.

[Pt{η^2-$Ph_2P(S)C{\equiv}CMe$}(dcpe)], 9. Solid $Ph_2P(S)C{\equiv}CMe$ (10 mg, 0.04 mmol) was added to a suspension of [Pt(C_2H_4)(dcpe)] (20 mg, 0.04 mmol) in diethyl ether (5 cm^3) at room temperature. Monitoring of the resulting yellow solution by ^{31}P NMR spectroscopy showed the reaction to be quantitative. Crystals suitable for X-ray analysis were obtained by layering a toluene solution of **9** with MeOH at −20 °C.

When a solution of **5** in C_6D_6 in an NMR tube was treated at room temperature with an excess of sulfur, complex **9** was formed instantly and quantitatively, as shown by ^{31}P NMR spectroscopy. IR (KBr): 3050 (w), 2922 (s), 2847 (s), 1697 (s, C≡C), 1445 (s), 1435 (s), 1098 (m), 645 (s) cm^{-1}. δ_H (300 MHz, C_6D_6) 0.95–2.00 (m, 48H, dcpe), 2.78 (dd, 3H, J(PC) 8.1, 2.7, J(PtH) 40.8, Me), 6.90–7.15 (m, 6H), 8.21–8.31 (m, 4H, Ph). δ_C (50.3 MHz, C_6D_6) 19.72 (t, J(PC) 9.8, Me), 23.85 (dd, J(PC) 25.7, 14.6, PCH_2), 25.66 (dd, J(PC) 28.1, 15.6, PCH_2), 26.20–30.20 (m, CH_2 of C_6H_{11}), 35.45 (br dd, J(PC) 23.0, 3.4, CH of C_6H_{11}), 35.95 (dd, J(PC) 23.9, 3.9, CH of C_6H_{11}), 119.25 (ddd, J(PC) 75.5, 74.2, 3.0, C^1), 128.03 (d, J(PC) 28.5, aromatic CH), 129.95 (d, J(PC) 3.0, aromatic CH), 132.12 (d, J(PC) 10.5, aromatic CH), 138.44 (dd, J(PC) 83.4, 2.9, aromatic C), 158.23 (ddd, J(PC) 71.1, 7.5, 3.6, J(PtC) 338.4, C^2). δ_P (80.96 MHz, C_6D_6) 29.1 (dd, ^3J(PP) 50.1, 45.9, J(PtP) 50.9, $P(S)Ph_2$), 67.6 (dd, ^2J(PP) 41.7, ^3J(PP) 45.9, J(PtP) 2951, dcpe), 69.0 (dd, ^2J(PP) 41.7, ^3J(PP) 50.1, J(PtP) 3376, dcpe). FAB-MS (NOPE, $C_{41}H_{61}P_3PtS$): m/z 875 [MH]$^+$, 791 [MH − Cy]$^+$.

[Pt{η^2-$Ph_2P(O)C{\equiv}CMe$}(dcpe)], 10. Solutions of **5** in diethyl ether or C_6D_6 were stirred in air at room temperature for 2–4 h. Monitoring of the reactions by ^{31}P NMR spectroscopy showed that **10** was formed quantitatively. Single crystals suitable for X-ray analysis were obtained by slow evaporation of an ether solution.

When a solution of $Ph_2P(O)C{\equiv}CMe$ (14 mg, 0.05 mmol) in ether (5 cm^3) was added to a suspension of [Pt(C_2H_4)(dcpe)]

Table 2 Crystal and structure refinement data for compounds $Ph_2PC{\equiv}CMe$, **5**, **6**, **8**, **9** and **10**

Compound	$Ph_2PC{\equiv}CMe$	**5**	**6**	**8**	**9**	**10**
Chemical formula	$C_{15}H_{13}P$	$C_{41}H_{61}P_3Pt$	$C_{41}H_{62}ClP_3Pt$	$C_{42}H_{64}P_3Pt^+I^-{\cdot}CH_2Cl_2$	$C_{41}H_{61}P_3PtS$	$C_{41}H_{61}OP_3Pt$
M	224.25	841.94	878.41	1068.82	874.00	857.94
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	8.0665(1)	10.1711(2)	15.7234(1)	12.0184(1)	10.0314(1)	9.5663(1)
b/Å	7.8531(1)	21.4981(4)	13.0059(1)	20.6516(2)	22.3462(2)	10.39139(1)
c/Å	19.9037(4)	18.1159(4)	19.9130(2)	19.0894(2)	17.5937(2)	20.3829(2)
α/°						97.0342(5)
β/°	96.5081(6)	100.6444(9)	96.7321(3)	103.5680(3)	91.7507(4)	100.9522(5)
γ/°						95.5804(4)
U/Å^3	1252.72(3)	3893.0(1)	4044.07(5)	4605.75(7)	3942.03(6)	1959.15(3)
D_x/g cm^{-3}	1.189	1.436	1.443	1.541	1.473	1.454
Z	4	4	4	4	4	2
μ (Mo Kα)/mm^{-1}	0.188	3.740	3.667	3.953	3.747	3.719
Total reflections	28529	39277	97423	96374	72750	57797
Unique reflections (R_{int})	2859 (0.054)	6888 (0.054)	11854 (0.041)	10687 (0.048)	9024 (0.073)	11489 (0.043)
Observed reflections	2230 [$I > 3\sigma(I)$]	6043 [$I > 2\sigma(I)$]	9407 [$I > 3\sigma(I)$]	9658 [$I > 3\sigma(I)$]	7877 [$I > 2\sigma(I)$]	10491 [$I > 2\sigma(I)$]
Absorp. corr. (trans. factors)	integration (0.948 to 0.983)	integration (0.569 to 0.777)	integration (0.568 to 0.687)	integration (0.616 to 0.756)	integration (0.781 to 0.893)	integration (0.544 to 0.751)
No. of parameters	197	406	192	470	415	440
R(observed data)	0.0387	0.0403	0.0484	0.0365	0.0453	0.0328
Rw (observed data)	0.0514	0.0487	0.0904	0.0425	0.0460	0.0376

(30 mg, 0.05 mmol) in diethyl ether (5 cm^3) at room temperature, the solution turned yellow instantly. The mixture was stirred for 1 h, and the ^{31}P NMR spectrum of the solution showed the formation of **10** to be quantitative. IR (KBr): 3052 (w), 2926 (s), 2849 (s), 1699 (m br, C≡C), 1446 (m), 1436(m), 1188 (m), 719(m) cm^{-1}. δ_H (300 MHz, C_6D_6) 0.95–2.05 (m, 48H, dcpe), 2.87 (dd, 3H, J(PC) 7.2, 1.8, J(PtH) 36, Me), 7.00–7.15 (m, 6H), 7.98 (ddd, 2H, J 12.9, 6.6, 2.7), 8.12 (dd, 2H, J 10.2, 6.3, Ph). δ_P (75.4 MHz, C_6D_6) 20.00 (t, J(PC) 10.4, Me), 23.80 (dd, J(PC) 25.0, 14.8, PCH_2), 25.55 (dd, J(PC) 27.4, 16.6, PCH_2), 26.00–30.10 (m, CH_2 of C_6H_{11}), 35.22 (dd, J(PC) 21.4, 4.4, CH of C_6H_{11}), 35.88 (dd, J(PC) 22.5, 5.5, CH of C_6H_{11}), 118.32 (app. dd, J(PC) 111.2, 63.7, C^1), 128.00 (d, J(PC) 11.8, aromatic CH), 130.03 (d, J(PC) 2.5, aromatic CH), 131.80 (d, J(PC) 9.9, aromatic CH), 139.03 (dd, J(PC) 103.6, 3.0, aromatic C), 158.41 (app. d, J(PC) 64.6, C^2). δ_P (80.96 MHz, C_6D_6) 12.3 (dd, ^3J(PP) 38.5, 35.4, J(PtP) 67.8, $P(O)Ph_2$), 68.5 (dd, ^2J(PP) 44.4, ^3J(PP) 38.5, J(PtP) 2981, dcpe), 69.0 (dd, ^2J(PP) 44.4, ^3J(PP) 35.4, J(PtP) 3343, dcpe). FAB-MS (NOPE, $C_{41}H_{61}OP_3Pt$): m/z 858 $[MH]^+$.

X-Ray crystallography

Crystal data, details of data collection, data processing, structure analysis and structure refinement are in Table 2. All crystals were mounted in silicone oil on a glass fibre and the data collected at −73 °C on a Nonius KappaCCD diffractometer (Mo Kα radiation, λ = 0.7107 Å) with use of the crystallographic software package maXus.[54] The intensities of the reflections were processed by use of the computer programs Denzo and Scalepak.[55] The structures of $Ph_2PC{\equiv}CMe$ and **5** were solved by direct methods (SIR92),[56] while the molecular structures of **6**, **8**–**10** were solved by the Patterson method (PATTY).[57] The structures were refined by use of the software package TEXSAN[58] unless stated otherwise.

The non-hydrogen atoms of $Ph_2PC{\equiv}CMe$ were refined anisotropically, while the hydrogen atoms were observed in a difference electron density map and refined with isotropic displacement factors. The maximum and minimum peaks in the final difference Fourier map were 0.21 and −0.24 e Å^{-3}, respectively. The non-hydrogen atoms of **5** were refined anisotropically by full-matrix least-squares. Hydrogen atoms were included at calculated positions (C–H 0.95Å) and periodically recalculated, but not refined. The maximum and minimum peaks in the final difference Fourier map were 0.85 and −1.26 e Å^{-3}, respectively.

In the crystal structure of **6**, the molecular species was disordered and present in two possible conformations in a 1 : 1 ratio. The program RAELS00[59] was used for constrained refinement and in the final cycle 192 variables were used to refine the 9407 observed reflections. The structure was modelled so that the phenyl rings C(4)–C(9) and C(10)–C(15), C(16) and the two cyclohexyl groups C(18)–C(23) and C(24)–C(29) were disordered, while the remainder of the molecule was not. All phenyl rings were constrained to have equal geometry relative to the atom P(3) and similar constraint was applied to the two cyclohexyl rings relative to P(1).[60] Restraints on some bond lengths were also imposed. Pt(1), Cl(1), C(16), C(16′) and C(17) were refined as isolated anisotropic atoms, while rigid body thermal parametrisations were used for the remaining non-hydrogen atoms.[60] Hydrogen atoms were located in geometrically sensible positions after each refinement cycle. The maximum and minimum peaks in the final difference Fourier map were 2.02 and −1.69 e Å^{-3}, respectively.

In the crystal structure of **[8]**I·CH_2Cl_2, the cationic molecular species and the iodide were clearly defined, but the solvent molecule was partially disordered. The non-hydrogen atoms of **8** were refined anisotropically by full-matrix least-squares. The hydrogen atoms H(1), H(2) and H(3) were located in a difference electron density map and refined positionally, but the other hydrogen atoms were included at calculated positions (C–H 0.95Å) and not refined. The maximum and minimum peaks in the final difference Fourier map were 1.60 and −1.32 e Å^{-3}, respectively.

In the structure of **9**, the non-hydrogen atoms were refined anisotropically by full-matrix least-squares. Hydrogen atoms were included at calculated positions (C–H 0.95Å) and periodically recalculated, but not refined. The hydrogen atoms of the methyl group were orientated to best-fit peaks in the difference electron density map. The maximum and minimum peaks in the final difference Fourier map were 1.16 and −1.41 e Å^{-3}, respectively.

In the crystal structure of **10**, one cyclohexyl ring of the dcpe ligand was disordered and appeared to be distributed over two sites in a 0.7 : 0.3 ratio. Refinement was originally carried out isotropically with restraints imposed upon the C–C bond distances for this ring, but the major conformation was subsequently refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions (C–H 0.95Å) and periodically recalculated; those of the disordered ring were calculated for the major orientation only with an

occupancy of 0.7. The hydrogen atoms of the methyl group were orientated to best-fit the difference electron density map. The maximum and minimum peaks in the final difference Fourier map were 0.84 and −1.30 e $Å^{-3}$, respectively.

The neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ values and mass attenuation coefficients were taken from ref. 61 for all structures.

CCDC reference numbers 168392–168397.

See http://www.rsc.org/suppdata/dt/b1/b107015k/ for crystallographic data in CIF or other electronic format.

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References

1 For early examples of η^1-$Ph_2PC{\equiv}CR$ complexes, see (*a*) R. B. King and A. Efraty, *Inorg. Chim. Acta*, 1970, **4**, 319; (*b*) K. S. Wheelock, J. H. Nelson and H. B. Jonassen, *Inorg. Chim. Acta*, 1970, **4**, 399; (*c*) R. T. Simpson and A. J. Carty, *J. Coord. Chem.*, 1973, **2**, 207.
2 H. N. Paik, A. J. Carty, K. Dymock and G. J. Palenik, *J. Organomet. Chem.*, 1974, **70**, C17.
3 S. Jacobson, A. J. Carty, M. Mathew and G. L. Palenik, *J. Am. Chem. Soc.*, 1974, **96**, 4330.
4 H. A. Patel, A. J. Carty and N. K. Hota, *J. Organomet. Chem.*, 1973, **50**, 247.
5 A. J. Carty, H. N. Paik and T. W. Ng, *J. Organomet. Chem.*, 1974, **74**, 279.
6 (*a*) B. C. Ward and J. L. Templeton, *J. Am. Chem. Soc.*, 1980, **102**, 1532; (*b*) T. M. Nickel, S. Y. W. Wau and M. J. Went, *J. Chem. Soc., Chem. Commun.*, 1989, 775; (*c*) A. K. Powell and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1992, 439.
7 M. A. Bennett, C. J. Cobley, A. D. Rae, E. Wenger and A. C. Willis, *Organometallics*, 2000, **19**, 1522.
8 M. A. Bennett, J. Castro, A. J. Edwards, M. R. Kopp, E. Wenger and A. C. Willis, *Organometallics*, 2001, **20**, 980.
9 N. M. Boag, M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 2170.
10 G. Butler, C. Eaborn and A. Pidcock, *J. Organomet. Chem.*, 1981, **210**, 403.
11 M.-R. Lequan, M.-J. Pouet and M.-P. Simonnin, *Org. Magn. Res.*, 1975, **7**, 392.
12 E. Louattani, A. Lledós, J. Suades, A. Alvarez-Larena and J. F. Piniella, *Organometallics*, 1995, **14**, 1053.
13 U. Rosenthal, G. Oehme, V. V. Burlakov, P. V. Petrovskii, V. B. Shur and M. E. Vol'pin, *J. Organomet. Chem.*, 1990, **391**, 119.
14 T. Bartik, B. Happ, M. Iglewsky, H. Bandmann, R. Boese, P. Heimbach, T. Hoffmann and E. Wenschuh, *Organometallics*, 1992, **11**, 1235.
15 E. O. Greaves, C. J. L. Lock and P. M. Maitlis, *Can. J. Chem.*, 1968, **46**, 3879.
16 U. Rosenthal, *Z. Anorg. Allg. Chem.*, 1981, **482**, 179.
17 M. A. Bennett, J. A. Johnson and A. C. Willis, *Organometallics*, 1996, **15**, 68.
18 T. G. Appleton and M. A. Bennett, *Inorg. Chem.*, 1978, **17**, 738.
19 S. O. Grim, R. P. Molenda and J. D. Mitchell, *J. Org. Chem.*, 1980, **45**, 250.
20 M. Duncan and M. J. Gallagher, *Org. Magn. Res.*, 1981, **15**, 37.
21 P. S. Pregosin and R. W. Kunz, ^{31}P- and ^{13}C-NMR of Transition Metal Phosphine Complexes, Springer Verlag, Berlin, 1979, p. 121.
22 T. A. Albright, W. J. Freeman and E. E. Schweizer, *J. Am. Chem. Soc.*, 1975, **97**, 2946.
23 M. J. Gallagher, *Aust. J. Chem.*, 1968, **21**, 1197.
24 M.-P. Simonnin and C. Charrier, *Org. Magn. Res.*, 1969, **1**, 27.
25 S. Otsuka, A. Nakamura and K. Tani, *J. Organomet. Chem.*, 1968, **14**, P30.
26 F. L. Bowden and R. Giles, *Coord. Chem. Rev.*, 1976, **20**, 81.
27 T. A. Albright, W. J. Freeman and E. E. Schweizer, *J. Org. Chem.*, 1975, **40**, 3437.
28 S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, 1976, **14**, 33.
29 J. Bart, *Acta Crystallogr., Sect. B*, 1969, **25**, 489.
30 G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond In Structural Chemistry and Biology*, International Union of Crystallography, Monographs on Crystallography 9, Oxford University Press, Oxford and New York, 1999.
31 M. Kadonaga, N. Yasuoka and N. Kasai, *J. Chem. Soc., Chem. Commun.*, 1971, 1597.
32 F. R. Hartley, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 6, p. 702.
33 C. M. Lukehart, A. T. McPhail, D. R. McPhail, J. B. Myers Jr. and H. K. Soni, *Organometallics*, 1989, **8**, 1007.
34 A. C. Dema, X. Li, C. M. Lukehart and M. D. Owen, *Organometallics*, 1991, **10**, 1197.
35 J. Ostermeier, W. Hiller and F. R. Kreissl, *J. Organomet. Chem.*, 1995, **491**, 283.
36 G. A. Acum, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Chem. Soc., Dalton Trans.*, 1995, 3049.
37 G. Conole, K. A. Hill, M. McPartlin, M. J. Mays and M. J. Morris, *J. Chem. Soc., Chem. Commun.*, 1989, 688.
38 J. Ipaktschi, T. Klotzbach and A. Dülmer, *Organometallics*, 2000, **19**, 5281.
39 S. Bresadola, B. Longato and F. Morandini, *J. Organomet. Chem.*, 1977, **128**, C5.
40 S. Bresadola, N. Bresciani-Pahor and B. Longato, *J. Organomet. Chem.*, 1979, **179**, 73.
41 V. V. Krivykh, E. S. Taits and M. I. Rybinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2866; V. V. Krivykh, E. S. Taits and M. I. Rybinskaya, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 2663.
42 V. V. Krivykh, E. S. Taits, P. V. Petrovskii, Y. T. Struchkov and A. I. Yanovskii, *Mendeleev Commun.*, 1991, 103.
43 W. Hewertson, I. C. Taylor and S. Trippett, *J. Chem. Soc. C*, 1970, 1835.
44 D. L. Hughes, A. J. L. Pombeiro, C. J. Pickett and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1984, 992.
45 J. Wolf and H. Werner, *Organometallics*, 1987, **6**, 1164.
46 S. M. Coughlan and G. K. Yang, *J. Organomet. Chem.*, 1993, **450**, 151.
47 C. P. Casey and J. T. Brady, *Organometallics*, 1998, **17**, 4620.
48 C. P. Casey, J. T. Brady, T. M. Boller, F. Weinhold and R. K. Hayashi, *J. Am. Chem. Soc.*, 1998, **120**, 12500.
49 C. Charrier, W. Chodkiewicz and P. Cadiot, *Bull. Soc. Chim. Fr.*, 1966, 1002.
50 A. J. Carty, N. K. Hota, T. W. Ng, H. A. Patel and T. J. O'Connor, *Can. J. Chem.*, 1971, **49**, 2706.
51 K. I. Booker-Milburn, in *Comprehensive Organic Functional Group Transformations*, ed. A. R. Katrizky, O. Meth-Cohn, C. W. Rees and S. V. Ley, Elsevier, Oxford, 1995, vol. 2, p. 1039.
52 N. Carr, L. Mole, A. G. Orpen and J. L. Spencer, *J. Chem. Soc., Dalton Trans.*, 1992, 2653.
53 D. J. Schwartz and R. A. Andersen, *J. Am. Chem. Soc.*, 1995, **117**, 4014.
54 S. Mackay, C. J. Gilmore, C. Edwards, N. Stewart and K. Shankland, maXus Computer Program for the Solution and Refinement of Crystal Structures, Nonius, The Netherlands, 1999.
55 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter Jr. and R. M. Sweet, Academic Press, New York, 1997, vol. 276, pp. 307–326.
56 A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
57 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The PATTY and DIRDIF Program System, Technical Report of the Crystallographic Laboratory, University of Nijmegen, Nijmegen, 1992.
58 TEXSAN: Single Crystal Structure Analysis Software, Vers. 1.8, Molecular Structure Corp., The Woodlands, TX, 1997.
59 A. D. Rae, RAELS00: A Comprehensive Constrained Least-Square Refinement Program, Australian National University, Canberra, ACT, 2000.
60 A. D. Rae, *Acta Crystallogr., Sect. A*, 1975, 560.
61 International Tables for Crystallography, Kluwer Academic, Dordrecht, 1992, vol. C.