

Generation of (η^2 -benzyne)bis(triphenylphosphine)platinum(0): orthometallation of the Pt(PPh₃)₂ complexes of benzyne (C₆H₄) and cyclohexyne (C₆H₈)

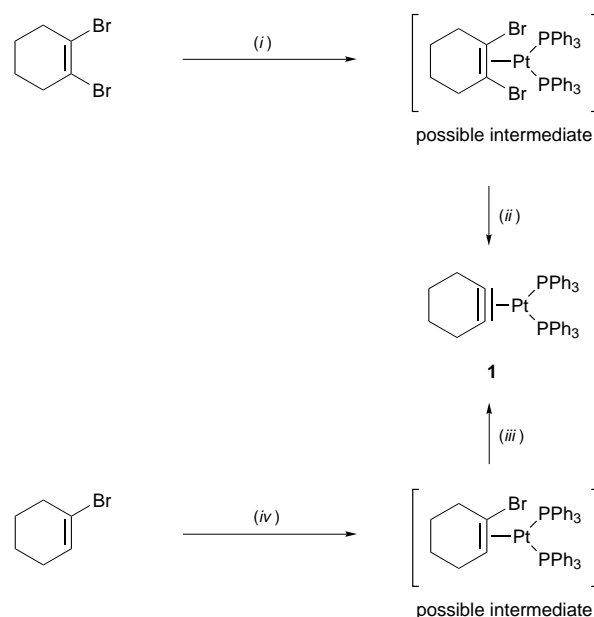
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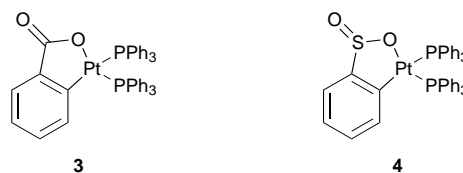
The benzyne–platinum(0) complex [Pt(PPh₃)₂(η^2 -C₆H₄)] has been generated by treatment of a mixture of [Pt(PPh₃)₂(η^2 -C₂H₄)] and chlorobenzene with 2,2,6,6-tetramethylpiperid-1-yl lithium at 0 °C and identified by comparison of its ³¹P NMR parameters with those of the cyclohexyne analogue, [Pt(PPh₃)₂(η^2 -C₆H₈)]. The compounds isolated from the reaction and identified by NMR spectroscopy and X-ray crystallography are the (2,2'-biphenyldiyl)platinum(II) complex [Pt(η^1 : η^1 -C₆H₄C₆H₄)(PPh₃)₂], formed by reaction of [Pt(PPh₃)₂(η^2 -C₆H₄)] with free benzyne, and the orthometallated (η^1 -phenyl)platinum(II) complex [Pt{C₆H₄(PPh₂)-2}(C₆H₅)(PPh₃)], formed by internal hydrogen-atom migration in [Pt(PPh₃)₂(η^2 -C₆H₄)]. The complex [Pt(PPh₃)₂(η^2 -C₆H₈)] undergoes a similar isomerization on heating in benzene to give the (η^1 -cyclohexen-1-yl)platinum(II) complex [Pt{C₆H₄(PPh₂)-2}(C₆H₉)(PPh₃)], whose structure has also been determined by X-ray crystallography.

Short-lived cyclic alkynes, such as cycloheptyne (C₇H₁₀), cyclohexyne (C₆H₈) and benzyne (C₆H₄) can be stabilized by complex formation with a variety of transition-metal fragments,^{1–3} including those of the zerovalent d¹⁰ metals ML₂ (M = Ni, Pd or Pt; L = various tertiary phosphines). A key compound in this work is the cyclohexyne complex [Pt(PPh₃)₂(η^2 -C₆H₈)] **1**, which was first prepared in high yield by the reduction of 1,2-dibromocyclohexene with 1% sodium amalgam in the presence of [Pt(PPh₃)₃] or [Pt(PPh₃)₂(η^2 -C₂H₄)].^{4,5} This reaction is believed to proceed *via* an undetected intermediate platinum(0) complex of 1,2-dibromocyclohexene (Scheme 1).^{3,6} More recently, Jones and co-workers⁷ have made complex **1** by an alternative method in which a mixture of 1-bromocyclohexene and [Pt(PPh₃)₃] is treated at room temperature with lithium diisopropylamide, LiNPrⁱ₂; a likely intermediate is a platinum(0) complex of 1-bromocyclohexene, which would probably undergo rapid dehydrohalogenation in the presence of LiNPrⁱ₂ (Scheme 1). This procedure has been extended to generate the Pt(PPh₃)₂ complexes of the tropylium analogue of benzyne (tropyne, C₇H₅), [Pt(PPh₃)₂(η^2 -C₇H₅)]⁺,⁸ and the Pt(PPh₃)₂ complexes of other cyclic alkynes.⁹

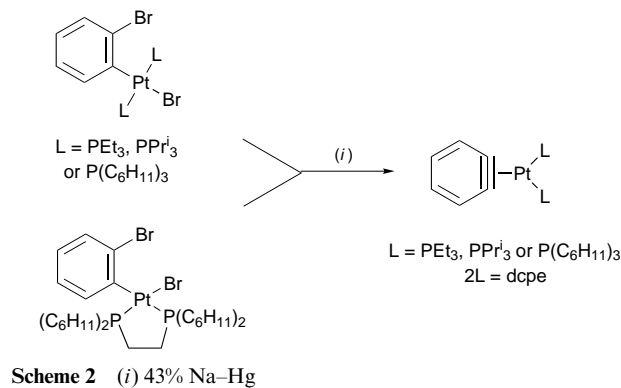
Platinum(0)–benzyne complexes [PtL₂(η^2 -C₆H₄)] [L₂ = dcpe, 2P(C₆H₁₁)₃, 2PEt₃, 2PPrⁱ₃; dcpe = 1,2-bis(dicyclohexylphosphino)ethane, (C₆H₁₁)₂PCH₂CH₂P(C₆H₁₁)₂] have been made by reduction of the appropriate (*o*-halogenoaryl)platinum(II) precursors with 43% sodium amalgam (Scheme 2);¹⁰ the weaker reducing agents 1% sodium amalgam or lithium, which are effective in forming nickel(0) complexes of benzyne and of 2,3-didehydronaphthalene from the corresponding nickel(II) precursors,^{11–13} do not work. However, all attempts to make the benzyne analogue of complex **1**, [Pt(PPh₃)₂(η^2 -C₆H₄)] **2**, by this procedure have failed, possibly because of preferential reductive cleavage of the P–Ph bond. Complex **2** also could not be obtained from the reaction of *cis*-[PtCl₂(PPh₃)₂] with *o*-Li₂-C₆H₄.¹⁴ Early attempts to trap benzyne,^{15,16} generated by thermal decomposition of benzenediazonium carboxylate or benzo-1,2,3-thiadiazole-1,1-dioxide, with [Pt(PPh₃)₄] or [Pt(PPh₃)₂(η^2 -C₂H₄)] were equally unsuccessful owing to the formation of chelate heterocyclic derivatives of platinum(II), such as compounds **3** and **4**, which did not fragment to give complex **2**; however, the formation of triphenylene in some of these



Scheme 1 (i) [Pt(PPh₃)₃] or [Pt(PPh₃)₂(η^2 -C₂H₄)]; (ii) 1% Na–Hg; (iii) LiNPrⁱ₂; (iv) [Pt(PPh₃)₃]



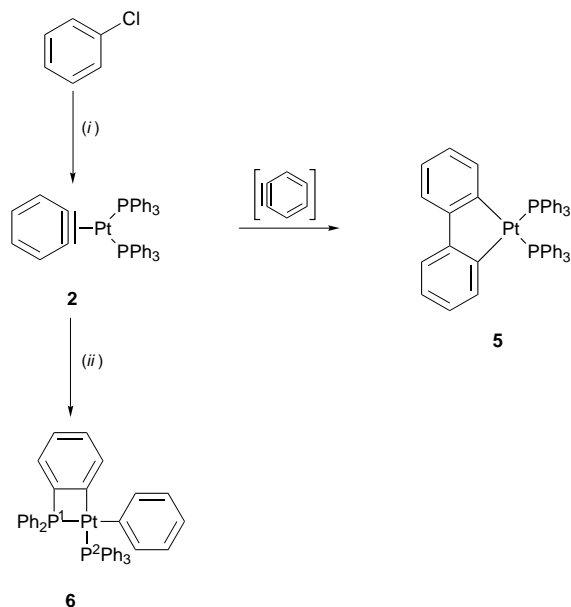
reactions was believed to indicate the possibility of organo-platinum intermediates. The work described here resulted from attempts to generate [Pt(PPh₃)₂(η^2 -C₆H₄)] **2** by a modification of Jones's procedure, *i.e.* by treatment of a mixture of [Pt(PPh₃)₂(η^2 -C₂H₄)] and chlorobenzene with the non-nucleophilic base 2,2,6,6-tetramethylpiperid-1-yl lithium, Li[N(CMe₂)CH₂CH₂CH₂CMe₂] (LiTMP). This reagent was chosen in the light of its reported reaction with chlorobenzene



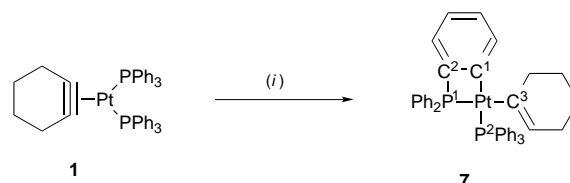
to generate benzyne, which could be trapped in moderate to good yield in the form of its Diels–Alder adducts with 1,3-diphenylisobenzofuran, 2,5-dimethylfuran, pyrrole, or *N*-methylisindole.¹⁷ This approach has also been used to synthesize a dinickel(0) complex of 1,2,4,5-tetrahydrobenzene (benz-1,4-diyne), [Ni₂(dcpe)₂(μ-1,2-η²:4,5-η²-C₆H₂)] by LiTMP-promoted dehydrohalogenation of the 4-fluorobenzyne–nickel(0) complex [Ni(dcpe)(η²-C₆H₃F-4)] in the presence of [Ni(dcpe)(η²-C₂H₄)].¹⁸

Results

A mixture of [Pt(PPh₃)₂(η²-C₂H₄)] and chlorobenzene was treated dropwise with approximately 4 equivalents of LiTMP at 0 °C. Monitoring by ³¹P NMR spectroscopy showed that only *ca.* 10% of [Pt(PPh₃)₂(η²-C₂H₄)] had undergone reaction. After the remaining LiTMP had been added, the ³¹P NMR spectrum showed, in addition to the singlet at δ_p 34.5 [¹J(PtP) 3741 Hz] due to unchanged [Pt(PPh₃)₂(η²-C₂H₄)], a new singlet at δ_p 28.2 [¹J(PtP) 3325 Hz] together with a small singlet at δ_p 29.0. The similarity of the ³¹P NMR parameters of the first formed species to those of the cyclohexyne complex [Pt(PPh₃)₂(η²-C₆H₈)] **1** [δ_p 28.3; ¹J(PtP) 3406 Hz]¹⁹ suggested that they could arise from the desired benzyne complex [Pt(PPh₃)₂(η²-C₆H₄)] **2**. Unfortunately, this species was not stable under the reaction conditions and attempts to isolate it failed; it decomposed to give two compounds whose relative amounts depended on temperature, and, more difficult to control, the amount of base in solution. In one experiment, a solution containing **2** was stored at –78 °C, but after 16 h the main species present was characterized by a singlet in the ³¹P NMR spectrum at δ 29.0 [¹J(PtP) 2003 Hz]. This compound was isolated in a pure state by preparative thin-layer chromatography and was shown by X-ray structural analysis (see below) to be the (2,2'-biphenyldiyl)platinum(II) complex, *cis*-[Pt(η¹:η¹-C₆H₄C₆H₄)(PPh₃)₂] **5**. It showed a parent-ion peak in its electron impact (EI)-mass spectrum. The magnitude of ¹J(PtP) is *ca.* 300 Hz greater than generally observed for neutral bis(tertiary arylphosphine)–η¹-aryl complexes of the type *cis*-[PtX(R)L₂],²⁰ *e.g.* for X = R = C₆H₅, L = PPh₃, values of ¹J(PtP) in C₆D₆ of 1763 Hz²⁰ and 1730 Hz²¹ have been reported. Compound **5** is believed to arise by reaction of the benzyne complex **2** with free benzyne at –78 °C (see Discussion) and can be isolated in 72% yield from reaction of a mixture of [Pt(PPh₃)₂(η²-C₂H₄)] and chlorobenzene with a large excess of LiTMP. At room temperature, a solution containing mainly **2** (and some **5**) was stable for at least 1 h, but after heating to 50 °C or, alternatively, after evaporation of the solvent at room temperature, the main species present, **6**, showed in its ³¹P NMR spectrum a pair of doublets at δ –55.0 and 21.2 [²J(PP) 10.9 Hz] assignable to inequivalent, mutually *cis* phosphorus atoms, P(1) and P(2), in a planar platinum(II) complex.²² The shielding of P(1) suggests that this phosphorus atom is part of a four-membered metallacycle,²³ *cf.* [Pt{C₆H₄(PPh₂)-2}]₂ (δ_p –52.3)²⁴



Scheme 3 (i) [Pt(PPh₃)₂(η²-C₂H₄)], LiTMP, 0 °C; (ii) room temperature



Scheme 4 (i) C₆H₆, reflux

and [Pt{C₆H₄(PPh₂)-2}(PPh₃)₂][CF₃SO₃] (δ_p –68.3),²⁵ and the remarkably low value of ¹J(PtP¹), 1021 Hz, indicates that P(1) is *trans* to a ligand of high *trans* influence, presumably σ-bonded carbon, *cf.* [Pt{C₆H₄(PPh₂)-2}]₂, 1352 Hz.²⁴ It should be noted, however, that ¹J(PtP) for the phosphorus atom *trans* to the σ-bonded carbon atom of the cycloplatinated ring in [Pt{C₆H₄(PPh₂)-2}(PPh₃)₂][CF₃SO₃] is 2006 Hz,²⁵ so these coupling constants can clearly span a wide range. The magnitude of ¹J(PtP²) in complex **6** is 2047 Hz, which allows P(2) to be assigned tentatively to PPh₃ *trans* to a σ-bonded carbon atom. The ³¹P NMR data, therefore, suggest the formulation of **6** as *cis*-[Pt{C₆H₄(PPh₂)-2}(η¹-C₆H₅)(PPh₃)]. This compound was also obtained in a pure state by thin-layer chromatography and its structure was confirmed by X-ray crystallography (see below). It is clearly an isomer of the benzyne complex **2** derived by migration of a hydrogen atom from triphenylphosphine to co-ordinated benzyne. The sequence of reactions occurring on treatment of [Pt(PPh₃)₂(η²-C₂H₄)] and chlorobenzene with LiTMP is summarized in Scheme 3.

The suggested origin of complex **6** receives additional support from the observation that the cyclohexyne complex [Pt(PPh₃)₂(η²-C₆H₈)] **1** undergoes a similar, though much slower, isomerization to the (η¹-cyclohexen-1-yl)platinum(II) complex [Pt{C₆H₄(PPh₂)-2}(η¹-C₆H₉)(PPh₃)] **7** (Scheme 4). This compound was isolated in good yield as a yellow solid when complex **1** was heated in benzene under reflux for 18 d and its identity was confirmed by X-ray crystallography (see below). Use of unrecrystallized samples of complex **1** also gave small amounts of *trans*-[PtBr(η¹-C₆H₉)(PPh₃)₂], presumably derived from NaBr impurity in the original preparation.⁴⁵ The ³¹P NMR spectrum of complex **7** is similar to that of **6**, consisting of a doublet at δ –52.8 [²J(PP) 10.9, ¹J(PtP) 861 Hz] due to the phosphorus atom P(1) in the cyclometallated four-membered ring and a doublet at δ 20.8 [²J(PP) 10.9, ¹J(PtP)

2144 Hz] due to the phosphorus atom P(2) *cis* to the cyclohexenyl group. The Pt–P couplings are reproduced in the ^{195}Pt NMR spectrum, which shows the expected doublet of doublets at $\delta -3981$ (relative to K_2PtCl_6). The vinylic proton of the η^1 -cyclohexen-1-yl group appears as a doublet of multiplets at $\delta 5.26$ [$J(\text{PH}) 11.2$, $J(\text{PtH}) 84$ Hz], the chemical shift and coupling constants being similar to those of other (η^1 -cyclohexen-1-yl)platinum(II) complexes^{5,19} and of $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)_2\}\{\eta^1\text{-C}(\text{CO}_2\text{Me})=\text{CHCO}_2\text{Me}\}(\text{PPh}_3)]$.²⁶ In the ^{13}C NMR spectrum of **7**, signals due to the quaternary carbon atoms (numbered as in Scheme 4) were located: a doublet of doublets at $\delta 149.70$ [$J(\text{PC}) 107.4$, 9.4 , $^1J(\text{PtC}) 905$ Hz] due to a carbon atom σ bonded to the metal, either that of the cycloplatinated ring (C^1) or of the η^1 -cyclohexen-1-yl group (C^3), a broad doublet at $\delta 153.20$ [$J(\text{PC}) 53.0$, $^2J(\text{PtC}) 32$ Hz] due to the remaining carbon atom (C^2) of the four-membered ring, and a broad doublet at $\delta 154.51$ [$J(\text{PC}) 117.1$, $^1J(\text{PtC}) 844$ Hz] due to C^3 or C^1 . The chemical shifts and coupling constants are similar to those of the cycloplatinated ring in $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)_2\}(\text{PPh}_3)]\text{-}[\text{CF}_3\text{SO}_3]$.²⁵ The magnitudes of $^1J(\text{PtP})$ *trans* to C_6H_5 in complex **7** (861 Hz), which is one of the smallest $^1J(\text{PtP})$ values reported for a phosphorus *trans* to a carbon atom, and of $^1J(\text{PtP})$ *trans* to C_6H_5 in complex **6** (1021 Hz) follow the same trend as observed for $^1J(\text{PtP})$ *trans* to the carbon σ -donor in $[\text{PtCl}(\text{R}')(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ [$\text{R}' = \text{C}_6\text{H}_5$, $^1J(\text{PtP}) = 1558$ Hz; $\text{R}' = \text{C}_6\text{H}_5$, $^1J(\text{PtP}) = 1613$ Hz],²⁷ and indicate that cyclohexen-1-yl has a slightly higher NMR *trans* influence than phenyl. However, the difference is too small to be reflected in the Pt–P bond lengths (see below).

Complex **7** was also formed when **1** was heated at 80°C in $[\text{H}_8]\text{toluene}$, but prolonged reaction in the refluxing solvent generated two more compounds, **8** and **9**, whose ^{31}P and ^{195}Pt NMR parameters were closely similar to, but clearly distinct from, those of **7** (see Experimental section); these compounds clearly contain the cycloplatinated unit $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)_2\}]$. The final solutions contained approximately equal amounts of compounds **7** and **8** and only minor amounts (5–10%) of **9**. Similar changes occurred when **1** was heated over several days in refluxing methylcyclohexane, thus eliminating the obvious possibility that the new compounds were isomeric tolyl complexes resulting from the oxidative addition of toluene to complex **7** and subsequent reductive elimination of cyclohexene. The compounds may be cyclohexen-2-yl or cyclohexen-3-yl isomers of complex **7** resulting from a metal-catalysed migration of the double bond in the six-membered ring. Unfortunately the compounds could not be separated by fractional crystallization or column chromatography, and attempts to promote a double-bond shift in complex **7** by heating it in the presence of a base (NEt_3) were unsuccessful.

Molecular structures of $[\text{Pt}(\eta^1\text{-}\eta^1\text{-C}_6\text{H}_4\text{C}_6\text{H}_4)(\text{PPh}_3)_2]$ **5**, *cis*- $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)_2\}(\eta^1\text{-C}_6\text{H}_5)(\text{PPh}_3)]$ **6** and *cis*- $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)_2\}(\eta^1\text{-C}_6\text{H}_5)(\text{PPh}_3)]$ **7**

The molecular geometry of complex **5** is shown in Fig. 1 together with atom numbering. Selected interatomic distances and angles are listed in Table 1. The molecule occupies a general position in the unit cell. The metal atom Pt(1) is in a distorted square-planar co-ordination environment, carbon atoms C(1) and C(1') being, respectively, 0.422 \AA above and 0.293 \AA below the plane defined by Pt(1) and the mutually *cis* phosphorus atoms. The aromatic rings of the biphenyldiyl ligand are planar, with a dihedral angle of 14.8° . The two Pt–C bond lengths [Pt(1)–C(1) $2.068(5)$, Pt(1)–C(1') $2.092(5)$ Å] are slightly but significantly different, this difference probably arising from crystal packing. The aromatic C–C bonds in the platinumacycle [C(1)–C(2) $1.421(6)$, C(1')–C(2') $1.427(6)$ Å] are longer than the remaining C–C bonds in the phenyl rings, which are in the usual range (1.366 – 1.393 Å). The separation between the linked

Table 1 Selected bond distances (Å) and angles ($^\circ$) for $[\text{Pt}(\eta^1\text{-}\eta^1\text{-C}_6\text{H}_4\text{C}_6\text{H}_4)(\text{PPh}_3)_2]$ **5**

Pt(1)–P(1)	2.333(1)	Pt(1)–P(2)	2.345(1)
Pt(1)–C(1)	2.068(5)	Pt(1)–C(1')	2.092(5)
C(1)–C(2)	1.421(6)	C(1')–C(2')	1.427(6)
C(2)–C(2')	1.466(7)	C(1)–C(6)	1.388(7)
C(1')–C(6')	1.388(6)		
P(1)–Pt(1)–P(2)	94.19(5)	C(1)–Pt(1)–C(1')	79.7(2)
P(1)–Pt(1)–C(1)	95.1(1)	P(1)–Pt(1)–C(1')	169.3(1)
P(2)–Pt(1)–C(1)	165.0(1)	P(2)–Pt(1)–C(1')	92.9(1)
Pt(1)–C(1)–C(2)	115.7(4)	Pt(1)–C(1')–C(2')	113.4(4)

Table 2 Selected bond distances (Å) and angles ($^\circ$) for *cis*- $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)_2\}(\eta^1\text{-C}_6\text{H}_5)(\text{PPh}_3)]$ **6**

Pt(1)–P(1)	2.330(2)	Pt(1)–P(2)	2.309(2)
Pt(1)–C(1)	2.052(7)	Pt(1)–C(8)	2.057(6)
P(1)–C(7)	1.806(7)	C(7)–C(8)	1.41(1)
C(1)–C(2)	1.40(1)	C(1)–C(6)	1.41(1)
P(1)–Pt(1)–P(2)	104.18(7)	P(1)–Pt(1)–C(1)	159.3(2)
P(1)–Pt(1)–C(8)	68.7(2)	P(2)–Pt(1)–C(1)	95.9(2)
P(2)–Pt(1)–C(8)	171.1(2)	C(1)–Pt(1)–C(8)	90.8(3)
Pt(1)–P(1)–C(7)	84.3(3)	P(1)–C(7)–C(8)	100.6(5)
C(7)–C(8)–C(9)	117.2(6)	Pt(1)–C(8)–C(7)	106.5(5)
Pt(1)–C(8)–C(9)	136.3(6)	C(8)–C(7)–C(12)	123.8(6)

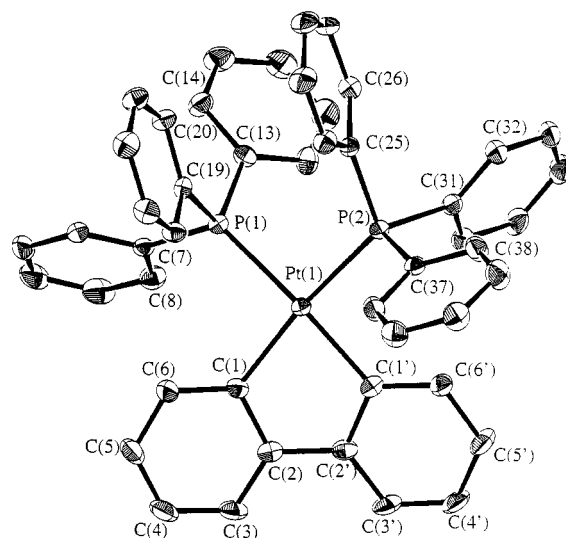


Fig. 1 An ORTEP²⁸ diagram of $[\text{Pt}(\eta^1\text{-}\eta^1\text{-C}_6\text{H}_4\text{C}_6\text{H}_4)(\text{PPh}_3)_2]$ **5** with atom labelling and 20% probability ellipsoids

carbon atoms of the two phenyl rings [C(2)–C(2') = $1.466(7)$ Å] is similar to those reported for other (2,2'-biphenyldiyl)platinum(II) complexes, *i.e.* $[\text{PtL}(\text{PPh}_3)_2]$ [$1.461(11)$ Å],²⁹ $[\text{PtL}'\text{-}(\text{cod})]$ [$1.486(10)$ Å],²⁹ and $[\text{PtL}'(\text{bipy})]$ [$1.493(14)$ Å]³⁰ [$\text{L} = 5,5'$ -bis(trifluoromethyl)-2,2'-biphenyldiyl; $\text{L}' = 5,5'$ -bis(*tert*-butyl)-2,2'-biphenyldiyl; $\text{cod} = \text{cycloocta-1,5-diene}$; $\text{bipy} = 2,2'$ -bipyridyl]. The Pt–C and Pt–P distances [Pt(1)–C(1) $2.068(5)$, Pt(1)–C(1') $2.092(5)$; Pt(1)–P(1) $2.333(1)$, Pt(1)–P(2) $2.345(1)$ Å] are also similar to those found in the 5,5'-bis(trifluoromethyl) derivative [Pt–C $2.058(7)$, $2.065(7)$; Pt–P $2.328(2)$, $2.346(2)$ Å].²⁹ Other bond lengths in complex **5** are unexceptional.

The molecular geometries of complexes **6** and **7** are very similar, and are shown in Figs. 2 and 3 together with the atom numbering. Selected interatomic distances and angles are given in Tables 2 and 3, respectively. In both compounds the metal atom lies almost in the co-ordination plane defined by the two mutually *cis* phosphorus atoms and the σ -bonded carbon atoms; the distances from the plane P(1), P(2), C(1) and C(8)

Table 3 Selected bond distances (Å) and angles (°) for *cis*-[Pt{C₆H₄(PPh₂)-2}(η¹-C₆H₉)(PPh₃)] **7**

Pt(1)–P(1)	2.336(1)	Pt(1)–P(2)	2.296(1)
Pt(1)–C(1)	2.054(5)	Pt(1)–C(8)	2.057(5)
P(1)–C(7)	1.799(5)	C(7)–C(8)	1.409(7)
C(1)–C(2)	1.361(8)	C(1)–C(6)	1.466(8)
P(1)–Pt(1)–P(2)	106.95(4)	P(1)–Pt(1)–C(1)	159.7(2)
P(1)–Pt(1)–C(8)	68.6(1)	P(2)–Pt(1)–C(1)	92.8(2)
P(2)–Pt(1)–C(8)	174.5(1)	C(1)–Pt(1)–C(8)	91.3(2)
Pt(1)–P(1)–C(7)	84.1(2)	P(1)–C(7)–C(8)	101.0(4)
C(7)–C(8)–C(9)	117.2(5)	Pt(1)–C(8)–C(9)	106.2(3)
Pt(1)–C(8)–C(9)	136.6(4)	C(8)–C(7)–C(12)	122.5(5)

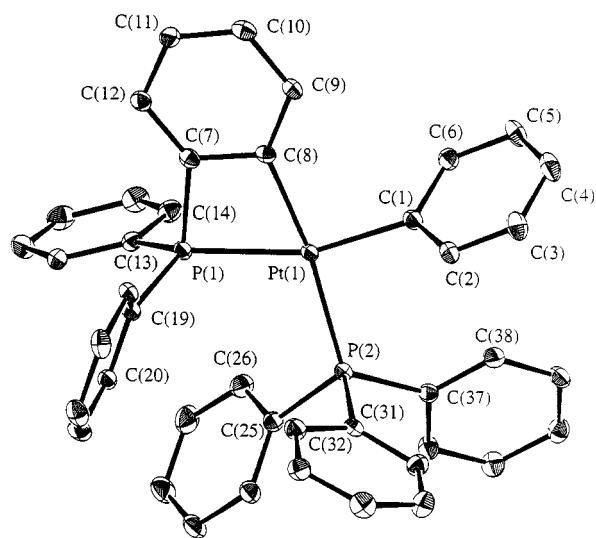


Fig. 2 An ORTEP diagram of *cis*-[Pt{C₆H₄(PPh₂)-2}(η¹-C₆H₅)(PPh₃)] **6** with atom labelling and 20% probability ellipsoids

are only 0.092 Å and 0.069 Å, respectively, and the bond carbon atoms C(1) and C(8) in both complexes are less than 0.2 Å below the plane defined by Pt(1), P(1) and P(2). The angle subtended at the metal atom in the orthometallated ring in both compounds is 69° (*cf.* 69° in [Pt{C₆H₄(PPh₂)-2}]₂);²⁴ there are corresponding increases from the ideal value of 90° in the valence angles P(1)–Pt(1)–P(2) [104 (6), 107° (7)]. The Pt–P distances in both four-membered rings [Pt(1)–P(1) 2.330(2) (6), 2.336(1) Å (7)] are comparable both to those in the cycloplatinated complexes [Pt{C₆H₄(PPh₂)-2}]₂ [2.297(1) Å]²⁴ and [Pt{C₆H₄(PPh₂)-2}{η¹-C(CO₂Me)=CH(CO₂Me)}(PPh₃)] [2.329(2) Å],³¹ and to the Pt–P bond length to the unmetallated PPh₃ ligand [Pt(1)–P(2) = 2.309(2) (6), 2.296(1) Å (7)]. The Pt–C distances in the four-membered ring of all four platinum complexes discussed above fall in the narrow range 2.056–2.063 Å, and are similar to the Pt–C₆H₅ bond length in **6** [Pt(1)–C(1) 2.052(7) Å] and to the Pt–C₆H₉ bond length in **7** [Pt(1)–C(1) 2.054(5) Å].

Discussion

Although the benzyne complex [Pt(PPh₃)₂(η²-C₆H₄)] **2** is generated by treatment of a mixture of chlorobenzene and [Pt(PPh₃)₂(η²-C₂H₄)] with LiTMP, the procedure is evidently not as successful as that used by Jones and co-workers⁷ to prepare the cyclohexyne complex [Pt(PPh₃)₂(η²-C₆H₈)] **1** (Scheme 1). In principle, there are two possible routes by which complex **2** could have been formed: (i) deprotonation of a transient intermediate dihapto chlorobenzene complex [Pt(PPh₃)₂(η²-C₆H₅Cl)], analogous to the intermediate 1-bromocycloheptene complex [Pt(PPh₃)₂(η²-C₇H₁₁Br)] detected by Jones and co-

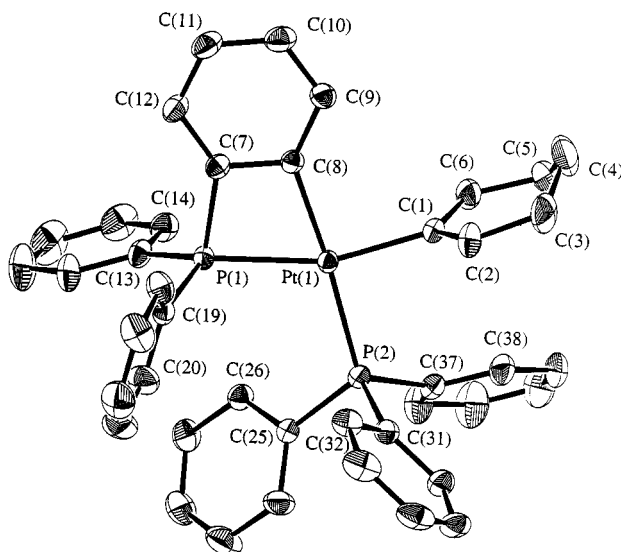


Fig. 3 An ORTEP diagram of *cis*-[Pt{C₆H₄(PPh₂)-2}(η¹-C₆H₉)(PPh₃)] **7** with atom labelling and 20% probability ellipsoids

workers⁷ in the preparation of the cycloheptyne complex [Pt(PPh₃)₂(η²-C₇H₁₀)]; (ii) deprotonation of chlorobenzene to give free benzyne, which is trapped by [Pt(PPh₃)₂(η²-C₂H₄)]. It is plausible that the vinylic halides 1-bromocyclohexene and 1-bromocycloheptene form much stronger π complexes than the aromatic halide chlorobenzene with platinum(0); hence free cyclohexyne or cycloheptyne are not formed whereas under similar reaction conditions free benzyne is readily generated. By whatever route complex **2** is formed, it is clearly capable of reacting rapidly with the highly reactive alkyne benzyne to give [Pt(η¹:η¹-C₆H₄C₆H₄)(PPh₃)₂]. This insertion is analogous to the first step, forming a benzonickelacyclopentadiene, of the double insertion of alkynes into nickel(0)–benzyne and nickel(0)–2,3-η-didehydronaphthalene bonds to give, respectively, substituted naphthalenes and anthracenes after reductive elimination of the nickel(0) fragment.^{3,11–13,32} Fewer reactions of this type are known with platinum(0) complexes: complex **1** is inert towards alkynes, although its derivatives [Pt(R''-PCH₂CH₂PR''₂)(η²-C₆H₈)] (R'' = Me, Et or C₆H₁₁) undergo monoinsertion with dimethyl acetylenedicarboxylate to give [Pt{C₆H₈C(CO₂Me)=C(CO₂Me)}(R''-PCH₂CH₂PR''₂)]³³. Benzyne has been reported to insert into the Ni–CH₂ bond of the metallacycle [Ni{C₆H₄(CMe₂CH₂)-2}(PMe₃)₂] to give, after reductive elimination, 9,9-dimethyl-9,10-dihydrophenanthrene.³⁴ It also inserts into the metal–phenylacetylide bond of the trichlorovinylnickel(II) complex *trans*-[Ni(C₂Ph)(C₂Cl₃)(PET₃)₂] to give *trans*-[Ni(C₆H₄C₂Ph-2)(C₂Cl₃)(PET₃)₂], together with the product of reductive elimination, C₆H₄(C₂Ph)-1-(C₂Cl₃)-2.³⁵

A second reason for the failure to isolate the benzyne complex **2** is that it readily isomerizes at or just above room temperature to the orthometallated complex *cis*-[Pt{C₆H₄(PPh₂)-2}(η¹-C₆H₅)(PPh₃)] **6**. The mechanism by which the hydrogen atom is transferred from PPh₃ to the unsaturated fragment is not known, but the process is clearly faster than the corresponding isomerizations of the cyclohexyne complex **1** to the cyclohexen-1-yl complex **7** and of the dimethyl acetylenedicarboxylate complex [Pt(PPh₃)₂(η²-MeO₂CC₂CO₂Me)] to the *cis*-1,2-bis(methoxycarbonyl)vinyl complex [Pt{C₆H₄(PPh₂)-2}(η¹-C(CO₂Me)=CH(CO₂Me)}(PPh₃)]^{26,31} which require long reaction times at elevated temperatures. The difference may reflect the relatively greater strain and weaker binding of benzyne to the platinum(0) centre. Other orthometallations of platinum(0)–triphenylphosphine complexes also generally require forcing conditions, *e.g.* irradiation at 254 nm for the

isomerization of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ to $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}\text{-}(\text{C}_2\text{H}_5)(\text{PPh}_3)]$ ³⁶ and elevated temperatures for the formation of dinuclear or polynuclear cycloplatinated complexes from $[\text{Pt}(\text{PPh}_3)_n]$ ($n = 2\text{--}4$).^{37–41}

Experimental

General procedures

All experiments were performed under an inert atmosphere with use of standard Schlenk techniques, and all solvents were dried and degassed prior to use. All reactions involving benzyne complexes were carried out under argon. The NMR spectra were recorded on the following spectrometers: Varian XL-200E (¹H at 200 MHz, ¹³C at 50.3 MHz, ³¹P at 80.96 MHz and ¹⁹⁵Pt at 42.83 MHz), Varian Gemini-300 BB (¹H at 300 MHz, ¹³C at 75.4 MHz and ³¹P at 121.4 MHz), Varian VXR-300 (¹H at 300 MHz and ¹³C at 75.4 MHz) and Varian VXR-500 (¹H at 500 MHz). The chemical shifts (δ) for ¹H and ¹³C are given in ppm relative to residual signals of the solvent, to external 85% H₃PO₄ for ³¹P and to external K₂PtCl₆ for ¹⁹⁵Pt. The spectra of all nuclei (except ¹H) were ¹H decoupled. The coupling constants (J) are given in Hz. Infrared spectra were measured in solid KBr or in solution (KBr cells) on Perkin-Elmer 683 or 1800 FT-IR spectrometers. Mass spectra were obtained by the electron impact (EI) method on a VG Micromass 7070F or a Fisons Instruments VG AutoSpec spectrometer.

Starting materials

The ethene complex $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ was prepared as described by Nagel.⁴² The cyclohexyne complex $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_6\text{H}_8)]$ **1**, obtained by a published procedure,⁵ was washed thoroughly with air-free water and recrystallized from toluene–hexane (1 : 6) before use.

Reaction of LiTMP with chlorobenzene in the presence of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$

In a typical experiment, a solution of LiTMP in tetrahydrofuran (thf) (10 cm³), prepared from 2,2,6,6-tetramethylpiperidine (0.23 cm³, 1.35 mmol) and LiBuⁿ (0.79 cm³ of 1.37 M solution in hexane, 1.08 mmol), was added over 1.5 h to a thf solution (10 cm³) at 0 °C containing $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ (200 mg, 0.27 mmol) and chlorobenzene (0.29 cm³, 2.7 mmol). After addition of 1 equivalent of base, monitoring by ³¹P NMR spectroscopy showed that only 10% of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ had reacted to form $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_6\text{H}_4)]$ **2**. After complete addition of the base and further stirring for 2 h at room temperature, the solution contained a mixture of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ [δ_{P} 34.5, $J(\text{PtP})$ 3741], $[\text{Pt}(\eta^1\text{-}\eta^1\text{-C}_6\text{H}_4\text{C}_6\text{H}_4)(\text{PPh}_3)_2]$ **5** and **2** in a ratio of 2.1 : 1 : 3.9. Attempts to isolate the benzyne complex were unsuccessful. For example, after removal of most of the toluene *in vacuo* and addition of hexane (20 cm³), the solution was left for 16 h at –78 °C but no crystallization occurred. After evaporation of the solvent, the ³¹P NMR spectrum of the residue showed the presence of a 3 : 1 mixture of compounds **5** and **2**, indicating that further reaction of **2** with free benzyne to give **5** had occurred. In another work-up, the reaction mixture was left at room temperature and the solvent was evaporated. The ³¹P NMR spectrum of the residue showed the presence of a 1.8 : 1 : 2.4 mixture of compounds **5**, **2** and **6** with only a trace of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$; rearrangement of **2** into the cyclometallated product **6** had occurred. Several fractions were combined and complexes **5** and **6** were separated by preparative TLC (silica gel, hexane–diethyl ether 5 : 1); **6** migrated faster than **5**. Yellow crystals of **5** and colourless crystals of **6** suitable for X-ray analysis were obtained from toluene–hexane and chlorobenzene–hexane, respectively. The amount of **6** was, however, insufficient for microanalysis.

In another experiment, the biphenyldiyl complex **5** was pre-

pared by adding chlorobenzene (0.72 cm³, 6.7 mmol) and a solution of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_2\text{H}_4)]$ (500 mg, 0.67 mmol) in thf (15 cm³) to a solution of LiTMP (2.68 mmol) in thf (20 cm³) at –60 °C. The solution was stirred for 2.5 h at 0 °C and 2 h at room temperature. As the ³¹P NMR spectrum of the solution showed that some **2** was still present, further LiBuⁿ (1 cm³ of 1.37 M solution in hexane) was added dropwise and the mixture was stirred for 16 h at room temperature. After evaporation of the solvent, the crude product was dissolved in diethyl ether and the solution was filtered through a silica gel column. Removal of the solvent afforded pure **5** (421 mg, 72%). Complex **2**: δ_{P} (80.96 MHz, C₆D₆) 28.2 [$J(\text{PtP})$ 3325]. Complex **5**: (Found: C, 65.6; H, 4.1. C₄₈H₃₈P₂Pt requires C, 66.1; H, 4.4%); δ_{H} (300 MHz, CD₂Cl₂) 7.00–7.70 (m, 34 H); δ_{C} (75.43 MHz, CD₂Cl₂) 127.9–128.4 (m), 128.75, 129.90, 129.99, 132.19, 132.32, 134.2–135.5 (m); δ_{P} (80.96 MHz, C₆D₆) 29.0 [$J(\text{PtP})$ 2003]; m/z (C₄₈H₃₈P₂Pt) 871 (M^+ , 5%), 262 (100), 228 (66), 183 (44), 154 (44), correct isotopic patterns. Complex **6**: δ_{H} (500 MHz, CD₂Cl₂) 6.75–7.40 (m, 34 H); δ_{C} (75.43 MHz, CD₂Cl₂) 126.27, 127.57, 127.69, 128.02, 128.15, 128.24, 129.44 [d, $J(\text{PC})$ 2.2], 129.52, 129.60 [d, $J(\text{PC})$ 2.7], 132.71, 132.86, 133.87, 134.03, 137.58 [$J(\text{PtC})$ 38.5, CH]; δ_{P} (121.4 MHz, C₆D₆) –55.0 [d, $J(\text{PP})$ 10.9, $J(\text{PtP})$ 1021, P(1)], 21.2 [d, $J(\text{PP})$ 10.9, $J(\text{PtP})$ 2047, P(2)]; m/z (C₄₂H₃₄P₂Pt) 795 (M^+ , 38%), 718 (5), 455 (5), 377 (6), 262 (100), 228 (24), 183 (62), 154 (35), correct isotopic patterns.

Preparation of *cis*- $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\eta^1\text{-C}_6\text{H}_9)(\text{PPh}_3)]$ **7**

A solution of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-C}_6\text{H}_8)]$ **1** (0.16 g, 0.2 mmol) in benzene (5 cm³) was stirred under reflux for 18 d and the solvent was removed by evaporation under reduced pressure. The yellow residue was recrystallized from CH₂Cl₂–hexane to give **7** as a pale yellow crystalline solid (96 mg, 75%) (Found: C, 63.5; H, 5.1. C₄₂H₃₈P₂Pt requires C, 63.1; H, 4.8%); m.p. 234 °C (decomp.); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr) 3040w, 2980w, 2920m, 2859w, 2810m, 1600w, 1588w, 1560m, 1480s, 1430s, 1308m, 1275m, 1095s, 1035m, 998m, 745s, 735s, 720s, 690s, 530s, 510s, 450m, 440m; δ_{H} (200 MHz, CD₂Cl₂) 0.35–0.55 (br, 4 H, CH₂), 1.80–2.00 (br, 2 H, CH₂), 2.05–2.25 (br, 2 H, CH₂), 5.26 [dm, 1 H, $J(\text{PH})$ 11.2, $J(\text{PtH})$ 84, =CH], 7.00–7.65 (m, 29 H, H^{arom}), 7.65–7.75 [m, 1 H, $J(\text{PtH})$ 57, Pt=C–CH^{ortho}]; δ_{C} (50.3 MHz, CD₂Cl₂) 24.39 [C(4)–H₂], 26.36 [d, $J(\text{PC})$ 5.7, $J(\text{PtC})$ 59.6, C(5)–H₂], 29.55 [d, $J(\text{PC})$ 9.6, $J(\text{PtC})$ 86.4, C(6)–H₂], 38.44 [d, $J(\text{PC})$ 4.5, $J(\text{PtC})$ 57.2, C(3)–H₂], 125.00 [m, $J(\text{PtC})$ 20, CH], 127.70 (m, CH), 128.15 [d, $J(\text{PC})$ 9.7, CH], 128.26 [d, $J(\text{PC})$ 9.7, CH], 128.62 [d, $J(\text{PC})$ 9.5, CH], 128.75 [d, $J(\text{PC})$ 9.5, CH], 129.97 (br s, CH), 130.25 (CH), 131.45 [d, $J(\text{PC})$ 32, C], 131.70 (m, CH), 133.30 [d, $J(\text{PC})$ 10.7, CH], 133.43 [d, $J(\text{PC})$ 10.7, CH], 134.0–134.6 (m, C), 134.58 [d, $J(\text{PC})$ 11.7, CH], 134.72 [d, $J(\text{PC})$ 11.7, CH], 138.25 [m, $J(\text{PtC})$ 39, CH], 149.70 [dd, $J(\text{PC})$ 107.4, 9.4, $J(\text{PtC})$ 905, C(112) or C(31)], 153.20 [br d, $J(\text{PC})$ 53.0, $J(\text{PtC})$ 32, C(111)], 154.51 [br d, $J(\text{PC})$ 117.1, $J(\text{PtC})$ 844, C(31) or C(112)]; δ_{P} (80.96 MHz, CD₂Cl₂) –52.8 [d, $J(\text{PP})$ 10.9, $J(\text{PtP})$ 861, P(1)], 20.8 [d, $J(\text{PP})$ 10.9, $J(\text{PtP})$ 2144, P(2)]; δ_{Pt} (42.83 MHz, CD₂Cl₂) –3981 [dd, $J(\text{PtP})$ 2144, 861].

Under the same conditions, samples of compound **1** that had not been freed from NaBr gave a *ca.* 4 : 1 mixture of complex **7** and *trans*- $[\text{PtBr}(\eta^1\text{-C}_6\text{H}_9)(\text{PPh}_3)_2]$, which could be almost completely separated by fractional crystallization from CH₂Cl₂–hexane. The latter compound was identified by comparison of its spectroscopic parameters with those of a sample prepared by treatment of complex **1** first with the calculated quantity of 0.1 M HCl in thf to give a mixture of *cis*- and *trans*- $[\text{PtCl}(\eta^1\text{-C}_6\text{H}_9)(\text{PPh}_3)_2]$ and then with NaBr to give the required product as the colourless *trans* isomer (Found: C, 56.3; H, 4.5. C₄₂H₃₉BrP₂Pt·0.25CD₂Cl₂ requires C, 55.3; H, 4.5%); m.p. 213 °C (decomp.); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr) 3070w, 3050w, 2920m, 2850m, 2820m, 1615w, 1585w, 1570w, 1480s, 1430s, 1095s, 740s, 690s, 520s, 510s, 495s; δ_{H} (200 MHz, CD₂Cl₂) 0.25–0.35 (br m, 2 H, CH₂), 0.40–0.55 (br m, 2 H, CH₂), 1.20–1.30 (br m, 2 H,

Table 4 Crystal and structure refinement data for [Pt(η^1 : η^1 -C₆H₄C₆H₄)(PPh₃)₂] **5**, *cis*-[Pt(C₆H₄PPh₂-2)(η^1 -C₆H₅)(PPh₃)] **6** and *cis*-[Pt(C₆H₄PPh₂-2)(η^1 -C₆H₉)(PPh₃)] **7**

Compound	5	6	7
Chemical formula	C ₄₈ H ₃₈ P ₂ Pt	C ₄₂ H ₃₄ P ₂ Pt·1.22C ₆ H ₅ Cl·0.28C ₆ H ₁₄	C ₄₂ H ₃₈ P ₂ Pt
<i>M</i>	964.01	795.78 + 162.38	799.79
Crystal system	Triclinic	Monoclinic	Monoclinic
<i>a</i> /Å	12.910(4)	10.910(3)	11.178(1)
<i>b</i> /Å	13.077(3)	22.913(4)	14.892(1)
<i>c</i> /Å	4.724(3)	16.877(4)	21.156(1)
α /°	74.05(2)		
β /°	79.12(2)	100.28(2)	98.20(1)
γ /°	65.70(2)		
<i>U</i> /Å ³	2170(1)	4151.0(17)	3485.7(4)
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no.14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>D</i> _c /g cm ⁻³	1.475	1.533	1.524
<i>Z</i>	2	4	4
<i>T</i> /K	293	298	293
<i>F</i> (000)	968	1915	1592
Colour, habit	Yellow, irregular	Colourless, trapezoidal	Colourless, block
Crystal size/mm	0.32 × 0.24 × 0.16	0.06 × 0.09 × 0.12	0.24 × 0.15 × 0.26
μ /cm ⁻¹	33.31	80.3	86.89
Diffractometer	Rigaku AFC6S	Rigaku AFC6R	Philips PW1100/20
X-Radiation	Mo-K α (graphite monochromated)	Cu-K α (graphite monochromated)	Cu-K α (graphite monochromated)
Scan mode	ω -2 θ	ω -2 θ	ω -2 θ
ω Scan width	0.80 + 0.34 tan θ	1.21 + 0.30 tan θ	1.2 + 0.142 tan θ
2 θ limits/°	50.1	120	128
<i>h</i> , <i>k</i> , <i>l</i> Ranges	(0, -16, -18) to (15, 16, 18)	(0, 0, -18) to (12, 25, 18)	(-13, 0, 0) to (12, 17, 24)
Total reflections	8057	6368	6228
Unique reflections	7681 (<i>R</i> _{int} = 0.021)	6176 (<i>R</i> _{int} = 0.015)	5798
Used reflections	6137 [<i>I</i> > 3 σ (<i>I</i>)]	4454 [<i>I</i> > 2 σ (<i>I</i>)]	5249 [<i>I</i> > 3 σ (<i>I</i>)]
Corrections (transmission factors)	Azimuthal scans (0.8806–1.0000)	Analytical (0.519–0.706)	Analytical (0.155–0.386)
Structure solution	Direct methods ^a (SHELXS 86, ⁴⁸ DIRDIF 94 ⁴⁹)	Direct methods ^b (SIR 92) ⁵³	Patterson method ^c (SHELXS 86) ⁴⁸
Refinement	Full-matrix least squares	Full-matrix least squares with conditions ⁵⁵	Full-matrix least squares
No. of parameters	523	455	406
<i>g</i> in Weighting scheme ^d	0.002	0.015	0.01
<i>R</i> (used reflections)	0.030	0.035	0.028
<i>R</i> ' (used reflections)	0.024	0.047	0.046
Goodness of fit	1.59	1.05	1.827
ρ_{\max} , ρ_{\min} /e Å ⁻³	0.83, -0.79	0.91, -0.75	0.4, -1.2

^a All calculations were performed by use of TEXSAN⁴³ with neutral atom scattering factors from Cromer and Waber,⁴⁴ Δf and $\Delta f'$ values from ref. 45 and mass attenuation coefficients from ref. 46. Anomalous dispersion effects were included in *F_c*.⁴⁷ ^b Structure solved with TEXSAN,⁵⁰ data reduction and refinement were performed using XTAL 3.4,⁵¹ with neutral atom scattering factors, Δf and $\Delta f'$ values from ref. 52. ^c Structure solved with SHELXS 86,⁴⁸ data reduction and refinement were performed using XTAL 3.0,⁵⁴ with neutral atom scattering factors, Δf and $\Delta f'$ values from ref. 52. ^d $w = 4F_o^2/[\sigma^2(F_o^2) + (gF_o^2)^2]$.

CH₂), 1.45–1.55 (br m, 2 H, CH₂), 5.21 [br s, 1 H, *J*(PtH) 69.0, =CH], 7.43 (br s, 18 H, H^{arom}), 7.70–7.85 (m, 12 H, H^{arom}); δ_C (50.3 MHz, CD₂Cl₂) 22.41 [C(4)–H₂], 24.60 [s, *J*(PtC) 54.2, C(5)–H₂], 28.97 [s, *J*(PtC) 81.0, C(6)–H₂], 37.14 [s, *J*(PtC) 40.1, C(3)–H₂], 126.20 [t, *J*(PC) 4.2, C(2)–H], 127.98 [t, *J*(PC) 5.2, CH], 130.47 (CH), 131.80 [t, *J*(PC) 27.7, *J*(PtC) 21.3, C^{arom}], 135.71 [t, *J*(PC) 5.8, CH], 138.10 [t, *J*(PC) 8.3, PtC(1)], *J*(PtC) not resolved for C(1) and C(2); δ_P (80.96 MHz, CD₂Cl₂) 24.8 [s, *J*(PtP) 3322]; δ_P (42.83 MHz, CD₂Cl₂) -4448 [t, *J*(PtP) 3323]; *m/z* (C₄₂H₃₉BrP₂Pt) 880 (*M*⁺, 5%), 846 (8), 800 (56), 719 (71), 307 (100), correct isotopic patterns.

Isomerization of complex 7. Qualitative NMR experiments showed that when complex **1** (40 mg) was heated in [²H₈]toluene (1.5 cm³) at various temperatures for 4 d, the formation of **7** was accompanied by an increasing amount of an isomer **8** and small amounts of a second isomer **9**. The proportions as determined by ³¹P NMR spectroscopy were 1.00:0.10:0.05 (80 °C), 1.00:1.00:0.15 (120 °C) and 1.00:1.60:0.05 (132 °C), respectively. Traces of other unidentified complexes were also observed. Complex **8**: δ_P (80.96 MHz, CD₂Cl₂) -55.4 [d, *J*(PP) 11.5, *J*(PtP) 1052.9, P(1)], 20.3 [d, *J*(PP) 11.5, *J*(PtP) 2061.4, P(2)]; δ_P (42.83 MHz, CD₂Cl₂) -3929 [dd, *J*(PtP) 2061, 1055]. Complex **9**: δ_P (80.96 MHz, CD₂Cl₂) -53.6 [d, *J*(PP) 11.0, *J*(PtP) 849, P(1)], 24.8 [d, *J*(PP) 11.0, *J*(PtP)

2154, P(2)]; δ_P (42.83 MHz, CD₂Cl₂) -3985 [dd, *J*(PtP) 2155, 851].

X-Ray crystallography of [Pt(η^1 : η^1 -C₆H₄C₆H₄)(PPh₃)₂] **5**, *cis*-[Pt(C₆H₄PPh₂-2)(η^1 -C₆H₅)(PPh₃)] **6** and *cis*-[Pt(C₆H₄PPh₂-2)(η^1 -C₆H₉)(PPh₃)] **7**

Selected crystal data, details of data collection, data processing, structure analysis and structure refinement are in Table 4.

The structure of complex **5** was solved by direct methods (SHELXS 86)⁴⁸ and was expanded using Fourier techniques (DIRDIF 94).⁴⁹ The calculations were performed using TEXSAN (version 1.6c).⁴³ The structure of **6** was solved by direct methods (SIR 92)⁵³ using TEXSAN (version 1.7).⁵⁰ One solvation molecule of chlorobenzene was identified in a general crystallographic position, plus further molecules of solvation about the centre of symmetry $\frac{1}{2}$, 0, 1 corresponding to disordered chlorobenzene and hexane molecules. The data reduction and refinement computations were performed with XTAL 3.4.⁵¹ The structure of **7** was solved by Patterson and Fourier-difference techniques (SHELXS 86).⁴⁸ Data reduction and refinement computations were performed with XTAL 3.0.⁵⁴ All non-hydrogen atoms were refined anisotropically by full-matrix least squares, except for the C atoms of the disordered solvation molecules in **6** which were restrained.⁵⁵ Hydrogen atoms

were included at calculated positions (C–H 0.95 Å) and held fixed.

CCDC reference number 186/799.

See <http://www.rsc.org/suppdata/dt/1998/271/> for crystallographic files in .cif format.

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