Heteronuclear Complexes of Platinum(II) and Copper(I) bridged by Alkynyl Ligands†

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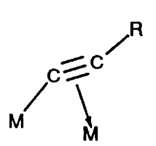
Reactions of *cis*-$[PtCl_2(PMe_2Ph)_2]$ with terminal alkynes RC_2H (R = Ph or Bu^t) and diethylamine in the presence of CuCl (up to 0.35 mol per mol Pt) yielded the complexes *cis*-$[PtCuCl(C_2R)_2(PMe_2Ph)_2]$. The crystal structure for R = Bu^t showed that both alkynyl ligands are σ bonded to Pt and η^2 co-ordinated to the Cu which has an approximately trigonal-planar geometry. The $Pt(C_2R)_2CuCl$ system is distorted from planarity. Similar reactions, but with more CuCl (1 mol per mol Pt), led to *trans*-$[PtCu_2Cl_2(C_2R)_2(PMe_2Ph)_2]$ (R = Bu^t). Treatment of the compound $[Pt(C_2Ph)_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $[Cu(MeCN)_4][BF_4]$ gave $[PtCu(MeCN)(C_2Ph)_2(dppe)][BF_4]$ which is believed to be structurally analogous to the neutral chloro complex. An acetone–acetonitrile solution of this complex deposited crystals of $[Pt_2Cu(C_2Ph)_4(dppe)_2][BF_4]$. The crystal structure of the latter contains orthogonal platinum co-ordination planes and each of the four alkynyl ligands is η^2 co-ordinated to a Cu atom in an approximately tetrahedral environment involving only carbon.

Alkynyl ligands can bridge metal centres in many ways.[1] Even bridging between two metal atoms occurs in three distinct modes, **A**–**C**. There are many examples of mode **A**, which can be regarded as the standard form when both metal atoms are transition metals. Mode **B** is much less common; it has been found for aluminium systems[2,3] and we have identified an example recently in a triosmium cluster.[4,5] The symmetrical form **C** is also fairly uncommon; the cluster $[Ru_3(\mu\text{-}C_2Bu^t)(\mu\text{-}\eta^2\text{-}C_2Bu^t)(PPh_2)_2(CO)_5(PPh_2C_2Bu^t)]$ contains alkynyl bridges of both types **A** and **C**.[6] When bonded to three or more metal atoms an even greater variety of co-ordination is found.

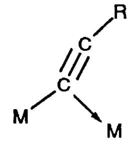
Organocopper compounds are widely used in organic synthesis,[7] although the nature of the reactive species is not always clear. Alkynylcopper systems have been studied for many years. The structure of the parent material $[\{Cu(C_2R)\}_n]$ remains unknown, although a polymeric structure with alkynyl bridges is probable. Some clue about the potential complexity in alkynylcopper systems comes from the structure of $[\{Cu(C_2Ph)(PMe_3)\}_4]$, in which two Cu atoms are co-ordinated differently to the other two; the copper atoms are linked to the alkynyl ligands through both σ and η^2 interactions.[8] It is not possible to describe the structure simply. In another recently reported polynuclear alkynylcopper compound, $[Cu_3(SC_6H_4CH_2NMe_2)_2(C_2Bu^t)]$, the C_2Bu^t ligand is linked to two metal atoms as in **C** but there is a further π interaction with a third copper atom.[9]

In mixed copper–transition metal compounds, σ co-ordination of alkynyl bridges at the transition metal and η^2 co-ordination at copper are favoured. Some structurally characterised compounds are $[RuCuCl(C_2Ph)(C_5H_5)(PPh_3)_2]$,[10] $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$[11] and $[Ir_2Cu_4(C_2Ph)_8(PPh_3)_2]$,[12,13] all of which contain bridges of type **A**. Recently a number of examples of alkynyl bridges between silver and platinum have been reported.[14–16]

To our knowledge, there are no examples of copper atoms bonded to more than three alkynyl ligands either in copper compounds or in mixed copper–transition metal compounds. Here we report an example of a complex with two alkynyl ligands bridging a platinum and a copper atom of a well known structural type as previously found for $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$[11] with bridges of type **A**. We also report here an unprecedented complex containing a copper atom tetrahedrally co-ordinated by four alkynyl groups. To our knowledge copper compounds of the type $[Cu(\eta^2\text{-alkyne})_4]^+$ have not been reported previously.



A



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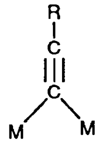

C

Results and Discussion

Syntheses.—Reactions of the complexes *cis*-$[PtCl_2(PMe_2Ph)_2]$ or $[PtCl_2(dppe)]$[17] (dppe = $Ph_2PCH_2CH_2PPh_2$) with diethylamine and terminal alkynes (RC_2H where R = Ph or Bu^t) in dichloromethane under reflux lead to the dialkynyl complexes *trans*-$[Pt(C_2R)_2(PMe_2Ph)_2]$ **1** (R = Bu^t) and **2** (R = Ph) and $[Pt(C_2R)_2(dppe)]$ **3** (R = Ph) of known type.[18] However, if the reaction of *cis*-$[PtCl_2(PMe_2Ph)_2]$ is carried out in the same way but in the presence of solid CuCl, the copper(I) chloride dissolves and mixed copper–platinum complexes are obtained. The nature of the product depends upon the amount of CuCl present. If a deficiency is used (< 0.35 mol CuCl per mol Pt) then a low yield of a white crystalline complex is obtained which we characterised as $[PtCuCl(C_2R)_2(PMe_2Ph)_2]$ **4** (R = Bu^t). Elemental analytical results were compatible with this formula. The $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra of **4** (Table 1) confirm that the tertiary phosphine ligands are *cis*, whereas the more stable form of $[Pt(C_2R)_2(PMe_2Ph)_2]$ is *trans*. The $^{13}C\text{-}\{^1H\}$ NMR spectrum shows C_α (alkynyl) signals with the ^{31}P couplings, 19.8 (*cis*) and 140.7 Hz (*trans*), consistent with a *cis* geometry at platinum. The methyl groups give a second-order multiplet which does not clearly identify the geometry.

Use of more CuCl (1 mol per mol Pt) in the above reaction leads to *trans*-$[PtCu_2Cl_2(C_2Bu^t)_2(PMe_2Ph)_2]$ **5**. Evidence for

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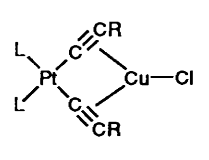
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

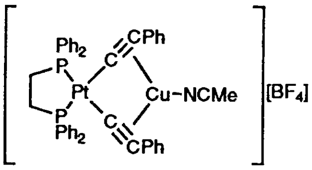
Table 1 Selected $^{31}P-\{^1H\}$ and $^{13}C-\{^1H\}$ NMR and IR data[a]

Compound	$^{31}P-\{^1H\}$ NMR[b]	$^{13}C-\{^1H\}$ NMR[c] C_α	C_β	IR/cm^{-1} $\nu(C\equiv C)$
1 *trans*-$[Pt(C_2Bu^t)_2L_2]$	−15.2 [2474]	90.0 (15.3) [941]	117.4 [256]	2112m
2 *trans*-$[Pt(C_2Ph)_2L_2]$	*d*	107.6 (30.5) [963]	109.6 (4.1) [264]	2116w
3 $[Pt(C_2Ph)_2(dppe)]$	40.1 [2280]	104.3 (15.3, 146.3) [1123]	112.1 (35.4) [307]	2116s
4 *cis*-$[PtCuCl(C_2Bu^t)_2L_2]$	−21.6 [2496]	71.3 (19.8, 140.7) [905]	123.0 (15.3) [286]	*e*
5 *trans*-$[PtCu_2Cl_2(C_2Bu^t)_2L_2]$	−12.7 [2347]	85.9[f]	121.8[f]	1983m, 1967m
6 $[PtCuCl(C_2Ph)_2(dppe)]$	38.8 [2289]	104.4 (15.5, 146.0) [1132]	112.0 (34.9) [307]	*e*
7 $[PtCuCl(C_2Bu^t)_2(dppe)]$	38.5 [2538]	70.1 (12.0, 134)	126.7 (31.2)	*e*
8 $[PtCu(MeCN)(C_2Ph)_2(dppe)][BF_4]$[g]	40.1 [2567]	82.0 (127.6)	115.7 (31.7) [290]	2082w, 2114w[h]
9 $[Pt_2Cu(C_2Ph)_4(dppe)_2][BF_4]$	40.1 [2490]	*e*	115.9 (33.0) [288]	2082w

[a] L = PMe_2Ph. NMR data (δ, *J* in Hz) for solutions in $CDCl_3$ unless stated otherwise; IR data for Nujol mulls. [b] *J*(PtP) in square brackets. [c] *J*(PC) in parentheses, *J*(PtP) in square brackets. [d] Not measured. [e] Not detected. [f] Broad signals, couplings not resolved. [g] $^{13}C-\{^1H\}$ NMR: δ 1.82 (CH_3CN); 117.5 (CH_3CN). [h] ν(CN) 2308 and 2282 cm^{-1}.



4 L = PMe_2Ph, R = Bu^t
6 L_2 = dppe, R = Ph
7 L_2 = dppe, R = Bu^t



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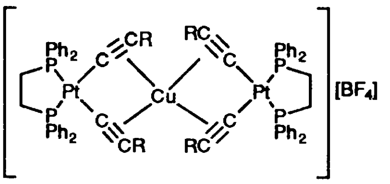


9 R = Ph

the *trans* geometry comes from ^1H and $^{13}C-\{^1H\}$ NMR spectra. The methyl groups of the PMe_2Ph ligands in $CDCl_3$ solution give virtual triplets: ^1H NMR, δ 1.97(t), apparent *J*(PH) 3.8 $[0.5|^2J(PH) + {}^4J(PH)|]$, *J*(PtH) 31.2 Hz; $^{13}C-\{^1H\}$ NMR, δ 14.9(t), apparent *J*(PC) 20.2 $[0.5|^1J(PC) + {}^3J(PC)|]$, *J*(PtC) 30.3 Hz. These data are characteristic of *trans* arrangements of the tertiary phosphines and may be compared with data for the parent compound *trans*-$[Pt(C_2Bu^t)_2(PMe_2Ph)_2]$: ^1H NMR, δ 2.09(t), apparent *J*(PH) 3.2, *J*(PtH) 32.3 Hz; $^{13}C-\{^1H\}$ NMR, δ 14.8(t), apparent *J*(PC) 20.2, *J*(PtC) 40.3 Hz. However, the mode of bonding of the alkynyl ligands to copper and the complete structure are still uncertain. As expected, similar reactions with the dppe complex $[PtCl_2(dppe)]$ give only the *cis* isomers of $[PtCuCl(C_2Ph)_2(dppe)]$ **6** and $[PtCuCl(C_2Bu^t)_2(dppe)]$ **7**.

Attempting to prepare cationic complexes related to **6** and **7** but with Cl replaced by a neutral ligand (MeCN), we treated $[Pt(C_2Ph)_2(dppe)]$ **3** with $[Cu(MeCN)_4][BF_4]$[19] and obtained the expected complex $[PtCu(MeCN)(C_2Ph)_2(dppe)][BF_4]$ **8** which is probably analogous to the neutral chloro complex **6**. In an attempt to grow crystals, a solution of compound **8** in acetonitrile–acetone was allowed to stand. However, the crystals deposited are characterised as $[Pt_2Cu(C_2Ph)_4(dppe)_2][BF_4]$ **9**. We presume that a by-product of this conversion is $[Cu(MeCN)_4][BF_4]$, liberated from compound **8**. The crystal structures of compounds **4** and **9** have been determined.

Structures of the Complexes.—The structure of compound **4** was confirmed by a single-crystal structure determination (Fig. 1). Selected bond lengths and angles are in Table 2, while Table 3 contains geometric details of the μ-σ:η^2-alkynyl ligands bridging the Pt and Cu atoms, together with corresponding data for compound **9** (see later). Compound **4** contains a *cis*-$Pt(C_2Bu^t)_2(PMe_2Ph)_2$ group with a CuCl unit bonded to the two alkyne groups in a similar fashion to that in $[ReCu(C_2C_6F_5)_2(CO)_3(PPh_3)_2]$ which contains a $Cu(PPh_3)$ group linked to two *cis*-$C_2C_6F_5$ ligands at rhenium.[11] The platinum atom in **4** is four-co-ordinate with a square-planar geometry and the copper is three-co-ordinate with an essentially trigonal-planar geometry. The Pt ⋯ Cu distance of 3.129(2) Å might be considered just short enough for there to be some direct bonding but we do not believe that there is any. Co-ordination of copper to the two alkynyl groups requires the metal atoms to approach each other this closely. The two C_2Bu^t groups are σ bonded to Pt and the Pt–C–C angles are 174(1) and 174.0(9)°, fairly close to linear. The copper atoms, on the other hand, are best regarded as η^2 co-ordinated to the alkynyl groups (see data in Table 3).

Table 2 Selected bond lengths (Å) and angles (°) for the compound $[PtCuCl(C_2Bu^t)_2(PMe_2Ph)_2]$ **4**

Pt ⋯ Cu	3.129(2)	Cu–C(1)	2.14(1)
Pt–P(1)	2.300(3)	Cu–C(2)	2.27(1)
Pt–P(2)	2.300(3)	Cu–C(4)	2.18(1)
Pt–C(1)	2.03(1)	Cu–C(5)	2.29(1)
Pt–C(4)	2.022(9)	C(1)–C(2)	1.22(2)
Cu–Cl	2.207(3)	C(4)–C(5)	1.22(1)
P(1)–Pt–P(2)	97.8(1)	Pt–C(4)–C(5)	174.0(9)
C(1)–Pt–P(2)	88.3(3)	C(1)–C(2)–C(3)	165(1)
C(4)–Pt–P(1)	89.3(3)	C(4)–C(5)–C(6)	166(1)
C(1)–Pt–C(4)	84.6(4)	Pt–Cu–Cl	165.9(1)
Pt–C(1)–C(2)	174(1)		

Ideally one would expect the Cu atom to lie in the platinum co-ordination plane, but Fig. 2 shows the displacement of the Cu atom (by 0.526 Å) out of the PtP_2 plane. The constraints necessary to maintain a square-planar platinum geometry seem to force the Cu atom to one side of the platinum co-ordination plane and the tertiary butyl groups to the other. The centres of the C–C bonds and the Cl atom define an approximately trigonal-planar geometry about Cu. The deviations of angles α and β from 180° (Table 3) ensure effective η^2 co-ordination, carbon atoms C(2) and C(5) being slightly further from Cu [2.27(1) and 2.29(1) Å] than C(1) and C(4) [2.14(1) and 2.18(1) Å]. The complex is stable in solution and we have found no evidence for CuCl dissociation.

A more interesting structure is that of compound **9** which is shown in Fig. 3; selected bond lengths and angles are in Table 4. The two square-planar platinum co-ordination planes are approximately orthogonal (dihedral angle between the PtP_2C_2 planes = 80.8°). This arrangement allows the two pairs of *cis*-alkynyl ligands to adopt bidentate co-ordination at copper. The

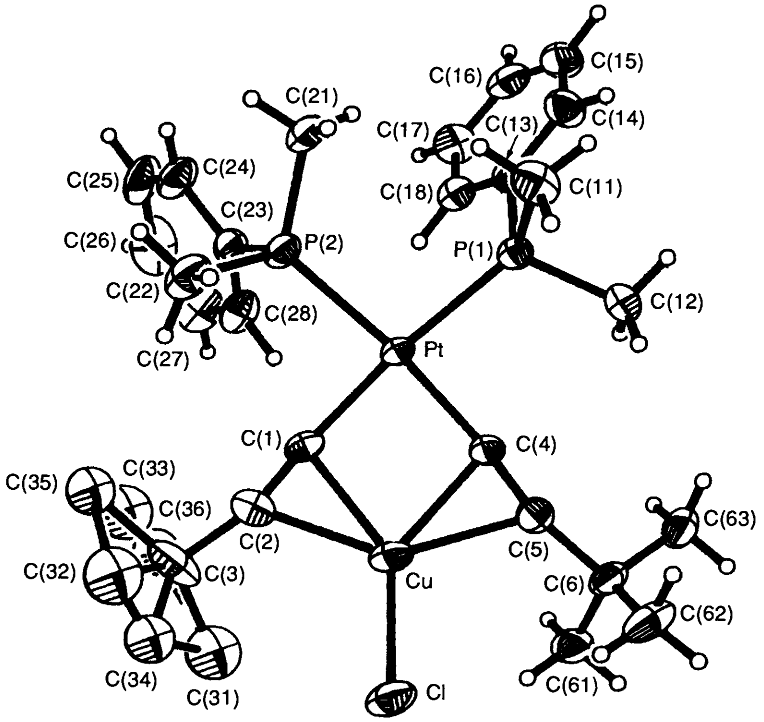
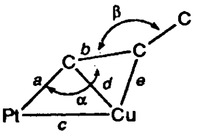


Fig. 1 Molecular structure of $[PtCuCl(C_2Bu^t)_2(PMe_2Ph)_2]$ **4**

Table 3 Geometric features of the alkynyl bridges between platinum and copper atoms; bond lengths (Å) and angles (°)



Compound		*a*	*b*	*c*	*d*	*e*	α	β
4	$C(1)C(2)Bu^t$	2.03(1)	1.22(2)	3.129(2)	2.14(1)	2.27(1)	174(1)	165(1)
	$C(4)C(5)Bu^t$	2.022(9)	1.22(1)	3.129(2)	2.18(1)	2.29(1)	174.0(9)	166(1)
9	C(1)C(2)Ph	2.01(3)	1.21(5)	3.133(5)	2.19(3)	2.41(3)	179(2)	174(3)
	C(3)C(4)Ph	2.05(3)	1.22(4)	3.133(5)	2.24(3)	2.41(3)	174(3)	169(3)
	C(5)C(6)Ph	2.00(3)	1.28(5)	3.088(5)	2.28(3)	2.49(3)	174(2)	166(3)
	C(7)C(8)Ph	2.02(3)	1.17(4)	3.088(5)	2.24(3)	2.39(4)	171(3)	167(4)

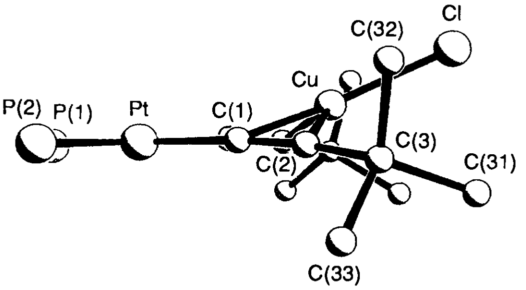


Fig. 2 Projection of a molecule of compound **4** in the PtP(1)P(2) plane showing the displacement of the CuCl group out of the platinum coordination plane. The organic groups at P(1) and P(2) are omitted

Table 4 Selected bond lengths (Å) and angles (°) for the compound $[Pt_2Cu(C_2Ph)_4(dppe)_2][BF_4]$ **9**

Pt(1) ··· Cu	3.133(5)	Cu–C(2)	2.41(3)
Pt(2) ··· Cu	3.088(5)	Cu–C(3)	2.24(3)
Pt(1)–P(1)	2.283(8)	Cu–C(4)	2.41(3)
Pt(1)–P(2)	2.275(9)	Cu–C(5)	2.28(3)
Pt(2)–P(3)	2.28(1)	Cu–C(6)	2.49(3)
Pt(2)–P(4)	2.275(8)	Cu–C(7)	2.24(3)
Pt(1)–C(1)	2.01(3)	Cu–C(8)	2.39(4)
Pt(1)–C(3)	2.05(3)	C(1)–C(2)	1.21(5)
Pt(2)–C(5)	2.00(3)	C(3)–C(4)	1.22(4)
Pt(2)–C(7)	2.02(3)	C(5)–C(6)	1.28(5)
Cu–C(1)	2.19(3)	C(7)–C(8)	1.17(4)
P(1)–Pt(1)–P(2)	86.4(3)	P(3)–Pt(2)–P(4)	87.1(3)
P(1)–Pt(1)–C(1)	93.3(8)	P(3)–Pt(2)–C(7)	90(1)
P(2)–Pt(1)–C(3)	91.4(8)	P(4)–Pt(2)–C(5)	89.2(8)
C(1)–Pt(1)–C(3)	90(1)	C(5)–Pt(2)–C(7)	94(1)

complex could be considered to be $[Cu(\eta^2\text{-alkyne})_4][BF_4]$, a type which we believe to be unknown previously. Treatment of a solution of $[Cu(MeCN)_4][BF_4]$ with an excess of PhC_2H in acetonitrile gave no reaction and the tetra(acetonitrile) compound was recovered. The particular nature of the bidentate diyne ligand, *cis*-$Pt(C_2Ph)_2(dppe)$, ensures that the copper atom is well embedded within the ligands and highly protected. In this case, unlike compound **4**, the Cu atom lies more closely in the PtP_2 planes. It is 0.120 Å out of the Pt(1)P(2)P(3) plane and 0.086 Å out of the Pt(2)P(3)P(4) plane. The geometries of the $Pt(C_2Ph)Cu$ bridges are normal and similar to those in compound **4** (Table 3).

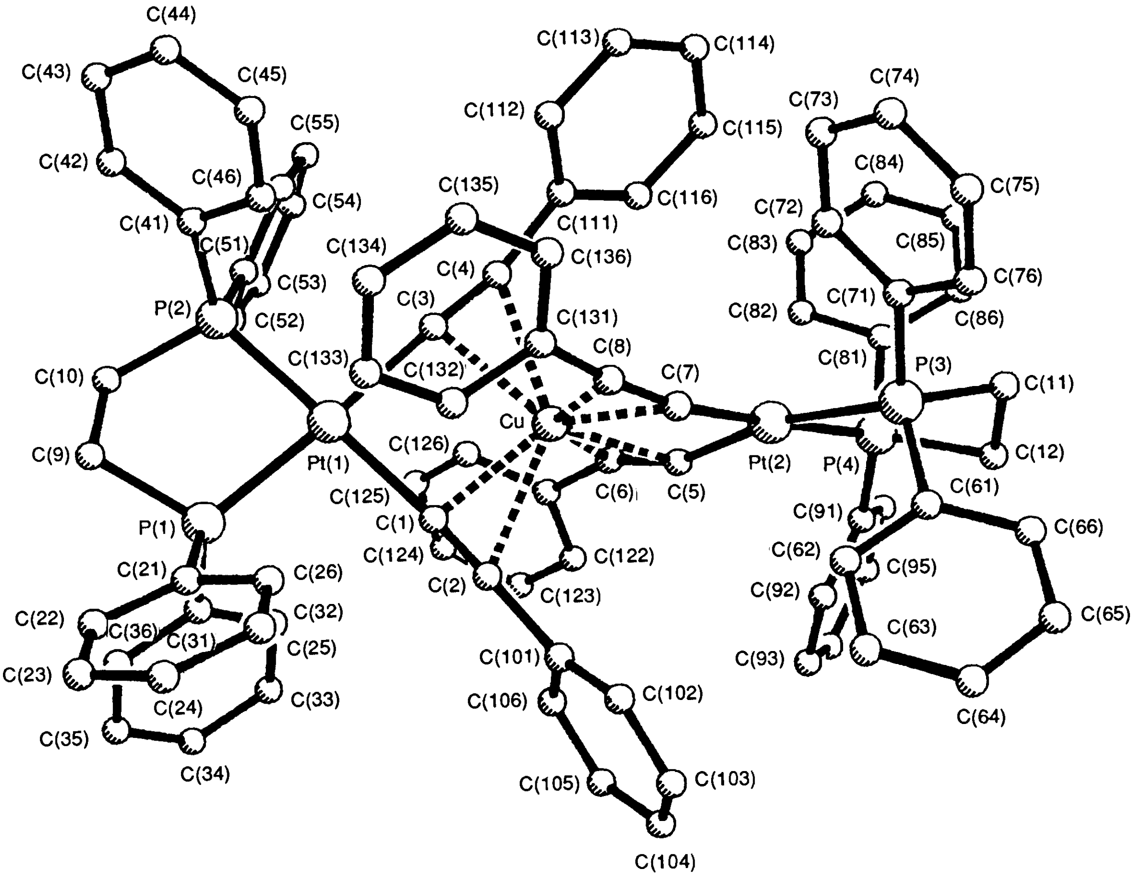


Fig. 3 Molecular structure of $[Pt_2Cu(C_2Ph)_4(dppe)_2]^+$ **9**, determined as its tetrafluoroborate salt. The Cu–C contacts are shown as broken lines for clarity

Experimental

The complexes *trans*-$[Pt(C_2R)(PMe_2Ph)_2]$ **1** (R = Bu^t) and **2** (R = Ph)[18] and $[Cu(MeCN)_4][BF_4]$[19] were synthesised as reported previously for the corresponding hexafluorophosphate salt.

Syntheses.—$[Pt(C_2Ph)_2(dppe)]$ **3**. Phenylethyne (0.65 g) was added to a solution of the complex $[PtCl_2(dppe)]$ (2.00 g) in dichloromethane (50 cm³) followed by addition of diethylamine (6 cm³) and copper(I) chloride (0.0067 g). The colourless solution with some suspended solid was refluxed for 4 h to give a clear pale yellow solution. The solvent was removed and the residue washed with water, dried *in vacuo*, and recrystallised from a dichloromethane–hexane mixture to give yellow needles of the product (1.82 g, 76%). IR spectrum (Nujol): ν(C≡C) 2116 cm⁻¹.

cis-$[PtCuCl(C_2Bu^t)_2(PMe_2Ph)_2]$ **4**. A solution of the complex *cis*-$[PtCl_2(PMe_2Ph)_2]$ (0.56 g) in dichloromethane was treated with diethylamine (0.18–0.25 g, 2.46–3.40 mol per mol Pt), Bu^tC_2H (0.20–0.37 g), and copper(I) chloride (0.035 g, 0.34 mol per mol Pt; no more CuCl than this must be used to obtain the required *cis* product) in a sealed thick-walled glass Carius tube under vacuum at 70 °C for 2 h. Longer reaction times gave considerably reduced yields. The tube was opened, the crystalline $[NH_2Et_2]Cl$ filtered off on filter-paper, and the solution evaporated to dryness. The residual pale yellow oil was washed with water to remove any remaining salt and dried. A solution of this oil in a dichloromethane–hexane mixture was cooled at around 0 °C overnight to give off-white needles of *trans*-$[Pt(C_2Bu^t)_2(PMe_2Ph)_2]$ (0.18–0.60 g, 27–87%) (characterising IR absorption at 2112 cm⁻¹). After separating off these needles, hexane was added to the pale yellow solution which was then stored at 0 °C for 1 d to give pale yellow crystals of product **4** (0.09–0.17 g, 12–21%) (Found: C, 46.05; H, 5.75; Cl, 4.90. $C_{28}H_{40}ClCuP_2Pt$ requires C, 45.90; H, 5.50; Cl, 4.85%). No acetylenic IR absorptions were observed in the region 1900–2100 cm⁻¹.

trans-$[PtCu_2Cl_2(C_2Bu^t)_2(PMe_2Ph)_2]$ **5**. A mixture of *cis*-$[PtCl_2(PMe_2Ph)_2]$ (0.65 g), copper(I) chloride (0.12 g, 1.0 mol per mol Pt), diethylamine (0.18 g, 2 mol per mol Pt), and Bu^tC_2H (0.40 g) in dichloromethane (50 cm³) in a Carius tube was degassed and the tube sealed and heated at 70–80 °C for 4 h. The tube was opened, the solvent removed, and the residue washed with water. After it had been dried, the residue was taken up in dichloromethane, hexane was added and the mixture cooled at 0 °C overnight to give compound **5** as off-white crystals (43%) (Found: C, 40.30; H, 4.70; Cl, 8.55. $C_{28}H_{40}Cl_2Cu_2P_2Pt$ requires C, 40.45; H, 4.85; Cl, 8.55%). IR (Nujol): ν(C≡C) 1983m and 1967m cm⁻¹.

$[PtCuCl(C_2Ph)_2(dppe)]$ **6**. A similar treatment of $[PtCl_2(dppe)]$ (0.54 g), PhC_2H (0.26 g), diethylamine (0.25 g), and CuCl (0.090 g) in dichloromethane at 70 °C for 4 h followed by crystallisation from dichloromethane–acetone gave the product **6**·CH_2Cl_2 as pale orange crystals (41%) (Found: C, 52.90; H, 3.75; Cl, 11.20. $C_{42}H_{34}CuClP_2Pt{\cdot}CH_2Cl_2$ requires C, 52.70; H, 3.70; Cl, 10.85%).

$[PtCuCl(C_2Bu^t)_2(dppe)]$ **7**. A similar treatment of $[PtCl_2(dppe)]$ (0.30 g), Bu^tC_2H (0.18 g), diethylamine (0.060 g), and CuCl (0.075 g, 1 mol per mol Pt) in dichloromethane at 70 °C for 4 h followed by crystallisation from dichloromethane–acetone gave product **7** as off-white crystals (67%) (Found: C, 51.95; H, 4.90; Cl, 5.85. $C_{38}H_{42}CuClP_2Pt{\cdot}0.25CH_2Cl_2$ requires C, 52.45; H, 4.65; Cl, 6.10%).

$[PtCu(MeCN)(C_2Ph)_2(dppe)][BF_4]$ **8**. A solution of the complex $[Pt(C_2Ph)_2(dppe)]$ (0.74 g) in dichloromethane (50 cm³) was mixed with an acetonitrile solution (5 cm³) of

Table 5 Crystal data and details of the data collection, structure solution and refinement for $[\mathrm{PtCuCl(C_2Bu^t)_2(PMe_2Ph)_2}]$ **4** and $[\mathrm{Pt_2Cu(C_2Ph)_4(dppe)_2}][\mathrm{BF_4}]$ **9**[a]

Compound	**4**	**9**
Formula	$\mathrm{C_{28}H_{40}ClCuP_2Pt}$	$\mathrm{C_{84}H_{68}BCuF_4P_4Pt_2}$
M	732.70	1741.93
Size/mm^3	0.28 × 0.40 × 0.48	0.46 × 0.22 × 0.35
Space group	$P2_1/n$	$P2_1/c$
a/Å	11.640(5)	16.259(7)
b/Å	15.465(6)	19.312(9)
c/Å	17.51(1)	27.241(8)
β/°	93.40(4)	106.98(3)
U/Å^3	3146(2)	8178(6)
D_c/g cm^{-3}	1.55	1.41
μ(Mo-Kα)/cm^{-1}	53.7	38.3
F(000)	1448	3432
No. of orientation reflections, 2θ range/°	25, 10–24	20, 10–23
Scan mode	ω–2θ	ω
2θ range/°	5–50	5–42
hkl range	0, 0, −21 to 14, 19, 21	0, 0, −28 to 17, 20, 28
Total data	6046	9174
Unique data	5522	8459
Rejection criterion	$I_o \leqslant 2\sigma(I_o)$	$I_o \leqslant 3\sigma(I_o)$
Reflections used	4143	4001
Parameters used	292	421
R	0.0536	0.0746
R'	0.0578	0.0749
g in weighting scheme	0.002 53	0.000 895
Maximum shift/e.s.d.	0.016[b]	0.13
Maximum difference peak/e Å^{-3}	2.49	1.16

[a] Common to both compounds: colourless crystals, monoclinic, $Z = 4$, Nicolet R3v/m diffractometer, molybdenum radiation, $\lambda = 0.710\,73$ Å, data collection temperature = 23 °C, corrections for Lorentz and polarisation effects, empirical absorption corrections (ψ scans), direct-methods structure solutions, $R = \Sigma(|F_o - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, w in weighting scheme $= 1/[\sigma^2(F) + gF^2]$. [b] 0.15 for disordered atoms of $\mathrm{Bu^t}$.

Table 6 Fractional atomic coordinates (× 10^4) for $[\mathrm{PtCuCl(C_2Bu^t)_2(PMe_2Ph)_2}]$ **4**

Atom	x	y	z
Pt	950(1)	8 243(1)	1 441(1)
Cu	3 411(1)	7 466(1)	1 307(1)
Cl	5 106(3)	6 842(2)	1 511(3)
P(1)	332(2)	9 483(2)	2 015(2)
P(2)	−813(2)	7 582(2)	1 247(2)
C(11)	−170(12)	9 343(9)	2 973(6)
C(12)	1 421(10)	10 296(8)	2 181(7)
C(13)	−798(9)	10 084(7)	1 472(6)
C(14)	−1 376(10)	10 757(8)	1 798(7)
C(15)	−2 178(11)	11 234(9)	1 374(9)
C(16)	−2 390(10)	11 069(9)	604(8)
C(17)	−1 835(11)	10 387(9)	279(7)
C(18)	−1 015(9)	9 911(7)	711(6)
C(21)	−1 997(10)	7 978(8)	1 786(7)
C(22)	−760(11)	6 459(9)	1 516(9)
C(23)	−1 368(9)	7 571(7)	252(7)
C(24)	−2 536(11)	7 381(9)	53(8)
C(25)	−2 923(13)	7 348(9)	−698(10)
C(26)	−2 189(19)	7 466(11)	−1 278(10)
C(27)	−1 043(13)	7 630(10)	−1 103(9)
C(28)	−645(11)	7 686(8)	−340(7)
C(1)	1 662(8)	7 213(8)	932(6)
C(2)	2 144(11)	6 646(8)	592(7)
C(3)	2 416(15)	5 890(10)	84(8)
C(31)	3 692(27)	6 073(21)	−264(17)
C(32)	2 364(29)	5 082(21)	609(18)
C(33)	1 463(30)	5 854(22)	−589(20)
C(34)	3 273(42)	5 265(31)	417(26)
C(35)	1 115(40)	5 439(31)	−146(27)
C(36)	2 088(42)	6 079(32)	−751(27)
C(4)	2 583(8)	8 689(7)	1 557(6)
C(5)	3 587(9)	8 912(7)	1 570(6)
C(6)	4 698(9)	9 398(8)	1 589(7)
C(61)	5 367(10)	9 154(8)	905(7)
C(62)	5 389(10)	9 180(11)	2 327(7)
C(63)	4 420(11)	10 389(8)	1 550(10)

$[\mathrm{Cu(MeCN)_4}][\mathrm{BF_4}]$ (0.30 g) and the mixture stirred at room temperature for 30 min. Evaporation to dryness and recrystallisation of the residue by addition of diethyl ether to an acetonitrile solution gave a pale yellow solid (0.88 g, 94%) (Found: C, 52.80; H, 3.65. $\mathrm{C_{44}H_{37}BCuF_4NP_2Pt{\cdot}0.25CH_2Cl_2}$ requires C, 52.70; H, 3.75%). Conductance (1.0 × 10^{-3} mol dm^{-3} in MeCN): $\Lambda_M = 115$ ohm^{-1} cm^2 mol^{-1}, consistent with a 1:1 electrolyte. Dichloromethane solutions at room temperature decompose slowly, turning from yellow to orange and depositing a little green precipitate.

$[\mathrm{Pt_2Cu(C_2Ph)_4(dppe)_2}][\mathrm{BF_4}]$ **9**. A solution of compound **8** in a mixture of acetone and acetonitrile was slowly evaporated at room temperature to give a deposit of colourless crystals of compound **9** (Found: C, 57.25; H, 3.90. $\mathrm{C_{84}H_{68}BCuF_4P_4Pt_2}$ requires C, 57.9; H, 3.95%). Conductance (0.8 × 10^{-3} mol dm^{-3} in MeCN): $\Lambda_M = 104$ ohm^{-1} cm^2 mol^{-1}, consistent with a 1:1 electrolyte.

Crystal Structure Determinations.—Crystal data and information on the intensity data collections, structure solutions and refinements for the two compounds are given in Table 5.

cis-$[\mathrm{PtCuCl(C_2Bu^t)_2(PMe_2Ph)_2}]$ **4**. A colourless crystal was obtained from dichloromethane. All non-hydrogen atoms were refined anisotropically except for those of one of the $\mathrm{Bu^t}$ groups, that centred on C(3), which was disordered. This group was best refined with one set of Me groups, C(31)–C(33), with a population of 0.65 and another with a different orientation, C(34)–C(36), with a population of 0.35. The disordered atoms were refined with a common isotropic thermal parameter for each set of carbon atoms. Hydrogen atoms were not included in the disordered group but were placed in all other sites in idealised positions riding on the C atoms with the C–H distance fixed at 0.96 Å and an isotropic thermal parameter of 0.08 Å^3. Fractional atomic coordinates for **4** are given in Table 6.

$[\mathrm{Pt_2Cu(C_2Ph)_4(dppe)_2}][\mathrm{BF_4}]$ **9**. A colourless crystal was formed over a period from a solution containing the complex $[\mathrm{PtCu(MeCN)(C_2Ph)_2(dppe)}][\mathrm{BF_4}]$ in acetone–acetonitrile.

Table 7 Fractional atomic coordinates (× 10^4) for $[Pt_2Cu(C_2Ph)_4(dppe)_2][BF_4]$ **9**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt(1)	1510(1)	422(1)	2400(1)	C(66)	3834(20)	3117(18)	−65(13)
Pt(2)	2436(1)	2929(1)	1228(1)	C(71)	4642(17)	3144(13)	1359(11)
Cu	1983(3)	1671(2)	1799(2)	C(72)	4772(20)	3069(14)	1869(12)
P(1)	955(6)	−665(4)	2208(3)	C(73)	5579(28)	2966(21)	2228(18)
P(2)	1637(6)	158(4)	3233(3)	C(74)	6255(24)	3040(17)	2029(14)
P(3)	3549(5)	3246(4)	927(3)	C(75)	6162(24)	3128(17)	1543(14)
P(4)	1837(5)	3975(4)	950(3)	C(76)	5325(22)	3177(17)	1157(14)
C(1)	1291(18)	681(15)	1658(12)	C(81)	1933(19)	4609(17)	1448(12)
C(2)	1146(19)	831(15)	2208(13)	C(82)	1635(21)	4426(18)	1877(13)
C(3)	2152(16)	1338(14)	2609(10)	C(83)	1723(22)	4826(19)	2288(14)
C(4)	2588(18)	1861(14)	2709(10)	C(84)	2122(23)	5416(21)	2311(15)
C(5)	1373(19)	2673(15)	1416(11)	C(85)	2439(22)	5671(20)	1915(14)
C(6)	745(18)	2489(14)	1582(11)	C(86)	2364(19)	5217(16)	1491(12)
C(7)	3043(18)	2030(16)	1488(11)	C(91)	711(18)	4008(15)	602(11)
C(8)	3385(20)	1535(17)	1698(12)	C(92)	346(22)	3443(18)	317(12)
C(9)	1112(20)	−1143(15)	2823(11)	C(93)	−570(25)	3429(22)	38(15)
C(10)	988(21)	−629(15)	3211(12)	C(94)	−1002(23)	3976(18)	93(13)
C(11)	3411(16)	4155(13)	773(10)	C(95)	−691(24)	4518(20)	357(13)
C(12)	2430(18)	4309(16)	522(11)	C(96)	194(19)	4566(16)	617(11)
C(21)	1488(24)	−1250(22)	1848(14)	C(101)	874(31)	975(21)	651(17)
C(22)	1429(30)	−1919(27)	1853(18)	C(102)	1437(48)	899(31)	365(26)
C(23)	1863(32)	−2394(32)	1643(20)	C(103)	1021(44)	1131(30)	−191(25)
C(24)	2207(34)	−2079(32)	1382(21)	C(104)	321(47)	1230(31)	−318(28)
C(25)	2486(47)	−1466(41)	1340(26)	C(105)	−375(63)	1110(41)	−227(33)
C(26)	1973(43)	−1026(43)	1566(26)	C(106)	17(42)	1057(28)	407(24)
C(31)	−172(21)	−695(17)	1879(12)	C(111)	3208(18)	2411(14)	2911(10)
C(32)	−596(22)	−118(18)	1659(12)	C(112)	4007(18)	2270(16)	3210(11)
C(33)	−1472(26)	−119(22)	1389(14)	C(113)	4615(21)	2822(16)	3366(12)
C(34)	−1908(27)	−763(21)	1361(15)	C(114)	4368(26)	3473(22)	3235(14)
C(35)	−1519(28)	−1317(24)	1575(15)	C(115)	3563(21)	3628(19)	2948(12)
C(36)	−655(22)	−1297(17)	1806(12)	C(116)	2982(18)	3115(14)	2767(11)
C(41)	2719(19)	21(15)	3663(12)	C(121)	−116(23)	2319(18)	1645(14)
C(42)	2861(24)	−300(17)	4148(13)	C(122)	−850(22)	2476(17)	1259(14)
C(43)	3713(24)	−324(19)	4450(15)	C(123)	−1653(24)	2289(18)	1321(15)
C(44)	4368(28)	−93(20)	4291(16)	C(124)	−1601(27)	1988(19)	1774(15)
C(45)	4226(30)	182(21)	3840(17)	C(125)	−955(24)	1832(18)	2157(15)
C(46)	3382(22)	249(17)	3493(14)	C(126)	−130(23)	2002(17)	2095(14)
C(51)	1205(20)	804(16)	3549(12)	C(131)	3991(27)	975(21)	1943(16)
C(52)	334(25)	888(21)	3485(15)	C(132)	3631(53)	377(38)	1974(28)
C(53)	−66(30)	1423(22)	3661(15)	C(133)	4060(71)	−330(64)	2222(37)
C(54)	462(25)	1877(19)	3985(14)	C(134)	4765(41)	−104(34)	2526(22)
C(55)	1340(25)	1817(19)	4081(14)	C(135)	5213(68)	364(48)	2476(35)
C(56)	1756(25)	1290(19)	3892(13)	C(136)	4508(56)	903(48)	2362(29)
C(61)	3557(18)	2771(15)	342(11)	B	3596(14)	6441(11)	716(7)
C(62)	3290(21)	2118(19)	270(14)	F(1)	3405(19)	5881(18)	583(12)
C(63)	3356(24)	1755(23)	−182(15)	F(2)	3041(24)	6813(19)	518(15)
C(64)	3657(22)	2104(21)	−537(15)	F(3)	3730(26)	6477(20)	1156(15)
C(65)	3888(23)	2751(21)	−483(15)	F(4)	4208(24)	6596(18)	609(13)

The crystal was not very strongly diffracting. Only the Pt, Cu and P atoms were refined anisotropically. The H atoms were included in the model in idealised positions and allowed to ride on the carbon atoms with C–H distances fixed at 0.96 Å and isotropic thermal parameters at 0.08 $Å^3$. The B–F distances were constrained to be equal within an idealised tetrahedron. Fractional atomic coordinates are given in Table 7.

All calculations were carried out using a MicroVax II computer running SHELXTL-PLUS.[20]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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