

Coordination of a monomeric diphosphido platinum complex as a bridging ligand†

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The reactions of *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ with [AuClPPh₃] or [Ag(OCIO₃)PPh₃] yield the neutral heterotrimeric complexes [M₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] (M = Au, Ag). Their structures have been established by X-ray diffraction studies and both complexes display M···M interactions but not Pt–M bonds. They are dynamic in solution, as demonstrated by ¹⁹F NMR spectroscopy, and M···M interactions seem to be present at low temperature.

Introduction

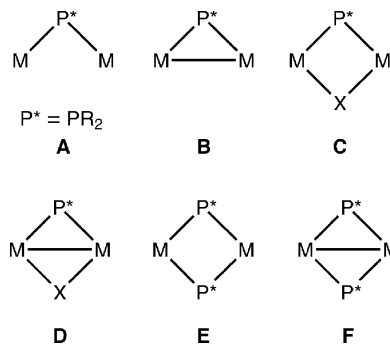
The capability of the PR₂ groups as versatile ligands in polynuclear complexes of palladium and platinum is well established. The classic coordination mode for this group is as a bridging ligand between two metal centres, although some examples of complexes in which a phosphido group acts as terminal ligand^{2–6} or as bridging ligand between three metal centres are known.^{7–16} In this context, choosing the appropriate synthetic procedure allows for many different structural situations: complexes showing a single PR₂ ligand without (Scheme 1, **A**^{17,18} and **B**^{19–24}) or with other bridging ligands (**C**^{25–28} and **D**^{28–32}) and complexes in which two phosphido groups are bridging the two metal centres (**E**^{33–36} and **F**^{37–42}). In these coordination modes the intermetallic distance ranges from typical metal–metal bond distances toward longer values.

In the course of our research on phosphido derivatives we have prepared *in situ* the mononuclear *cis*-Li₂[Pt(C₆F₅)₂(PPh₂)₂]⁴³ which shows two terminal diphenylphosphido ligands. This complex has been used as a building block for the designed synthesis of polynuclear derivatives in which the mononuclear platinum fragment acts as a chelate metalloligand. In this paper we study the behaviour of *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ towards the electrophilic fragment “MPPh₃⁺” (M = Ag, Au).

Results and discussion

The reaction of *cis*-Li₂[Pt(C₆F₅)₂(PPh₂)₂] with AuClPPh₃ or [Ag(OCIO₃)PPh₃] (1 : 2 molar ratio) affords the neutral heterotrimeric complexes [M₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂], M = Au **1**, Ag **2**, in which each P atom is bonded to a M centre. In this process the nucleophilic complex *cis*-

[Pt(C₆F₅)₂(PPh₂)₂]²⁻ acts as a bridging metalloligand towards the two M centres. The structures of complexes **1** and **2** have been determined by X-ray diffraction and are shown, along with the atom-labelling schemes, in Fig. 1 and 2, respectively. Selected bond distances and angles are listed in Tables 1 and 2, respectively. For complex **1**, two practically identical molecules are found in the asymmetrical unit and the structural parameters of only one of them will be used in this discussion. The two [M₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] (**1** and **2**) complexes exhibit very similar structures. In both cases the platinum atoms lie in the centre of a square-planar environment with the pentafluorophenyl and diphenylphosphido ligands in a *cis* disposition. The bond distances and angles involving the platinum centre are very similar in **1** and **2**. The diphosphido ligands are acting as a bridge between the platinum centres and the gold (**1**) or silver (**2**) ones. In all the cases, the Pt···M distances are too long for Pt–Au or Pt–Ag bonds to be considered (*vide infra*). Both Au in **1** and Ag in **2** complete their coordination sphere with a PPh₃ ligand. The P–M–P angle is almost linear (M = Au (**1**) 165.0(1) and 167.5(1)°; M = Ag (**2**) 162.8(1) and 156.1(1)°). In each complex, one of the M metal atoms lies almost in the same plane as the square Pt coordination plane (Au(2) in **1** and Ag(1) in **2**) while the other (Au(1) in **1** and Ag(2) in **2**) is clearly outside this plane, by almost 2 Å, due to the orientation imposed by the phosphido bridging ligand (see Fig. 1(b) and 2(b)). The Pt···M distances are shorter with the M atoms



Scheme 1

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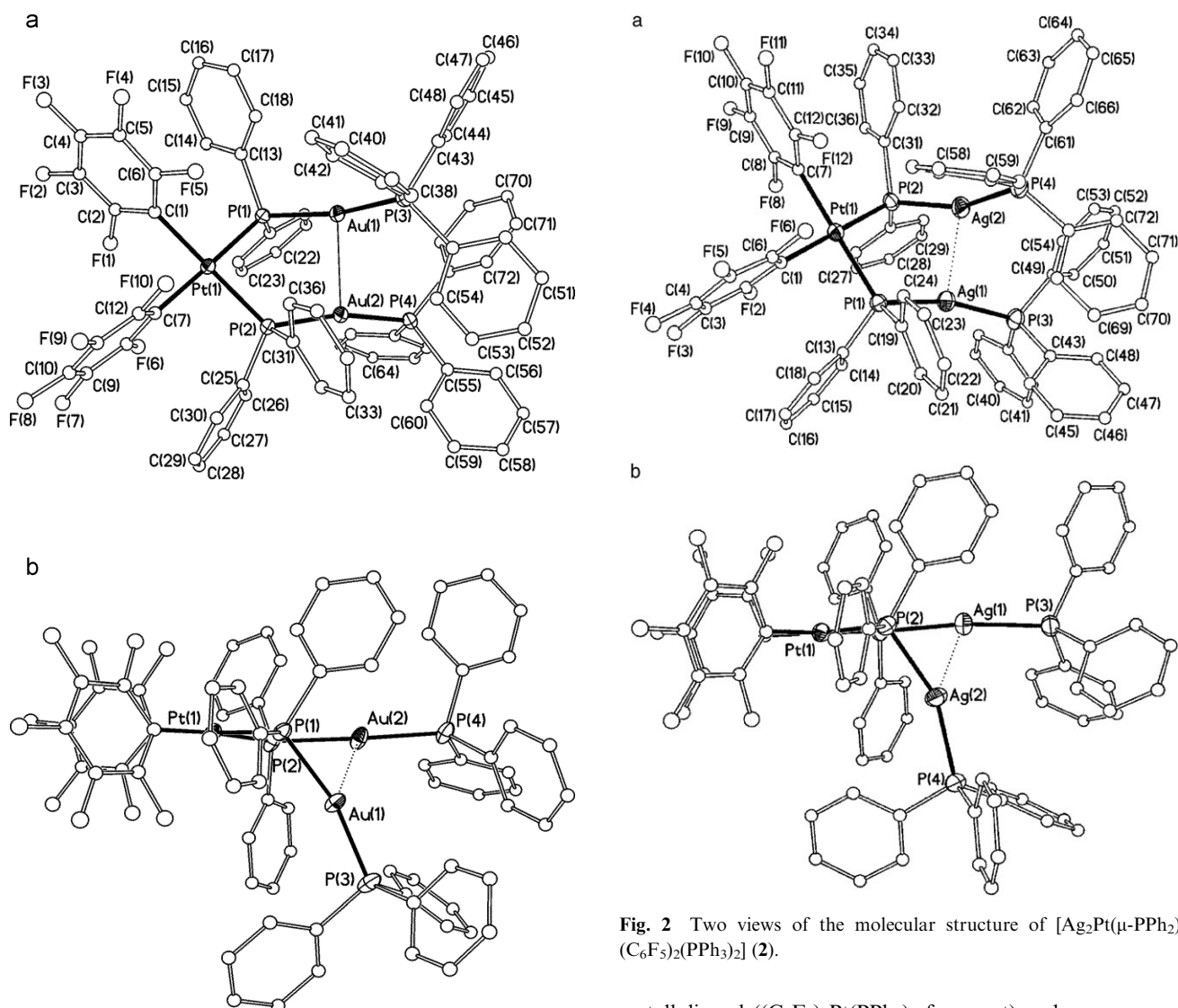


Fig. 1 Two views of the molecular structure of [Au₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] (1).

located outside the square plane (Pt(1)···Au(1) 3.772(1) Å, Pt(1)···Ag(2) 3.686(1) Å vs. Pt(1)···Au(2) 4.064(1) Å, Pt(1)···Ag(1) 4.068(1) Å) and also the Pt–P–M angles are narrower (Pt(1)–P(1)–Au(1) 109.3(1)°, Pt(1)–P(2)–Ag(2) 103.7(1)° vs. Pt(1)–P(2)–Au(2) 122.4(1)°, Pt(1)–P(1)–Ag(1) 117.2(1)°). This configuration of **1** and **2** is probably adopted in order to avoid the steric repulsions caused by the bulky PPh₃ ligands attached to Au and Ag.

Relatively short Au···Au (3.072(1) Å) and Ag···Ag (3.016(1) Å) distances are observed. It is well established that two-coordinate gold(I) complexes with linear coordination self associate through short Au···Au contacts^{44–52} and complexes with Ag···Ag interactions are also known.^{53–59} These interactions between closed-shell d¹⁰ metal centres play an important role in determining the solid-state structures and, especially with gold(I), they have attracted considerable experimental and theoretical attention.⁶⁰ The heterotrinnuclear complexes **1** and **2** combine a d⁸ metal centre and two d¹⁰ metal centres. The two gold or silver atoms are bridged by only one

Fig. 2 Two views of the molecular structure of [Ag₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] (2).

metalloligand ((C₆F₅)₂Pt(PPh₂)₂ fragment) and a more open dihedral angle between the two Pt–P–M planes (longer M···M distance) could result in a less crowded structure, however the gold–gold and silver–silver interactions determine the solid-state structures.

The IR spectra of **1** and **2** in the 800 cm⁻¹ region show two absorptions in agreement with the presence of the *cis*-“Pt(C₆F₅)₂” fragment.^{61,62} The ¹⁹F NMR spectra of **1** and **2** (CDCl₃ or CD₂Cl₂ solution, respectively) at low temperature show five signals of equal intensity: two of them with platinum satellites due to the *o*-F atoms and three high-field signals due to *m*- and *p*-F atoms, while, in solid state, all ten F atoms are inequivalent. This pattern indicates the equivalence of the two C₆F₅ groups and the inequivalence of both halves within each ring. The dynamic process between **A** and **C** in Scheme 2 may explain these spectra. The process assumes the maintenance of the M···M interaction and the rotation of the dinuclear “(PPh₂–M–PPh₃)₂” fragment around the Pt–P bonds, *i.e.* the presence in solution of a C₂ axis through the Pt centre and the midpoint of the M–M vector (Scheme 2, **B**). As can be seen, the dynamic process makes the *o*-F¹ with *o*-F¹⁰ atoms and the *o*-F⁵ with *o*-F⁶ atoms equivalent, giving rise to two signals in the *o*-F region. For the *m*-F atoms, the equivalence of F² with

Table 1 Selected bond lengths (Å) and angles (°) for [Au₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] · 1.5CH₂Cl₂ (**1** · 1.5CH₂Cl₂)

Molecule 1			Molecule 2				
Pt(1)–C(7)	2.054(6)	Au(2)–P(4)	2.3091(16)	Pt(2)–C(79)	2.057(5)	Au(4)–P(8)	2.3022(15)
Pt(1)–P(2)	2.3023(15)	Pt(1)–P(1)	2.2952(16)	Pt(2)–P(5)	2.3059(15)	Pt(2)–P(6)	2.2982(16)
Au(1)–Au(2)	3.0723(4)	Au(1)–P(1)	2.3284(15)	Au(3)–Au(4)	3.1548(4)	Au(3)–P(5)	2.3320(15)
Pt(1)–C(1)	2.061(6)	Au(2)–P(2)	2.3353(16)	Pt(2)–C(73)	2.061(5)	Au(4)–P(6)	2.3173(15)
Au(1)–P(3)	2.3054(16)			Au(3)–P(7)	2.3025(15)		
C(7)–Pt(1)–C(1)	85.4(2)	C(7)–Pt(1)–P(1)	178.08(16)	C(79)–Pt(2)–C(73)	87.8(2)	C(79)–Pt(2)–P(6)	92.73(15)
C(1)–Pt(1)–P(1)	93.34(16)	C(7)–Pt(1)–P(2)	93.08(15)	C(73)–Pt(2)–P(6)	175.60(17)	C(79)–Pt(2)–P(5)	174.18(16)
C(1)–Pt(1)–P(2)	175.65(17)	P(1)–Pt(1)–P(2)	88.26(6)	C(73)–Pt(2)–P(5)	91.22(15)	P(6)–Pt(2)–P(5)	88.71(5)
P(3)–Au(1)–P(1)	164.96(6)	P(4)–Au(2)–P(2)	167.52(6)	P(7)–Au(3)–P(5)	161.87(6)	P(8)–Au(4)–P(6)	169.23(6)

F⁹ and F⁴ with F⁷ also gives two signals and finally only one signal appears for the two equivalent *p*-F atoms.

The strength of these attractive Au···Au interactions has been shown to be comparable to that of hydrogen bonding and in some cases they are strong enough to persist in solution at low temperature.^{63–66} In complexes **1** and **2** both the Au···Au and the Ag···Ag interactions seem to be maintained in solution at low temperature.

The ¹⁹F NMR spectra of solutions of **1** and **2** at room temperature show three signals in 2 : 2 : 1 intensity ratio due to *o*-F, *m*-F and *p*-F atoms, respectively. This pattern indicates that, in solution, the two pentafluorophenyl groups are equivalent and moreover, within each ring the two *o*-F atoms and the two *m*-F atoms are equivalent. The free rotation of the pentafluorophenyl groups around the Pt–C_{ipso} in the structures of the Scheme 2 can explain the spectra at room temperature. Nevertheless it is important to note that a dynamic process involving the “PPh₂–M–PPh₃” fragments can produce a mirror plane on the NMR time scale. The dynamic process shown in Scheme 3 is in accord with the spectra at room temperature and indicates the breaking-off of the d¹⁰–d¹⁰ interaction (Scheme 3, **A**), as would be expected at room temperature. The rotations around the Pt–P bonds make the two halves equivalent within each C₆F₅ ring (Scheme 3, **B**) as well as the two pentafluorophenyl groups (Scheme 3, **C**).

These results unambiguously show that the *cis*-“Pt(C₆F₅)₂(PPh₂)₂” fragment, which behaves as a bridging metalloligand towards Au(I) and Ag(I) compounds, not only allows the Au···Au or Ag···Ag interactions in the solid state but also in solution at low temperature. The gold complex [Au₃(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂]⁺,⁵⁴ analogous to **1**, shows the *cis*-“Au(C₆F₅)₂(PPh₂)₂” fragment which behaves as a bridging metalloligand towards Au(I) centres. Its ¹⁹F NMR spectrum⁵⁴

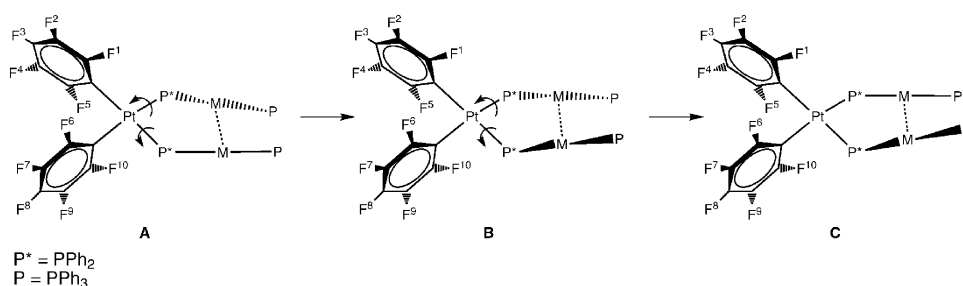
Table 2 Selected bond lengths (Å) and angles (°) for [Ag₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] (**2**)

Pt(1)–C(7)	2.078(6)	Ag(2)–P(2)	2.3850(15)
Pt(1)–P(1)	2.3391(14)	Pt(1)–P(2)	2.3008(14)
Ag(1)–Ag(2)	3.0156(6)	Ag(1)–P(1)	2.4274(15)
Pt(1)–C(1)	2.081(6)	Ag(2)–P(4)	2.3965(15)
Ag(1)–P(3)	2.4071(16)		
C(7)–Pt(1)–C(1)	88.4(2)	C(7)–Pt(1)–P(2)	91.36(16)
C(1)–Pt(1)–P(2)	178.09(16)	C(7)–Pt(1)–P(1)	177.93(17)
C(1)–Pt(1)–P(1)	93.22(16)	P(2)–Pt(1)–P(1)	86.94(5)
P(3)–Ag(1)–P(1)	162.84(5)	P(3)–Ag(1)–Ag(2)	105.62(4)
P(1)–Ag(1)–Ag(2)	81.82(4)	P(2)–Ag(2)–P(4)	156.12(6)

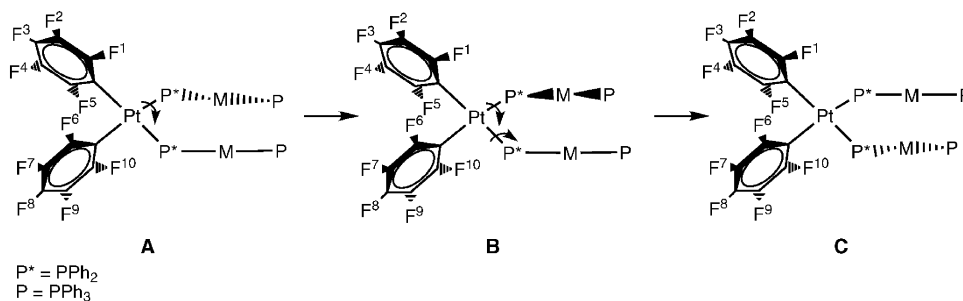
at room temperature is analogous to those observed in **1** and **2** but, unfortunately, the spectrum at low temperature and its solid-state structure have not been reported and a comparison of the behaviour of the *cis*-“M(C₆F₅)₂(PPh₂)₂” fragments when M = Pt and Au cannot be made.

The ³¹P{¹H} NMR spectrum of **1** at room temperature shows a signal centred at 42.7 ppm due to P atoms of PPh₃ ligands and a signal with platinum satellites centred at 25.9 ppm due to the phosphido groups. Each signal appears as a doublet of different intensities and separated by 247 Hz. Taking into account the dynamic behaviour proposed from the ¹⁹F NMR, the four P atoms in **1** become an AA'BB' spin system. Considering other P–P couplings in some of our related phosphido derivatives,^{28,43} it can be expected that the ⁴J(PPh₂–PPh₃) value in **1** (³J(PPh₂–PPh₃) if the Au···Au interaction is considered) as well as the coupling between the P atoms of the two PPh₃ ligands should be zero. The coupling between the P atoms of the two phosphido ligands merits some comments. In all our derivatives we have always observed ²J(*cis*-(PPh₂–PPh₂)), coupling between both P atoms in the “M(μ-PPh₂)₂M” systems, but this coupling is not observed when the two *cis* phosphido groups are bridging “M(μ-PPh₂)M(μ-PPh₂)M” fragments.^{9,28,39,43} Moreover in the only reported clusters in which the *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ fragment acts as a bridging ligand, the *cis*-PPh₂–PPh₂ coupling is not observed.⁹ Accordingly the ²J(PPh₂–PPh₂) value in **1** would be expected to be zero. All these facts allow the analysis of the spectrum of **1** as a simple AB spin system for the P atoms. The highfield signal shows platinum satellites (see Experimental section). The ²J(PPh₂–PPh₃) value in the linear PPh₂–Au–PPh₃ arrangement in **1** (247 Hz) lies within the same range as in PPh₂–M–PPh₃ (M = Pt, Pd) arrangements^{23,27} and the dinuclear gold complex [Au₂(μ-PPh₂)(C₆F₅)₃(PPh₃)].⁵⁴ Moreover it is very different to the striking value of 629 Hz reported for the analogous gold complex [Au₃(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂]⁺.⁵⁴ The ³¹P{¹H} NMR spectrum of **1** at 213 K is the same as that observed at room temperature. The ³¹P{¹H} NMR spectrum of **2** shows, even at 183 K (CH₂Cl₂ solution), very broad and overlapped signals from 0 to 20 ppm due to the presence of ¹⁰⁹Ag and ¹⁰⁷Ag centres (I = ½) bonded to the inequivalent P atoms, along with more similar values for the two chemical shifts of the PPh₂ and PPh₃ groups, and therefore the spectrum cannot be analysed.

In all our previous works the mononuclear diphosphido complex *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ reacted with platinum or palladium complexes as a chelate metalloligand.^{35,43} The



Scheme 2



Scheme 3

presence of a *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ fragment acting as a bridging ligand between two platinum centres has only been observed for the tetranuclear clusters [Pt₄(μ-PPh₂)₄(C₆F₅)₄L]ⁿ⁻ (L = C₆F₅, n = 1; L = PPh₃ or py, n = 0).⁹ The synthesis of these clusters can not be carried out directly from *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ but rather through an elaborate synthetic design. The synthesis of **1** and **2** demonstrate the ability of this platinum complex to also react directly as a bridging metalloligand. This behaviour allows the *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ complex to be related to the bis(diphenylphosphino)methane ligand for which a rich chemistry, with both chelate and bridging coordination is well established. The main difference is the square-planar or tetrahedral environment of the platinum or carbon atoms, respectively, along with the anionic nature of the bidentate metalloligand and this result offers a new way of future research.

Conclusion

The structures of the new complexes **1** and **2** show that the *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ complex can act as a bridge between two gold(i) or silver(i) centres. Thus, the adequate synthetic procedure allows the *cis*-[Pt(C₆F₅)₂(PPh₂)₂]²⁻ anion to act as a chelate or bridging bidentate metalloligand. The Au(i)···Au(i) and Ag(i)···Ag(i) distances in **1** and **2** and their variable-temperature NMR studies are in agreement with a d¹⁰···d¹⁰ interaction in the solid state as well as in solution at low temperature.

Experimental

Materials and methods

C and H analyses were performed with a Perkin-Elmer 240B microanalyser. IR spectra were recorded on a Perkin-Elmer

Spectrum One spectrophotometer (Nujol mulls between polyethylene plates in the range 4000–350 cm⁻¹). NMR spectra were recorded on a Varian Unity 300 instrument with CFCl₃ and 85% H₃PO₄ as external references for ¹H, ¹⁹F and ³¹P, respectively. Literature methods were used to prepare the starting materials *cis*-[Pt(C₆F₅)₂(PPh₂H)₂],⁴³ [AuCl(PPh₃)]⁶⁷ and [AgOClO₃(PPh₃)].⁶⁸

Syntheses

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

[M₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂], M = Au (**1**). To a colourless solution of *cis*-[Pt(C₆F₅)₂(PPh₂H)₂] (0.200 g, 0.222 mmol) in thf (10 mL) at -78 °C was added *n*-butyllithium (2.5 M in hexanes, 0.180 mL, 0.450 mmol) under an argon atmosphere. The yellow solution was stirred for 5 min and [AuCl(PPh₃)] (0.220 g, 0.445 mmol) was added. The reaction solution was allowed to reach room temperature, stirred for 3 h, and evaporated to dryness. CH₂Cl₂ (25 mL) was added to the resulting residue and the solution was filtered through Celite and evaporated to ca. 0.5 mL. Et₂O (15 mL) was added and **1** crystallised as a white solid, which was filtered off, washed with Et₂O (2 × 1 mL) and vacuum-dried, 0.323 g, 80%. Anal. Calc. for Au₂C₇₂H₅₀F₁₀P₄Pt: C, 47.57; H, 2.77. Found: C, 47.62; H, 3.10%. IR/cm⁻¹ (X-sensitive C₆F₅) 788, 776 (Nujol). ¹⁹F NMR (CDCl₃, 295 K): δ -117.7 (³J_{PtF} = 324 Hz, 4F, *o*-F), -166.1 (4F, *m*-F), -166.7 (2H, *p*-F) ppm. ¹⁹F NMR (CDCl₃, 213 K): δ -117.7 (³J_{PtF} = 373 Hz, 2F, *o*-F), -1178.5 (³J_{PtF} = 334 Hz, 2F, *o*-F), -165.0 (2F, *m*-F), -165.9 (2F, *m*-F), -166.0 (2F, *p*-F) ppm. ³¹P{¹H} NMR (CDCl₃, 295 K): δ 42.6 (PPh₃), 26.0 (¹J_{PtP} = 1979 Hz, PPh₂) ppm, 2J(PPh₃-PPh₂) = 247 Hz.

Table 3 Crystal data and structure refinement for [Au₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] · 1.5CH₂Cl₂ (**1** · 1.5CH₂Cl₂) and [Ag₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] (**2**)

	1 · 1.5CH ₂ Cl ₂	2
Empirical formula	C ₇₂ H ₅₀ F ₁₀ P ₄ PtAu ₂ · 1.5CH ₂ Cl ₂	C ₇₂ H ₅₀ F ₁₀ P ₄ PtAg ₂
<i>M_r</i>	1945.41	1639.83
<i>T</i> /K	100(1)	223(1)
<i>λ</i> /Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	30.4401(14)	12.6820(10)
<i>b</i> /Å	21.4415(10)	23.978(3)
<i>c</i> /Å	22.4453(11)	21.791(3)
<i>β</i> /°	110.9598(8)	101.224(1)
<i>V</i> /Å ³	13680.3(11)	6499.66(13)
<i>Z</i>	8	4
<i>D_c</i> /g cm ⁻³	1.889	1.676
<i>μ</i> (Mo-Kα)/mm ⁻¹	6.600	2.913
Diffractometer	Bruker Smart Apex	Enraf Nonius Kappa CCD
<i>θ</i> Range/°	1.69–25.02	2.98–27.88
Data collected	74456	72340
Independent data (<i>R_{int}</i>)	24104 (0.0331)	15283 (0.0727)
Data/restraints/parameters	24104/0/1690	11407/0/802
Goodness-of-fit on <i>F</i> ²	1.018	1.030
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0320	<i>R</i> 1 = 0.0316
	<i>wR</i> 2 = 0.0578	<i>wR</i> 2 = 0.0874
<i>R</i> Indices (all data)	<i>R</i> 1 = 0.0502	<i>R</i> 1 = 0.0519
	<i>wR</i> 2 = 0.0603	<i>wR</i> 2 = 0.1236
Goodness-of-fit = [Σ <i>w</i> (<i>F_o</i> ² - <i>F_c</i> ²)/(<i>N_{obs}</i> - <i>N_{param}</i>)] ^{0.5} ; <i>R</i> 1 = Σ(<i>F_o</i> - <i>F_c</i>)/Σ <i>F_o</i> ; <i>wR</i> 2 = [Σ <i>w</i> (<i>F_o</i> ² - <i>F_c</i> ²) ² /Σ <i>w</i> (<i>F_o</i> ²) ²] ^{0.5} .		

[M₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂], **M** = **Ag** (**2**). Complex **2** was prepared as a white solid using a similar procedure from *cis*-Li₂[Pt(C₆F₅)₂(PPh₂)₂] (0.277 mmol) and [AgOClO₃(PPh₃)] (0.260 g, 0.554 mmol) and stirred for 30 min (0.345 g, 76%). Anal. Calc. for Ag₂C₇₂H₅₀F₁₀P₄Pt: C, 52.73; H, 3.07. Found: C, 52.85; H, 3.31%. IR/cm⁻¹ (X-sensitive C₆F₅) 789, 777 (Nujol) ¹⁹F NMR (CDCl₃, 295 K): δ -118.3 (³*J*_{PtF} = 347 Hz, 4F, *o*-F), -167.0 (4F, *m*-F), -167.9 (2F, *p*-F) ppm. ¹⁹F NMR (CD₂Cl₂, 183 K): δ -116.7 (³*J*_{PtF} = 391 Hz, 2F, *o*-F), -117.7 (³*J*_{PtF} = 321 Hz, 2F, *o*-F), -164.7 (2F, *m*-F), -165.6 (2F, *m*-F), -166.1 (2F, *p*-F) ppm.

X-Ray structure determinations of [Au₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] · 1.5CH₂Cl₂ (1** · 1.5CH₂Cl₂) and [Ag₂Pt(μ-PPh₂)₂(C₆F₅)₂(PPh₃)₂] (**2**).** Crystal data and other details of the structure analyses are presented in Table 3. Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into solutions of approx. 0.020 g of the complexes in 3 mL of CH₂Cl₂. The structures were solved by Patterson and Fourier methods, and refined using the program SHELXL-97.⁶⁹ All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms were constrained to idealised geometries and assigned isotropic displacement parameters equal to 1.2 times the *U*_{iso} values of their respective parent atoms. For **1** · 1.5CH₂Cl₂, two mole-

cules of CH₂Cl₂ show some kind of disorder. In one of them, one of the Cl atoms (Cl(4)) is disordered over two sets of positions that were refined with partial occupancy 0.70/0.30. In the other one, two different moieties are occupying the same region of the space, and are refined with occupancy 0.55/0.45. No hydrogen atoms were added to the disordered dichloromethane molecules. Full-matrix least-squares refinement on *F*² of these models converged to the final residual indices given in Table 3.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517726j

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References

- Part 20: I. Ara, N. Chauche, J. Forniés, C. Fortuño, A. Kribii and A. C. Tspis, *Organometallics*, 2006, DOI: 10.1021/om0508029.
- A. Handler, P. Peringer and E. P. Muller, *J. Chem. Soc., Dalton Trans.*, 1990, 3725.
- D. K. Wicht, I. V. Kourkine, B. M. Lew, J. M. Nthenge and D. S. Glueck, *J. Am. Chem. Soc.*, 1997, **119**, 5039.
- D. K. Wicht, I. Kovacic, D. S. Glueck, L. M. Liable-Sans, C. D. Incarvito and A. L. Rheingold, *Organometallics*, 1999, **18**, 5141.
- M. A. Zhuravel, D. S. Glueck, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2002, **21**, 3208.
- D. K. Wicht, S. N. Paisner, B. M. Lew, D. S. Glueck, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, C. M. Harr and S. P. Nolan, *Organometallics*, 1998, **17**, 652.
- E. Alonso, J. Forniés, C. Fortuño, A. Martín and A. G. Orpen, *Chem. Commun.*, 1996, 231.
- E. Alonso, J. Forniés, C. Fortuño, A. Martín and A. G. Orpen, *Organometallics*, 2000, **19**, 2690.
- E. Alonso, J. Forniés, C. Fortuño, A. Martín and A. G. Orpen, *Organometallics*, 2003, **22**, 2723.
- L. R. Falvello, J. Forniés, C. Fortuño, A. Martín and A. P. Martínez-Sariñena, *Organometallics*, 1997, **16**, 5849.
- J. F. Corrigan, S. Doherty and N. J. Taylor, *J. Am. Chem. Soc.*, 1992, **114**, 7557.
- G. W. Rabe, S. Kheradman, L. M. Liable-Sands, I. A. Guzei and A. L. Rheingold, *Angew. Chem., Int. Ed.*, 1998, **37**, 1404.
- C. Frenzel, F. J. Somoza, S. Blaurock and E. Hey-Hawkins, *J. Chem. Soc., Dalton Trans.*, 2001, 3115.
- A. Eichhofer, D. Fenske and W. Holstein, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 242.
- U. Englich, K. Hassler, K. Ruhlandt-Senge and F. Unlig, *Inorg. Chem.*, 1998, **37**, 3532.
- E. Hey-Hawkins and E. Sattler, *J. Chem. Soc., Chem. Commun.*, 1992, 775.
- E. Alonso, J. Forniés, C. Fortuño, A. Martín, G. M. Rosair and A. J. Welch, *Inorg. Chem.*, 1997, **36**, 4426.
- T. Mizuta, M. Onishi, T. Nakazono, H. Nakazawa and K. Miyoshi, *Organometallics*, 2002, **21**, 717.
- P. Leoni, E. Vichi, S. Lencioni, M. Pasquali, E. Chiarentin and A. Albinati, *Organometallics*, 2000, **19**, 3062.
- P. Leoni, F. Marchetti, M. Pasquali, L. Marchetti and A. Albinati, *Organometallics*, 2002, **21**, 2167.
- R. Bender, P. Braunstein, A. Dedieu, P. D. Ellis, B. Huggins, P. D. Harvey, E. Sappa and A. Tiripicchio, *Inorg. Chem.*, 1996, **35**, 1223.
- P. Leoni, M. Pasquali, M. Sommovigo, A. Albinati, P. S. Pregosin and H. Ruegger, *Organometallics*, 1996, **15**, 2047.
- E. Alonso, J. Forniés, C. Fortuño, A. Martín and A. G. Orpen, *Organometallics*, 2001, **20**, 850.

- 24 L. R. Falvello, J. Forniés, C. Fortuño, F. Durán and A. Martín, *Organometallics*, 2002, **21**, 2226.
- 25 N. Chaouche, J. Forniés, C. Fortuño, A. Kribii, A. Martín, P. Karipidis, A. C. Tsipis and C. A. Tsipis, *Organometallics*, 2004, **23**, 1797.
- 26 I. Ara, N. Chaouche, J. Forniés, C. Fortuño, A. Kribii, A. C. Tsipis and C. A. Tsipis, *Inorg. Chim. Acta*, 2005, **358**, 1377.
- 27 E. Alonso, J. Forniés, C. Fortuño and M. Tomás, *J. Chem. Soc., Dalton Trans.*, 1995, 3777.
- 28 J. Forniés, C. Fortuño, R. Gil and A. Martín, *Inorg. Chem.*, 2005, **44**, 9534.
- 29 C. Archambault, R. Bender, P. Braunstein and Y. Dusausoy, *J. Chem. Soc., Dalton Trans.*, 2002, 4084.
- 30 R. Bender, S. E. Bouaoud, P. Braunstein, Y. Dusausoy, N. Merabet, J. Raya and D. Rouag, *J. Chem. Soc., Dalton Trans.*, 1999, 735.
- 31 P. Leoni, M. Pasquali, L. Fadini, A. Albinati, P. Hofmann and M. Metz, *J. Am. Chem. Soc.*, 1997, **119**, 8625.
- 32 R. Bender, P. Braunstein, S. E. Bouaoud, D. Rouag, P. D. Harvey, S. Golhen and L. Ouahab, *Inorg. Chem.*, 2002, **41**, 1739.
- 33 M. Itazaki, Y. Nishihara and K. Osakada, *Organometallics*, 2004, **23**, 1610.
- 34 R. H. Heyn and C. H. Gorbitz, *Organometallics*, 2002, **21**, 2781.
- 35 E. Alonso, J. M. Casas, J. Forniés, C. Fortuño, A. Martín, A. G. Orpen, C. A. Tsipis and A. C. Tsipis, *Organometallics*, 2001, **20**, 5571.
- 36 I. V. Kourkine, M. B. Chapman, D. S. Glueck, K. Eichele, E. Wasylshen, G. P. A. Yap, L. M. Liable-Sands and A. L. Rheingold, *Inorg. Chem.*, 1996, **35**, 1478.
- 37 P. Leoni, M. Pasquali, A. Fortunelli, G. Germano and A. Albinati, *J. Am. Chem. Soc.*, 1998, **120**, 9564.
- 38 E. Alonso, J. M. Casas, F. A. Cotton, X. J. Feng, J. Forniés, C. Fortuño and M. Tomás, *Inorg. Chem.*, 1999, **38**, 5034.
- 39 L. R. Falvello, J. Forniés, C. Fortuño and F. Martínez, *Inorg. Chem.*, 1994, **33**, 6242.
- 40 P. Leoni, G. Chiaradonna, M. Pasquali and F. Marchetti, *Inorg. Chem.*, 1999, **38**, 253.
- 41 J. Forniés, C. Fortuño, S. Ibáñez, A. Martín, A. C. Tsipis and C. A. Tsipis, *Angew. Chem., Int. Ed.*, 2005, **44**, 2407.
- 42 E. Alonso, J. Forniés, C. Fortuño, A. Martín and A. G. Orpen, *Organometallics*, 2003, **22**, 5011.
- 43 J. Forniés, C. Fortuño, R. Navarro, F. Martínez and A. J. Welch, *J. Organomet. Chem.*, 1990, **394**, 643.
- 44 J. Vicente, M. T. Chicote, I. Saura-Llamas, M. C. Lagunas, M. C. Ramírez de Arellano, P. González-Herrero, M. D. Abrisqueta and R. Guerrero, in *Metal Clusters in Chemistry*, ed. P. Braunstein, L. Oro and P. R. Raithby, Weinheim, 1999, pp. 493–508.
- 45 H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3.
- 46 H. Schmidbaur, *Chem. Soc. Rev.*, 1995, 391.
- 47 P. Pyykko, *Chem. Rev.*, 1997, **97**, 597.
- 48 K. Nomiya, R. Noguchi, K. Ohsawa and K. Tsuda, *J. Chem. Soc., Dalton Trans.*, 1998, 4101.
- 49 Y.-A. Lee and R. Eisenberg, *J. Am. Chem. Soc.*, 2003, **125**, 7778.
- 50 S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Inorg. Chem.*, 2004, **43**, 7234.
- 51 F. Jiang, M. M. Olmstead and A. L. Balch, *J. Chem. Soc., Dalton Trans.*, 2000, 4098.
- 52 W. J. Hunks, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2002, **41**, 4590.
- 53 J.-R. Li, X.-H. Bu, J. Jiao, W.-P. Du, X.-H. Xu and R.-H. Zhang, *Dalton Trans.*, 2005, 464.
- 54 M. C. Blanco, E. J. Fernández, J. M. López-de-Luzuriaga, M. E. Olmos, O. Crespo, M. C. Gimeno, A. Laguna and P. G. Jones, *Chem.-Eur. J.*, 2000, **6**, 4116.
- 55 P. L. Caradoc-Davies, L. R. Hanton and K. Lee, *Chem. Commun.*, 2000, 783.
- 56 D. L. Reger, R. F. Semeniuc, B. Captain and M. D. Smith, *Inorg. Chem.*, 2005, **44**, 2995.
- 57 Q.-X. Liu, F.-B. Xu, Q.-S. Li, X.-S. Zeng, X.-B. Leng, Y. L. Chou and Z.-Z. Zhang, *Organometallics*, 2003, **22**, 309.
- 58 Y. Kang, S. S. Lee, K.-M. Park, S. H. Lee, S. O. Kang and J. Ko, *Inorg. Chem.*, 2001, **40**, 7027.
- 59 J. Zank, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1999, 415.
- 60 H. Schmidbaur, *Nature*, 2001, **413**, 31.
- 61 E. J. Maslowsky, in *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, 1997.
- 62 R. Usón and J. Forniés, *Adv. Organomet. Chem.*, 1988, **28**, 219.
- 63 T. L. Stott, M. O. Wolf and B. O. Patrick, *Inorg. Chem.*, 2005, **44**, 620.
- 64 A. L. Balch, E. Y. Fung and M. M. Olmstead, *J. Am. Chem. Soc.*, 1990, **112**, 5181.
- 65 D. E. Harwell, M. D. Mortimer, C. B. Knobler, F. A. L. Anet and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1996, **118**, 2679.
- 66 H. de la Riva, A. Pintado-Alba, M. Nieuwenhuyzen, C. Hardacre and M. C. Lagunas, *Chem. Commun.*, 2005, 4970.
- 67 R. Usón and A. Laguna, *Inorg. Synth.*, 1982, **21**, 71.
- 68 F. A. Cotton, L. R. Falvello, R. Usón, J. Forniés, M. Tomás, J. M. Casas and I. Ara, *Inorg. Chem.*, 1987, **26**, 1366.
- 69 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.