

Unsymmetrical complexes containing the linear tetraphosphine ligand DPPEPM

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Abstract

The tetraphosphine DPPEPM reacts with $[\text{PtMe}_2(\text{cod})]$ to produce $[\text{PtMe}_2(\text{DPPEPM-PP})]$ (**1**) in near quantitative yield. On standing in solution, the free P atoms become oxidized to give $[\text{PtMe}_2(\text{DPPEPM}(\text{O})_2\text{-PP})]$ (**1a**), which has been characterized by X-ray crystallography. In contrast, reactions of DPPEPM with $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$) yield ionic products of the form $[\text{M}(\text{DPPEPM-PP})_2]\text{MCl}_4$ (**3**, **4**). When a solution of the platinum complex was allowed to stand, crystals of $[\text{Pt}(\mu\text{-Cl})(\mu\text{-DPPEPM})_2]\text{Cl}_3$ (**5**) were obtained. In a third set of reactions, treatment of $[\text{PtClR}(\text{cod})]$ ($\text{R} = \text{Me}, \text{Ph}$) or $[\text{PdClMe}(\text{cod})]$ with DPPEPM gives species of the type $[\text{MR}(\text{DPPEPM-PPP})]\text{Cl}$ (**6–8**), in which one of the internal P atoms is uncoordinated. Reactions of $[\text{PtR}_2(\text{DPPEPM-PP})]$ with $[\text{PtR}'_2(\text{cod})]$ or $[\text{MCl}_2(\text{cod})]$ ($\text{M} = \text{Pd}, \text{Pt}$), or of $[\text{PtR}(\text{DPPEPM-PPP})]\text{Cl}$ with $[\text{MCl}_2(\text{cod})]$, lead to unsymmetrical bimetallic complexes. $[\text{PtMe}_2(\mu\text{-DPPEPM})\text{PdCl}_2]$ (**11**) and $[\text{PtClPh}(\mu\text{-DPPEPM})\text{PdCl}_2]$ (**14**) have been characterized crystallographically. Trimetallic complexes of the form $[\{\text{PtR}_2(\mu\text{-DPPEPM})\}_2\text{M}][\text{MCl}_4]$ ($\text{M} = \text{Pd}, \text{Pt}$, **15–17**) are produced by reaction of $[\text{PtR}_2(\text{DPPEPM-PP})]$ with $[\text{MCl}_2(\text{cod})]$.

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1. Introduction

Diphosphine ligands such as bis(diphenylphosphino)methane (dppm) have been used for nearly 30 years in the construction of bimetallic complexes [1–6]. A range of structures has been identified and a wealth of reaction chemistry has been uncovered. The usually observed *trans* arrangement of phosphine units leads to good complex stability [7–13]. We have been able to prepare a series of thermally stable hydridopalladium (II) derivatives bridged by dppm ligands [14–18], for example, whereas palladium (II) hydrides are generally observed only as unstable reaction intermediates. Although a number of well-defined

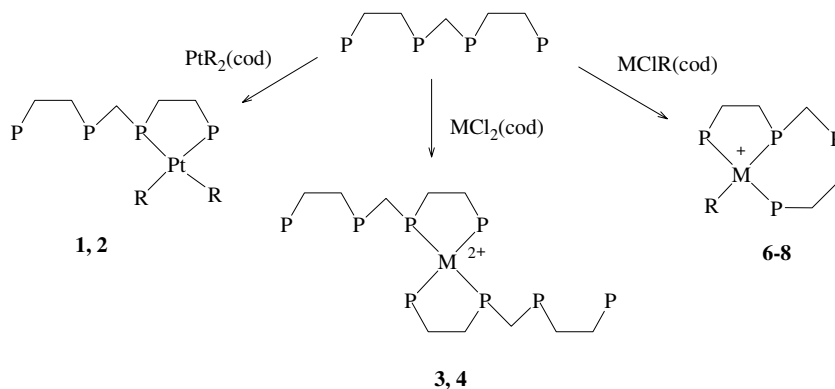
reactions have been observed, the drawback to this high complex stability is that dppm-bridged species rarely exhibit catalytic activity.

It has been reasoned that use of a linear tetraphosphine, which is capable of both bridging and chelating functions, should confer greater reactivity on a bimetallic system by maintaining a *cis* orientation of the remaining groups coordinated to the metals. Indeed, rhodium complexes containing bis{(diethylphosphinoethyl)phenylphosphino}methane ligands have been shown to be more effective hydroformylation catalysts than their monomeric analogues [19]. We have reported previously the synthesis and structures of symmetrical, bimetallic complexes of platinum and palladium containing the bis{(diphenylphosphinoethyl)phenylphosphino}methane (DPPEPM) ligand [20]. We report here on approaches to unsymmetrical, heterobimetallic complexes with DPPEPM. A preliminary report of some of this work has appeared [21].

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Scheme 1.

2. Results and discussion

When the DPPEPM ligand is allowed to react with 2 mol equiv. of $[MCl_2(cod)]$ ($M = Pd, Pt$) or $[PtR_2(cod)]$, the products are symmetrical, bimetallic complexes of the form $[M_2X_4(\mu-DPPEPM)]$ [20]. In contrast, when 1 mol equiv. of $[PtR_2(cod)]$ ($R = Me, Ph$) is added slowly to a suspension of *meso*-DPPEPM in acetone, monometallic complexes of the form $[PtR_2(DPPEPM-PP)]$ (**1**, $R = Me$; **2**, $R = Ph$) are obtained in nearly quantitative yield (small amounts of $[Pt_2R_4(\mu-DPPEPM)]$ are also formed, and these are difficult to separate, making it difficult to obtain satisfactory microanalyses) (Scheme 1). If the addition is performed in reverse order, i.e., if DPPEPM is added to $[PtR_2(cod)]$, mixtures of products are obtained. In **1**, for example, the $^{31}P\{^1H\}$ NMR spectrum consists of four resonances, two arising from the P atoms coordinated to platinum (with couplings to ^{195}Pt of ca 1800 Hz, typical of P atoms lying *trans* to alkyl substituents), and two that have low frequency chemical shifts similar to those found in the free ligand. The 1H NMR spectrum exhibits two signals due to the non-equivalent methyl groups, and the signals expected for the DPPEPM ligand. The high-resolution mass spectrum reveals the presence of the parent ion, as well as peaks associated with single oxidation of the parent. Crystals formed on standing in chloroform solution, and these proved to be of the double oxidation product $[PtMe_2(DPPEPM(O)_2-PP)]$ (**1a**). The uncoordinated P atoms in **1** could be deliberately oxidized using elemental sulfur, giving rise to $[PtMe_2(DPPEPM(S)_2-PP)]$ (**1b**), a species that exhibits four high frequency ^{31}P resonances.

The molecular structure of **1a** is shown in Fig. 1 and selected bond distances and angles are presented in Table 1. The structure reveals that two P atoms are coordinated to platinum, whereas the other two have been oxidized. The geometry at platinum is approximately square planar, the sum of the angles about the metal center being 360.1° . The larger angles are those between P and C atoms, whereas the smallest angle (83.8°) is that between the smaller methyl groups. The Pt–P and Pt–C distances are unremarkable. The central P–C–P angle in the ligand is $116.0(4)^\circ$, similar to that found in DPPEPM(S)₄ [20].

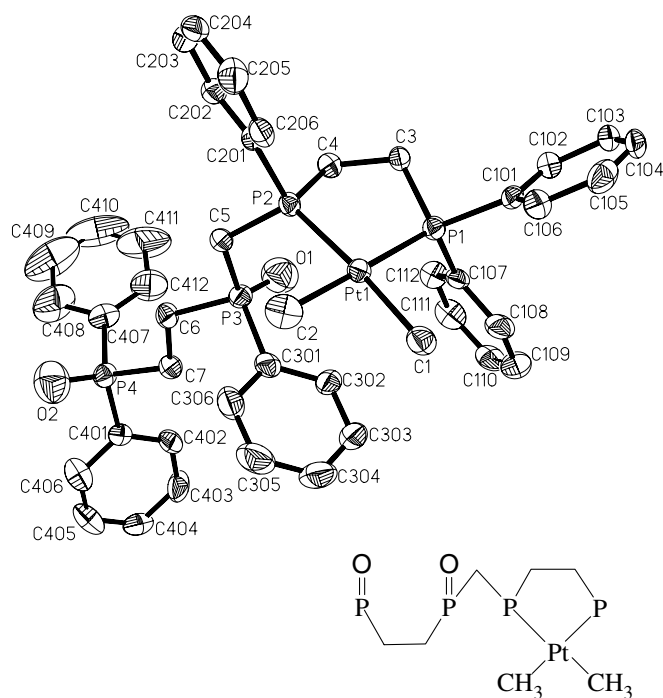


Fig. 1. Molecular structure of **1a**, with atoms represented by thermal ellipsoids at the 50% level.

Table 1
Selected bond distances (Å) and angles ($^\circ$) for **1a**

Pt–C(1)	2.095(8)	Pt–C(2)	2.095(9)
Pt–P(1)	2.263(2)	Pt–P(2)	2.254(2)
P(3)–O(1)	1.450(8)	P(4)–O(2)	1.410(8)
C(1)–Pt–C(2)	83.8(4)	C(1)–Pt–P(1)	97.3(2)
C(1)–Pt–P(2)	175.8(2)	C(2)–Pt–P(1)	179.0(3)
C(2)–Pt–P(2)	92.7(3)	P(1)–Pt–P(2)	86.28(8)
P(2)–C(5)–P(3)	116.0(4)		

Obviously, this compound is generated by slow air oxidation of **1**, and it provides further evidence for the formation of the monometallic species.

We anticipated that when 1 mol equiv. of $[MCl_2(cod)]$ ($M = Pd, Pt$) was introduced similarly to an acetone suspension of DPPEPM it might form an analogous monometallic

complex of the form $[\text{MCl}_2(\text{DPPEPM-PP})]$. The major product does indeed show signals due to coordinated and uncoordinated P atoms in its ^{31}P NMR spectrum, but it is clear from the $^1J_{\text{PtP}}$ values in the platinum complex that the coordinated P atoms lie *trans* to other P atoms rather than chlorides. The free P atoms appear at -12.7 and -27.7 , whereas the coordinated P atoms are observed at 34.3 ($^1J_{\text{PtP}} = 2370$ Hz) and 44.7 ($^1J_{\text{PtP}} = 2665$ Hz). Thus, the cation is postulated to be $[\text{Pt}(\text{DPPEPM-PP})_2]^{2+}$ (**4**) (Scheme 1), and this has been confirmed by its high-resolution mass spectrum. The palladium complex (**3**) exhibits similar ^{31}P NMR data. In each case, the ^1H NMR spectrum exhibits two widely spaced, broad resonances due to the central CH_2 group of the DPPEPM ligand. With ^{31}P -decoupling, these simplify to doublets, with $^2J_{\text{HH}} = 16$ Hz. In the case of **4**, these signals appear at 0.87 and 4.55 ppm, whereas they are observed at 0.91 and 4.35 ppm in the palladium analogue **3**. The origin of this disparity is unclear. In **4**, eight resonances may be detected for the $\text{PCH}_2\text{CH}_2\text{P}$ hydrogens, and these may be separated into two sets of four hydrogens based on COSY experiments.

Whereas the identity of the cation in each of these reactions has been established, the anion is invisible to ^1H and ^{31}P NMR spectroscopy. Although $[\text{MCl}_2(\text{cod})]$ and DPPEPM were allowed to react in a 1:1 ratio, the cations contain two ligands per metal. This might suggest that half of the metal precursor should be left unreacted, but monitoring the reaction by ^1H NMR spectroscopy indicated that no $[\text{MCl}_2(\text{cod})]$ remained. Consistent with this observation, when 2 mol equiv. of DPPEPM was added to $[\text{PtCl}_2(\text{cod})]$, half of the ligand remained unreacted. Thus, DPPEPM and the metal complex react in a 1:1 ratio, and we suggest that the anions are PtCl_4^{2-} and PdCl_4^{2-} . The colors of the reaction solutions range from yellow in the case of platinum, to orange for palladium, which might be consistent with the presence of the tetrachlorometallates. The isolated complexes are off-white and yellow, respectively, but these may not contain the MCl_4^{2-} ions (vide infra). Several attempts to detect PtCl_4^{2-} by ^{195}Pt NMR spectroscopy were unsuccessful, perhaps due to the low solubility of the complex. Attempts to identify the anion using negative ion FAB mass spectrometry were also inconclusive, perhaps due to decomposition of the anion in the solvent used (acetonitrile). Thus, we can only infer the nature of the anion from stoichiometry and further reaction, rather than by direct observation.

Attempts to grow crystals of **3** or **4** as their MCl_4^{2-} salts were unsuccessful. When a chloroform solution of the platinum complex was allowed to evaporate slowly, yellow crystals were obtained, but these proved to be of a bimetallic complex $[\text{Pt}_2(\mu\text{-Cl})(\mu\text{-DPPEPM})_2]\text{Cl}_3$ (**5**). This has the same overall formulation, and evidently it is produced by a complex rearrangement of $[(\text{4})\text{PtCl}_4]$, involving displacement of chlorides from PtCl_4^{2-} by attack of the free P atoms of the cation. One of the chlorides remains coordinated and assumes a bridging role. The molecular structure of the $[\text{Pt}_2(\mu\text{-Cl})(\mu\text{-DPPEPM})_2]^{3+}$ cation is shown in Fig. 2, and

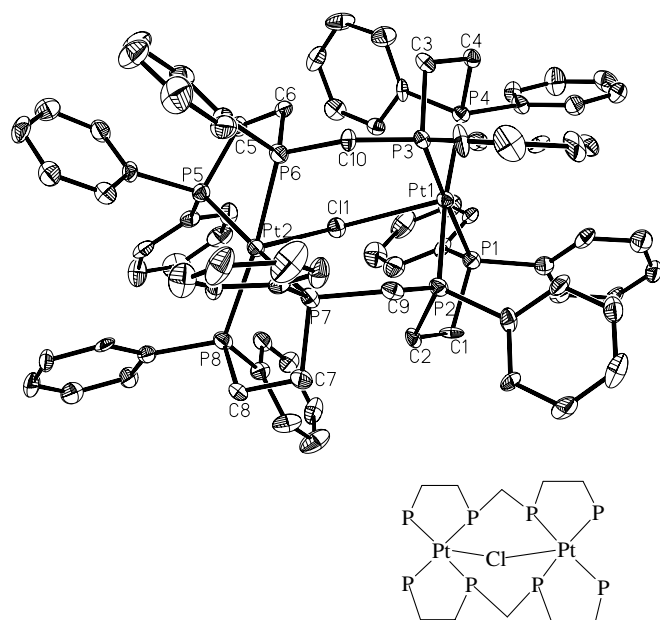


Fig. 2. Molecular structure of **5**, with atoms represented by thermal ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for **5**

Pt(1)–Cl	2.852(2)	Pt(2)–Cl	2.775(2)
Pt(1)–P(1)	2.357(2)	Pt(2)–P(5)	2.358(2)
Pt(1)–P(2)	2.323(2)	Pt(2)–P(6)	2.323(2)
Pt(1)–P(3)	2.319(2)	Pt(2)–P(7)	2.308(2)
Pt(1)–P(4)	2.344(2)	Pt(2)–P(8)	2.339(2)
Pt(1)–Cl–Pt(2)	109.91(7)	P(5)–Pt(2)–P(6)	80.76(8)
P(1)–Pt(1)–P(2)	81.90(8)	P(5)–Pt(2)–P(7)	173.44(8)
P(1)–Pt(1)–P(3)	175.34(9)	P(5)–Pt(2)–P(8)	100.41(8)
P(1)–Pt(1)–P(4)	99.02(8)	P(6)–Pt(2)–P(7)	94.02(8)
P(2)–Pt(1)–P(3)	94.72(8)	P(6)–Pt(2)–P(8)	171.36(9)
P(2)–Pt(1)–P(4)	173.83(8)	P(7)–Pt(2)–P(8)	84.15(8)
P(3)–Pt(1)–P(4)	84.01(8)	P(5)–Pt(2)–Cl	80.99(8)
P(1)–Pt(1)–Cl	81.51(8)	P(6)–Pt(2)–Cl	86.07(7)
P(2)–Pt(1)–Cl	85.06(7)	P(7)–Pt(2)–Cl	102.74(8)
P(3)–Pt(1)–Cl	101.46(8)	P(8)–Pt(2)–Cl	102.57(8)
P(4)–Pt(1)–Cl	101.11(7)	P(3)–C(10)–P(6)	123.3(5)
P(2)–C(9)–P(7)	122.7(5)		

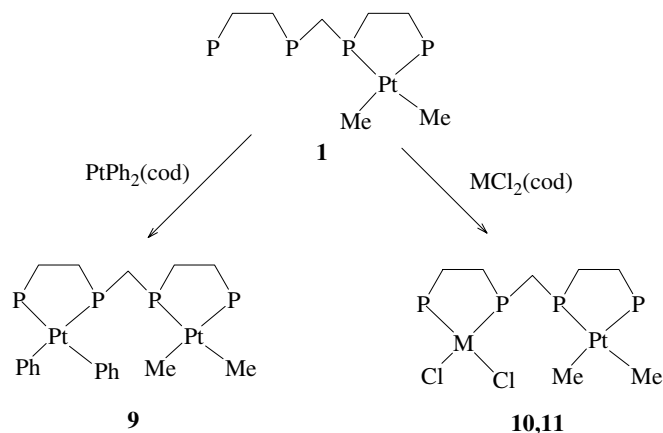
selected bond distances and angles are given in Table 2. The cation is composed of two platinum centers, each of which exhibits approximately square pyramidal geometry. Each platinum is chelated by two $\text{PCH}_2\text{CH}_2\text{P}$ units from two different DPPEPM ligands in the square plane, the axial site being occupied by the chloride, which bridges the two metals. The PtP_4 units are nearly planar, the sums of the angles about platinum being 359.3° and 359.7° . The platinum atoms are located 0.096 and 0.131 Å out of the mean plane of their four P atoms. The two P_4 planes are inclined at an angle of 62° , and this results in two smaller ($80.99(8)$ – $86.07(7)^\circ$) and two larger ($101.11(7)$ – $102.74(8)^\circ$) P–Pt–Cl angles at each platinum. The Pt–Pt distance is 4.61 Å. The Pt–P distances range from $2.308(2)$ to $2.358(2)$ Å, and the P–Pt–P angles range from $80.76(8)^\circ$ to $100.41(8)^\circ$. The smaller angles are found for the chelated

diphosphine units. The chloride bridges the two metals in an unsymmetrical fashion (Pt–Cl 2.775(2) and 2.852(2) Å), with a Pt–Cl–Pt angle of 109.91(7)°. This angle is considerably greater than those found in dppe-bridged complexes [22]. The P–C–P angles are much greater at 122.7(5)° and 123.3(5)° than in previously characterized complexes [20], perhaps due to the need to maintain the two PtP₄ units at an optimal distance from one another, and this may involve some strain within the tetraphosphine ligands. Very few solid state structures have been reported for five-coordinate platinum or palladium complexes with four P atoms and one chloride in their coordination sphere [23–29], and this represents the first in which the chloride serves as a bridging ligand.

Reactions of [PtClR(cod)] (R = Me, Ph) or [PdClMe(cod)] with DPPEPM follow a third pathway to give **6–8**. When the metal complex is allowed to react with 1 mol equiv. of DPPEPM, the chloride is displaced and DPPEPM acts as a tridentate ligand, with one of the internal P atoms remaining uncoordinated (Scheme 1). On standing in solution, this free P atom becomes oxidized. The solid state structure of [PtMe(DPPEPM(O)-PPP)]Cl has been determined [21], and peaks due to the oxidized product are found in the mass spectrum of [PtMe(DPPEPM-PPP)]Cl (**6**) and in the ³¹P NMR spectrum of [PdMe(DPPEPM-PPP)]Cl (**8**). The ³¹P NMR spectra of the [MR(DPPEPM-PPP)]⁺ cations contain four resonances, one at low frequency due to the uncoordinated P atom, two that exhibit large ²J_{PP} coupling constants (ca 380 Hz) indicative of their mutually *trans* disposition, and a fourth that shows couplings to the other three P atoms. In the platinum complexes, the free P atom does not exhibit coupling to ¹⁹⁵Pt, the two mutually *trans* P atoms have couplings in the range 2700–2850 Hz, and the P atom *trans* to the organic ligand shows the smallest ¹J_{PtP} value (1700–1800 Hz).

Complexes of the type [PtR₂(DPPEPM-PP)] (**1**, **2**) have two uncoordinated P atoms that should be available to coordinate a second metal center, thus permitting the formation of heterobimetallic derivatives. Indeed, reaction of **1** with [PtPh₂(cod)] or [MCl₂(cod)] (M = Pd, Pt), or of **2** with [PdCl₂(cod)], does result in unsymmetrical species as the major products **9–12** (although traces of symmetrical species are always detected) (Scheme 2). In each case, these complexes exhibit four high frequency resonances in their ³¹P NMR spectra, indicating that all four P atoms are coordinated. In the case of [PtMe₂(μ-DPPEPM)PtPh₂] (**9**), all four signals have small ¹J_{PtP} values (1654–1820 Hz), whereas in [PtMe₂(μ-DPPEPM)PtCl₂] (**10**) there are two smaller and two larger couplings.

The solid state structure of **10** has been reported previously [21]. Here we report the structure of its palladium analogue [PtMe₂(μ-DPPEPM)PdCl₂] (**11**). Its molecular structure is shown in Fig. 3, and selected bond distances and angles are presented in Table 3. The PtMe₂ and PdCl₂ units are disordered over both sites, but this has been modeled successfully using partial occupancies (see Section 4).



Scheme 2.

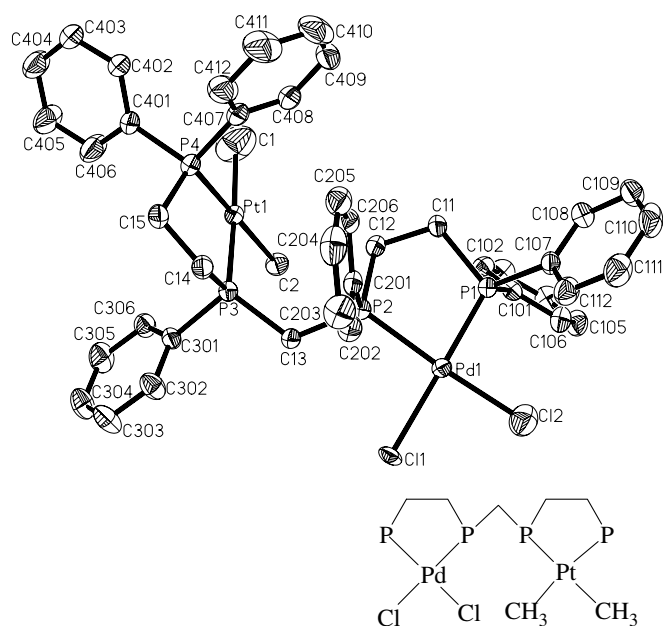


Fig. 3. Molecular structure of **11**, with atoms represented by thermal ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

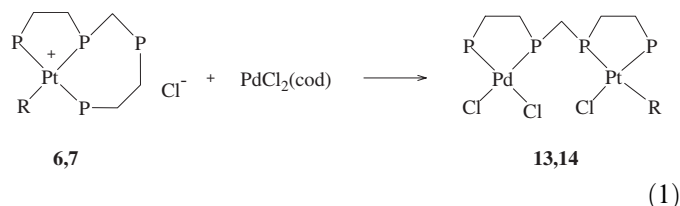
Table 3
Selected bond distances (Å) and angles (°) for **11**

Pt–C(1)	2.1993(13)	Pt–C(2)	2.3327(12)
Pt–P(3)	2.2797(10)	Pt–P(4)	2.2234(10)
Pd–Cl(1)	2.3381(11)	Pd–Cl(2)	2.231(2)
Pd–P(1)	2.2177(9)	Pd–P(2)	2.2849(9)
C(1)–Pt–C(2)	90.12(5)	C(1)–Pt–P(3)	176.49(4)
C(1)–Pt–P(4)	90.77(4)	C(2)–Pt–P(3)	93.23(4)
C(2)–Pt–P(4)	178.96(4)	P(3)–Pt–P(4)	85.89(4)
Cl(1)–Pd–Cl(2)	88.58(7)	Cl(1)–Pd–P(1)	173.68(4)
Cl(1)–Pd–P(2)	94.55(4)	Cl(2)–Pd–P(1)	91.37(7)
Cl(2)–Pd–P(2)	175.98(6)	P(1)–Pd–P(2)	85.79(3)
P(2)–C(13)–P(3)	120.60(19)		

The structure consists of two approximately square planar units (the sums of the angles at Pt and Pd are 360.0° and 360.3°, respectively), rotated away from each other around

the flexible PCH₂P bridge, giving a Pt–Pd distance of 6.35 Å. The P–C–P angle of 120.6(19)° is similar to that in the diplatinum complex, and larger than the analogous angle in **1a**. It is likely that the angle increases in order to accommodate the presence of two metal centers.

When [PtClR(cod)] (R = Me, Ph) is allowed to react with DPPEPM, ionic complexes **6** and **7** are formed (vide supra), which contain one free P atom, that we considered might be available for further coordination. When [PtCl₂(cod)] or [PdCl₂(cod)] is added, displacement of cyclooctadiene does take place, but cleavage of one of the Pt–P bonds occurs and the free chloride becomes coordinated to give [PtClR(μ-DPPEPM)MCl₂] (**13**, M = Pt, R = Me; **14**, M = Pd, R = Ph) (Eq. (1)). The products have been characterized by NMR spectroscopy and, in the case of the phenyl complex, by high-resolution mass spectrometry and X-ray crystallography.



The molecular structure of **14** is displayed in Fig. 4, and selected bond distances and angles are given in Table 4. This structure is not disordered over the metal-containing sites. It consists of two metal square planes (the sums of the angles are 360.0 for Pt and 360.1 for Pd) rotated away from each other to give a Pt–Pd distance of 6.20 Å. The Pt–P distances differ by 0.08 Å, the longer bond involving the internal P atom that lies *trans* to the phenyl group [30]. In contrast, the Pd–P distances are identical to each other, as are the Pd–Cl distances. The P–C–P angle is 124.1(4)°, larger than those found in **10** and **11**.

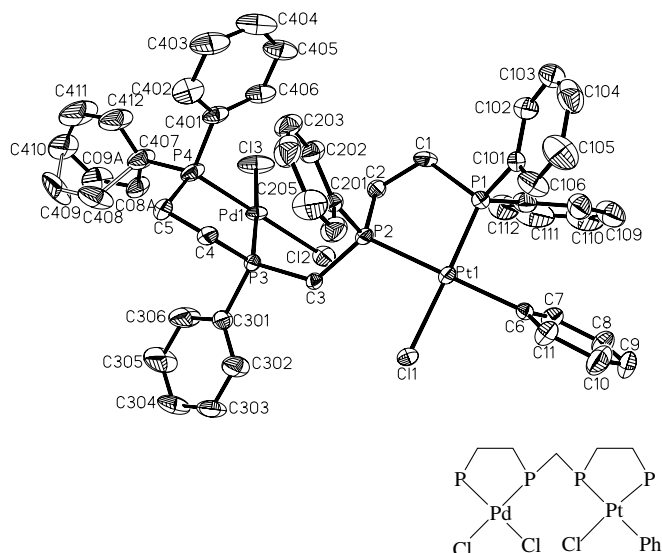
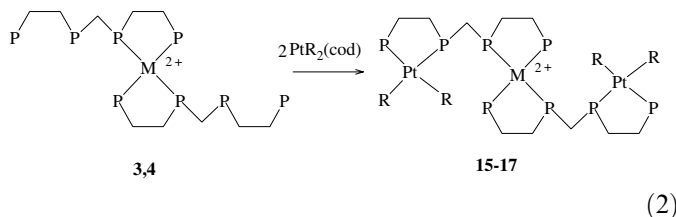


Fig. 4. Molecular structure of **14**, with atoms represented by thermal ellipsoids at the 50% level. Hydrogen atoms have been omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) for **14**

Pt–Cl(1)	2.3612(17)	Pt–C(6)	2.101(6)
Pt–P(1)	2.2165(18)	Pt–P(2)	2.2972(16)
Pd–Cl(2)	2.3586(19)	Pd–Cl(3)	2.368(2)
Pd–P(3)	2.2286(18)	Pd–P(4)	2.227(2)
Cl(1)–Pt–C(6)	87.97(18)	Cl(1)–Pt–P(1)	178.27(6)
Cl(1)–Pt–P(2)	93.05(6)	C(6)–Pt–P(1)	93.68(18)
C(6)–Pt–P(2)	177.2(2)	P(1)–Pt–P(2)	85.32(6)
Cl(2)–Pd–Cl(3)	93.11(8)	Cl(2)–Pd–P(3)	89.56(7)
Cl(2)–Pd–P(4)	174.48(7)	Cl(3)–Pd–P(3)	176.80(8)
Cl(3)–Pd–P(4)	91.71(8)	P(3)–Pd–P(4)	85.71(7)
P(2)–C(3)–P(3)	124.1(4)		

In **3** and **4**, one diphosphine unit of each ligand is coordinated, leaving two diphosphine moieties available for further bonding. This presents the possibility of forming trimetallic derivatives. Thus, reaction of [MCl₂(cod)] with DPPEPM, followed by [PtR₂(cod)] (R = Me, Ph), leads to trimetallic complexes of the form [{PtR₂(μ-DPPEPM)}₂M][MCl₄] (**15**, M = Pt, R = Me; **16**, M = Pd, R = Me; **17**, M = Pd, R = Ph) (Eq. (2)). Again, the cations have been identified by NMR spectroscopy and high resolution mass spectrometry, whereas the anions are postulated as PtCl₄²⁻ or PdCl₄²⁻ based on the reaction stoichiometry. In each case the ³¹P NMR spectrum contains four resonances. The mixed metal complexes exhibit two signals with ¹J_{PtP} values around 1700 Hz, due to the P atoms attached to platinum, and two signals with no satellites. In **15**, there are two resonances with couplings of ca 1800 Hz, due to the P atoms lying *trans* to methyl groups, and signals at 30.3 (¹J_{PtP} = 2375 Hz) and 43.1 ppm (¹J_{PtP} = 2693 Hz), due to the P atoms coordinated to the central platinum. The resonance with the larger coupling is assigned to the terminal P atoms, because they are Ph₂PR moieties, and the other to the internal PhPR₂ units. It has not proved possible to isolate these complexes in pure form, but each of the trimetallic cations has been characterized by its high resolution mass spectrum. A cluster of peaks corresponding to the cation itself is observed and, in addition, a set of peaks due to the cation plus a chlorine atom is found. The latter must involve abstraction of Cl from the anion.



3. Summary

Careful addition of the appropriate metal complex to the tetradentate ligand DPPEPM leads to complexes of the form [PtR₂(DPPEPM-PP)] (**1**, **2**), [M(DPPEPM-PP)₂][MCl₄] (**3**, **4**) or [MR(DPPEPM-PPP)]Cl (**6–8**). Each of these has uncoordinated P atoms that can be utilized in

the formation of bi- or trimetallic derivatives. Thus, the free P atom(s) in **1** or **2**, or in **6–8**, may be used to generate heterobimetallic species, whereas the two pairs of free P atoms in **3** or **4** allow formation of trimetallic complexes of the type $[\{\text{PtR}_2(\mu\text{-DPPEPM})\}_2\text{M}][\text{MCl}_4]$ (**15–17**).

4. Experimental section

All reactions were carried out under an atmosphere of argon. Solvents were distilled prior to use. $[\text{PtCl}_2(\text{cod})]$, $[\text{PdCl}_2(\text{cod})]$, $[\text{PtR}_2(\text{cod})]$ (R = Me, Ph), $[\text{PtClR}(\text{cod})]$ (R = Me, Ph), and $[\text{PdClMe}(\text{cod})]$ were prepared as reported previously [22,31–34]. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker ARX-500 or Avance 300, or a Varian Unity plus 300 spectrometer. High-resolution mass spectra (HRMS) were obtained in FAB mode, on a JEOL M Station-JMS700, using nitrobenzyl alcohol (NBA) as solvent.

4.1. Synthesis of $[\text{PtMe}_2(\text{DPPEPM-PP})]$ (**1**)

An acetone solution (3.0 mL) of $[\text{PtMe}_2(\text{cod})]$ (0.015 g, 0.045 mmol) was added dropwise, with constant stirring, to a suspension of DPPEPM (0.030 g, 0.045 mmol) in acetone (0.8 mL). The almost colorless solution was allowed to stir for another 10 min, then the solvent was removed under reduced pressure. The residue was washed several times with pentane and precipitated from acetone/pentane as an off-white powder (0.021 g, 53%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP -28.7 (dd, $^2J_{\text{PP}} = 68$ Hz, $^3J_{\text{PP}} = 31$ Hz), -12.4 (d, $^3J_{\text{PP}} = 31$ Hz), 42.0 (dd, $^2J_{\text{PP}} = 68$ Hz, $^3J_{\text{PP}} = 4$ Hz, $^1J_{\text{PtP}} = 1814$ Hz), 49.4 (d, $^3J_{\text{PP}} = 4$ Hz, $^1J_{\text{PtP}} = 1829$ Hz). ^1H NMR (acetone- d_6): δH 0.41 (dd, $^3J_{\text{PH}} = 7$ Hz, $^2J_{\text{PtH}} = 63$ Hz, CH_3), 0.47 (dd, $^3J_{\text{PH}} = 7$ Hz, $^2J_{\text{PtH}} = 63$ Hz, CH_3), 1.9–3.1 (several m, $\text{PCH}_2\text{CH}_2\text{P}$, PCH_2P), 7.0–7.5 (m, C_6H_5). HRMS: calc. for $^{12}\text{C}_{42}\text{H}_{43}\text{P}_4^{195}\text{Pt}^+$ ($\text{M} - \text{CH}_3$) $^+$, 866.1963; observed, 866.2022; calc. for $^{12}\text{C}_{42}\text{H}_{43}\text{OP}_4^{195}\text{Pt}^+$ ($\text{MO} - \text{CH}_3$), 882.1912; observed, 882.1905. Crystals of $[\text{PtMe}_2\{\text{DPPEPM}(\text{O})_2\text{-PP}\}]$ (**1a**) were obtained from CDCl_3 solution.

4.2. Synthesis of $[\text{PtPh}_2(\text{DPPEPM-PP})]$ (**2**)

This complex was prepared similarly from $[\text{PtPh}_2(\text{cod})]$ (0.020 g, 0.045 mmol) and DPPEPM (0.030 g, 0.045 mmol) and isolated as a pale yellow powder (0.026 g, 57%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP -28.0 (dd, $^2J_{\text{PP}} = 74$ Hz, $^3J_{\text{PP}} = 30$ Hz, $^3J_{\text{PtP}} = 62$ Hz), -12.8 (d, $^3J_{\text{PP}} = 30$ Hz), 37.9 (d, $^2J_{\text{PP}} = 74$ Hz, $^1J_{\text{PtP}} = 1723$ Hz), 41.6 (s, $^1J_{\text{PtP}} = 1733$ Hz).

4.3. Synthesis of $[\text{PtMe}_2(\mu\text{-DPPEPM}(S)_2\text{-PP})]$ (**1b**)

An acetone- d_6 solution (1.0 mL) of $[\text{PtMe}_2(\text{cod})]$ (0.005 g, 0.015 mmol) was added dropwise, with constant shaking, to a suspension of DPPEPM (0.010 g, 0.015 mmol) in acetone- d_6 (0.2 mL) in an NMR tube. To this solution elemental

sulfur (0.001 g, 0.0038 mmol) was added, and a yellow solution formed. $^{31}\text{P}\{^1\text{H}\}$ NMR: δP 41.4 (d, $^2J_{\text{PP}} = 10$ Hz, $^1J_{\text{PtP}} = 1825$ Hz), 49.6 (d, $^2J_{\text{PP}} = 10$ Hz, $^1J_{\text{PtP}} = 1829$ Hz), 44.7 (br, 2P). ^1H NMR: δH 0.15 (dd, $^3J_{\text{PH}} = 8$ Hz, $^2J_{\text{PtH}} = 70$ Hz, CH_3), 0.34 (dd, $^3J_{\text{PH}} = 7$ Hz, $^2J_{\text{PtH}} = 71$ Hz, CH_3), 1.9–2.9 (several m, $\text{PCH}_2\text{CH}_2\text{P}$), 3.6–3.8 (br m, PCH_2P), 6.8–7.8 (m, C_6H_5).

4.4. Synthesis of $[\text{Pd}(\text{DPPEPM-PP})_2]\text{PdCl}_4$ (**3**)

A solution of $[\text{PdCl}_2(\text{cod})]$ (0.013 g, 0.045 mmol) in acetone (3.0 mL) was added dropwise to a suspension of DPPEPM (0.030 g, 0.045 mmol) in acetone (0.8 mL) with constant stirring. The solution darkened and it was allowed to stir for another 10 min, and the solvent was evaporated. The residue was washed several times with pentane and precipitated from acetone/pentane to give the product as a yellow powder (0.028 g, 75%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP -26.9 (ddd, $^3J_{\text{PP}} = 32$ Hz, $^2J_{\text{PP}} = ^4J_{\text{PP}} = 16$ Hz), -12.6 (d, $^3J_{\text{PP}} = 32$ Hz), 47.4 (5-line pattern, $^2J_{\text{PP}} = 16$ Hz), 57.3 (apparent t, $^2J_{\text{PP}} = 16$ Hz). ^1H NMR (acetone- d_6): δH 0.86 (m, 1H, PCH_2P), 1.2–2.8 (several m, $\text{PCH}_2\text{CH}_2\text{P}$), 4.31 (d, $^2J_{\text{HH}} = 16$ Hz, 1H, PCH_2P), 6.8–8.3 (m, C_6H_5). $^1\text{H}\{^{31}\text{P}\}$ NMR (acetone- d_6): δH 0.86 (d, $^2J_{\text{HH}} = 16$ Hz, 1H, PCH_2P), 1.3–2.6 (several m, $\text{PCH}_2\text{CH}_2\text{P}$), 4.32 (d, $^2J_{\text{HH}} = 16$ Hz, 1H, PCH_2P), 6.8–8.3 (m, C_6H_5).

4.5. Synthesis of $[\text{Pt}(\text{DPPEPM-PP})_2]\text{PtCl}_4$ (**4**)

This complex was prepared analogously and isolated as an off-white powder in 70% yield. $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP -27.7 (ddd, $^3J_{\text{PP}} = 32$ Hz, $^2J_{\text{PP}} = ^4J_{\text{PP}} = 18$ Hz), -12.7 (d, $^3J_{\text{PP}} = 32$ Hz), 34.3 (5-line pattern, $J_{\text{PP}} = 18$ Hz, $^1J_{\text{PtP}} = 2370$ Hz), 44.7 (apparent t, $^2J_{\text{PP}} = 18$ Hz, $^1J_{\text{PtP}} = 2665$ Hz). ^1H NMR (acetone- d_6): δH 0.87 (m, 1H, PCH_2P), 1.2–2.7 (several m, $\text{PCH}_2\text{CH}_2\text{P}$), 4.55 (d, $^2J_{\text{HH}} = 16$ Hz, 1H, PCH_2P), 6.9–8.1 (m, C_6H_5). $^1\text{H}\{^{31}\text{P}\}$ NMR (acetone- d_6): δH 0.87 (d, $^2J_{\text{HH}} = 16$ Hz, 1H, PCH_2P), 1.2–2.8, (several m, $\text{PCH}_2\text{CH}_2\text{P}$), 4.32 (d, $^2J_{\text{HH}} = 16$ Hz, 1H, PCH_2P), 6.9–8.1 (m, C_6H_5). HRMS: calc. for $^{12}\text{C}_{82}\text{H}_{81}\text{P}_8^{195}\text{Pt}^+$ (MH^+), 1508.3887; observed, 1508.3933. Crystals, which proved to be $[\text{Pt}_2(\mu\text{-Cl})(\mu\text{-DPPEPM})_2]\text{Cl}_3$ (**5**), were obtained by slow evaporation of a CDCl_3 solution.

4.6. Synthesis of $[\text{PtMe}(\text{DPPEPM-PPP})]\text{Cl}$ (**6**)

A solution of $[\text{PtClMe}(\text{cod})]$ (0.016 g, 0.045 mmol) in acetone (3.0 mL) was added dropwise to a suspension of DPPEPM (0.030 g, 0.045 mmol) in acetone (0.8 mL). A colorless solution formed, which was allowed to stir for another 10 min. The solvent was removed under vacuum, and the residue was washed with pentane, then dissolved in acetone. Addition of pentane gave the product as a white powder (0.027 g, 85%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP -19.5 (dd, $^2J_{\text{PP}} = 24$, $^3J_{\text{PP}} = 9$ Hz), 28.9 (ddd, $^2J_{\text{PP}} = 384$, 19, $^3J_{\text{PP}} = 9$ Hz, $^1J_{\text{PtP}} = 2833$ Hz), 43.7 (ddd, $^2J_{\text{PP}} = 24$,

19, 5 Hz, $^1J_{\text{PtP}} = 1785$ Hz), 54.8 (dd, $^2J_{\text{PP}} = 384$, 5 Hz, $^1J_{\text{PtP}} = 2718$ Hz). ^1H NMR (acetone- d_6): δH 0.34 (q, $^3J_{\text{PH}} = 6$ Hz, $^2J_{\text{PtH}} = 30$ Hz, CH_3), 1.4–1.5, 2.3–2.9, 3.2–3.4 (m, $\text{PCH}_2\text{CH}_2\text{P}$), 3.89–3.93, 4.08–4.20 (m, PCH_2P) 7.2–8.0 (m, C_6H_5). HRMS: calc. for $^{12}\text{C}_{42}\text{H}_{43}\text{P}_4^{195}\text{Pt}^+$ (M^+), 866.1963; observed, 866.1987. A cluster of peaks around m/z 882 due to $[\text{PtMe}\{\text{DPPEPM}(\text{O})\text{-PPP}\}]^+$ was also observed.

4.7. Synthesis of $[\text{PtPh}(\text{DPPEPM-PPP})\text{Cl}]$ (7)

A solution of $[\text{PtClPh}(\text{cod})]$ (0.006 g, 0.015 mmol) in acetone- d_6 (0.8 mL) was added dropwise to a suspension of DPPEPM (0.010 g, 0.015 mmol) in acetone- d_6 (0.3 mL) to give a colorless solution. $^{31}\text{P}\{^1\text{H}\}$ NMR: δP -20.4 (dd, $^2J_{\text{PP}} = 24$, $^3J_{\text{PP}} = 6$ Hz), 23.3 (ddd, $^2J_{\text{PP}} = 375$, 19, $^3J_{\text{PP}} = 6$ Hz, $^1J_{\text{PtP}} = 2834$ Hz), 39.6 (ddd, $^2J_{\text{PP}} = 24$, 19, 6 Hz, $^1J_{\text{PtP}} = 1733$ Hz), 47.8 (dd, $^2J_{\text{PP}} = 375$, 6 Hz, $^1J_{\text{PtP}} = 2721$ Hz).

4.8. Synthesis of $[\text{PdMe}(\text{DPPEPM-PPP})\text{Cl}]$ (8)

An acetone- d_6 solution (1.0 mL) of $[\text{PdClMe}(\text{cod})]$ (0.004 g, 0.015 mmol) was added dropwise to a suspension of DPPEPM (0.010 g, 0.015 mmol) in acetone- d_6 (0.2 mL) to give a pale yellow solution. $^{31}\text{P}\{^1\text{H}\}$ NMR: δP -17.0 (dd, $^2J_{\text{PP}} = 26$ Hz, $^3J_{\text{PP}} = 11$ Hz), 31.3 (ddd, $^2J_{\text{PP}} = 374$, 37 Hz, $^3J_{\text{PP}} = 11$ Hz), 39.3 (ddd, $^2J_{\text{PP}} = 37$, 26, 26 Hz), 56.0 (dd, $^2J_{\text{PP}} = 374$, 26 Hz). ^1H NMR: δH 0.38 (q, $^3J_{\text{PH}} = 6$ Hz, CH_3), 1.3–2.5 (several m, $\text{PCH}_2\text{CH}_2\text{P}$), 3.01–3.05, 4.68–4.72 (m, PCH_2P), 7.0–7.7 (m, C_6H_5). In addition, signals were detected in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{PdMe}\{\text{DPPEPM}(\text{O})\text{-PPP}\}]\text{Cl}$: δP 28.5 (ddd, $^2J_{\text{PP}} = 374$, 38 Hz, $^3J_{\text{PP}} = 16$ Hz), 34.5 (d, $^2J_{\text{PP}} = 16$ Hz), 35.6 (dd, $^2J_{\text{PP}} = 38$, 26 Hz), 56.3 (dd, $^2J_{\text{PP}} = 374$, 26 Hz).

4.9. Synthesis of $[\text{PtMe}_2(\mu\text{-DPPEPM})\text{PtPh}_2]$ (9)

An acetone solution (3.0 mL) of $[\text{PtMe}_2(\text{cod})]$ (0.015 g, 0.045 mmol) was added dropwise, with constant stirring, to a suspension of DPPEPM (0.030 g, 0.045 mmol) in acetone (0.8 mL). An almost colorless solution formed. Solid $[\text{PtPh}_2(\text{cod})]$ (0.020 g, 0.045 mmol) was added slowly and the mixture was allowed to stir for a further 10 min before the solvent was removed. The residue was washed several times with pentane and dissolved in acetone. Addition of pentane resulted in precipitation of the product as a pale yellow powder (0.022 g, 47%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP 32.3 (d, $^2J_{\text{PP}} = 6$ Hz, $^1J_{\text{PtP}} = 1654$ Hz), 40.5 (d, $^2J_{\text{PP}} = 6$ Hz, $^1J_{\text{PtP}} = 1734$ Hz), 40.6 (d, $^2J_{\text{PP}} = 7$ Hz, $^1J_{\text{PtP}} = 1820$ Hz), 48.8 (d, $^2J_{\text{PP}} = 7$ Hz, $^1J_{\text{PtP}} = 1811$ Hz). ^1H NMR (acetone- d_6): δH 0.40 (dd, $^3J_{\text{PH}} = 7$ Hz, $^2J_{\text{PtH}} = 66$ Hz, CH_3), 0.47 (dd, $^3J_{\text{PH}} = 7$ Hz, $^2J_{\text{PtH}} = 66$ Hz, CH_3), 1.0–3.4 (several m, $\text{PCH}_2\text{CH}_2\text{P}$, PCH_2P), 6.4–7.8 (m, C_6H_5). HRMS: calc. for $^{12}\text{C}_{42}\text{H}_{43}\text{P}_4^{195}\text{Pt}_2^+$ ($\text{M} - \text{CH}_3$, $2\text{C}_6\text{H}_5$) $^+$, 1061.1611; observed, 1061.1636.

4.10. Synthesis of $[\text{PtMe}_2(\mu\text{-DPPEPM})\text{PtCl}_2]$ (10)

A solution of $[\text{PtMe}_2(\text{cod})]$ (0.015 g, 0.045 mmol) in acetone (3.0 mL) was added dropwise to a suspension of DPPEPM (0.030 g, 0.045 mmol) in acetone (0.8 mL). To the resulting nearly colorless solution was added $[\text{PtCl}_2(\text{cod})]$ (0.017 g, 0.045 mmol), and the solution was allowed to stir for another 10 min. The solvent was removed under vacuum, and the residue was washed several times with pentane and isolated from acetone/pentane as a yellow powder (0.027 g, 52%). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP 36.4 (s, $^1J_{\text{PtP}} = 3535$ Hz), 39.2 (s, $^1J_{\text{PtP}} = 1743$ Hz), 41.5 (s, $^1J_{\text{PtP}} = 3648$ Hz), 48.5 (s, $^1J_{\text{PtP}} = 1786$ Hz).

4.11. Synthesis of $[\text{PtMe}_2(\mu\text{-DPPEPM})\text{PdCl}_2]$ (11)

This complex was prepared similarly and obtained as a yellow powder in 60% yield. $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP 40.3 (s, $^1J_{\text{PtP}} = 1740$ Hz), 48.9 (s, $^1J_{\text{PtP}} = 1795$ Hz), 61.0 (s), 64.8 (s). HRMS: calc. for $^{12}\text{C}_{43}\text{H}_{46}\text{P}_4^{106}\text{Pd}^{195}\text{Pt}^{35}\text{Cl}^+$ ($\text{M} - \text{Cl}$) $^+$, 1022.0921; observed, 1022.0896. Crystals of $[\text{PtMe}_2(\mu\text{-DPPEPM})\text{PdCl}_2]$ suitable for an X-ray diffraction study were grown by slow evaporation of an acetone- d_6 solution.

4.12. Synthesis of $[\text{PtPh}_2(\mu\text{-DPPEPM})\text{PdCl}_2]$ (12)

This complex was prepared similarly from $[\text{PtPh}_2(\text{cod})]$ and DPPEPM, followed by addition of $[\text{PtCl}_2(\text{cod})]$, and isolated as a yellow solid in 55% yield. $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP 33.7 (s, $^1J_{\text{PtP}} = 1650$ Hz), 40.2 (s, $^1J_{\text{PtP}} = 1727$ Hz), 64.1 (s), 64.3 (s). ^1H NMR (acetone- d_6): 1.0–3.0 (several m, $\text{PCH}_2\text{CH}_2\text{P}$), 3.3–3.8 (br m, PCH_2P), 6.7–8.3 (m, C_6H_5).

4.13. Synthesis of $[\text{PtClMe}(\mu\text{-DPPEPM})\text{PtCl}_2]$ (13)

A solution of $[\text{PtClMe}(\text{cod})]$ (0.005 g, 0.015 mmol) in acetone (0.8 mL) was added dropwise to a suspension of DPPEPM (0.010 g, 0.015 mmol) in acetone (0.3 mL). To the resulting colorless solution was added $[\text{PtCl}_2(\text{cod})]$ (0.005 g, 0.015 mmol). The solvent was removed and the residue was washed with pentane and dried in vacuo. $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP 39.5 (d, $^2J_{\text{PP}} = 18$ Hz, $^1J_{\text{PtP}} = 3581$ Hz), 39.7 (s, $^1J_{\text{PtP}} = 3654$ Hz), 41.2 (s, $^1J_{\text{PtP}} = 4256$ Hz), 41.4 (d, $^2J_{\text{PP}} = 18$ Hz, $^1J_{\text{PtP}} = 1688$ Hz).

4.14. Synthesis of $[\text{PtClPh}(\mu\text{-DPPEPM})\text{PdCl}_2]$ (14)

This complex was prepared analogously from $[\text{PtClPh}(\text{cod})]$, DPPEPM and $[\text{PdCl}_2(\text{cod})]$, and isolated as a pale yellow solid. $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6): δP 36.4 (s, $^1J_{\text{PtP}} = 4258$ Hz), 37.3 (d, $^2J_{\text{PP}} = 24$ Hz, $^1J_{\text{PtP}} = 1605$ Hz), 62.4 (dd, $^2J_{\text{PP}} = 24$, 10 Hz), 64.3 (d, $^2J_{\text{PP}} = 10$ Hz). HRMS: calc. for $^{12}\text{C}_{47}\text{H}_{45}\text{P}_4^{106}\text{Pd}^{195}\text{Pt}^{35}\text{Cl}_2^+$ ($\text{M} - \text{Cl}$) $^+$, 1104.0531; observed, 1104.0524. Crystals of $[\text{PtPhCl}(\mu\text{-DPPEPM})\text{PdCl}_2]$ suitable

for an X-ray diffraction study were grown by slow evaporation of an acetone- d_6 solution.

4.15. Synthesis of [$\{PtMe_2(\mu-DPPEPM)\}_2Pt\}][PtCl_4]$ (15)

An acetone solution (3.0 mL) of $[PtCl_2(cod)]$ (0.017 g, 0.045 mmol) was added dropwise to a suspension of DPPEPM (0.030 g, 0.045 mmol) in acetone (0.8 mL). $[PtMe_2(cod)]$ (0.015 g, 0.045 mmol) was added and the mixture was allowed to stir for another 10 min, and the solvent was removed. The residue was washed several times with pentane and the product was isolated from acetone/pentane as a colorless powder (0.035 g, 68%). $^{31}P\{^1H\}$ NMR (acetone- d_6): δ P 30.3 (apparent t, $^2J_{PP} = 16$ Hz, $^1J_{PtP} = 2375$ Hz), 40.2 (d, $^2J_{PP} = 9$ Hz, $^1J_{PtP} = 1790$ Hz), 43.1 (apparent t, $^2J_{PP} = 16$ Hz, $^1J_{PtP} = 2693$ Hz), 49.7 (d, $^2J_{PP} = 9$ Hz, $^1J_{PtP} = 1791$ Hz). 1H NMR (acetone- d_6): δ H 0.17 (dd, $^3J_{PH} = 7$ Hz, $^2J_{PtH} = 70$ Hz, CH₃), 0.35 (dd, $^3J_{PH} = 7$ Hz, $^2J_{PtH} = 71$ Hz, CH₃), 1.1–2.7 (several m, PCH₂CH₂P), 3.10–3.14, 5.22–5.27 (m, PCH₂P), 6.7–7.7 (m, C₆H₅). HRMS: calc. for $^{12}C_{86}H_{93}P_8^{195}Pt_3^+$ (MH⁺), 1958.4122; observed, 1958.3901. A cluster of peaks around m/z 1992 due to (M + Cl)⁺ was also observed.

4.16. Synthesis of [$\{PtMe_2(\mu-DPPEPM)\}_2Pd\}][PdCl_4]$ (16)

This complex was prepared analogously from $[PdCl_2(cod)]$ and DPPEPM, followed by $[PtMe_2(cod)]$, and obtained as a yellow solid in 70% yield. $^{31}P\{^1H\}$ NMR (acetone- d_6): δ P 41.1 (apparent t, $^2J_{PP} = 8$ Hz, $^1J_{PtP} = 1756$ Hz), 43.5 (unresolved m), 49.4 (d, $^2J_{PP} = 8$ Hz, $^1J_{PtP} = 1789$ Hz), 56.0 (apparent t, $^2J_{PP} = 15$ Hz). 1H

NMR (acetone- d_6): δ H 0.23 (dd, $^3J_{PH} = 7$ Hz, $^2J_{PtH} = 70$ Hz, CH₃), 0.36 (dd, $^3J_{PH} = 8$ Hz, $^2J_{PtH} = 71$ Hz, CH₃), 1.3–2.8 (several m, PCH₂CH₂P), 3.34–3.39, 5.02–5.07 (m, PCH₂P), 6.6–7.7 (m, C₆H₅). $^1H\{^{31}P\}$ NMR (acetone- d_6): δ H 0.23 (s, $^2J_{PtH} = 70$ Hz, CH₃), 0.36 (s, $^2J_{PtH} = 71$ Hz, CH₃), 1.3–2.8 (several m, PCH₂CH₂P), 3.34 (d, $^2J_{HH} = 15$ Hz, 1H, PCH₂P), 5.02 (d, $^2J_{HH} = 15$ Hz, 1H, PCH₂P), 6.6–7.7 (m, C₆H₅). HRMS: calc. for $^{12}C_{86}H_{93}P_8^{106}Pd^{195}Pt_2^+$ (MH⁺), 1869.3509; observed, 1869.3434. A cluster of peaks around m/z 1904 due to (M + Cl)⁺ was also observed.

4.17. Synthesis of [$\{PtPh_2(\mu-DPPEPM)\}_2Pd\}][PdCl_4]$ (17)

This complex was prepared analogously from $[PdCl_2(cod)]$ and DPPEPM, followed by $[PtPh_2(cod)]$, and obtained as a yellow solid in 65% yield. $^{31}P\{^1H\}$ NMR (acetone- d_6): δ P 33.9 (d, $^2J_{PP} = 7$ Hz, $^1J_{PtP} = 1654$ Hz), 43.3 (t, $^2J_{PP} = 15$ Hz), 44.1 (d, $^2J_{PP} = 7$ Hz, $^1J_{PtP} = 1703$ Hz), 54.8 (t, $^2J_{PP} = 15$ Hz). 1H NMR (acetone- d_6): δ H 1.3–2.4 (several m, PCH₂CH₂P), 3.62–3.73, 4.95–5.01 (m, PCH₂P), 6.3–8.6 (m, C₆H₅). HRMS: calc. for $^{12}C_{106}H_{100}P_8^{106}Pd^{195}Pt_2^{35}Cl^+$ (M + Cl)⁺, 2151.3745; observed, 2151.3738.

4.18. X-ray crystallography

Crystals of appropriate dimensions were mounted on glass fibers in random orientations. Preliminary examination and data collection were performed using a Bruker SMART Charge Coupled Device (CCD) Detector system single crystal X-ray diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) equipped with a sealed tube X-ray source. Preliminary unit cell constants were

Table 5
Crystallographic data for **1a**, **5**, **11** and **14**

	1a	5	11	14
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group, Z	$P2_1/c$, 4	$P2_1/n$, 4	$P\bar{1}$, 2	$P\bar{1}$, 2
a (Å)	13.188(3)	14.278(3)	12.3272(3)	13.1936(4)
b (Å)	15.424(2)	21.400(4)	13.7559(4)	14.0729(5)
c (Å)	19.507(4)	29.452(6)	13.9446(4)	15.9353(5)
α (°)	90	90	104.613(2)	114.430(2)
β (°)	96.447(18)	98.372(13)	101.693(2)	109.842(2)
γ (°)	90	90	99.907(2)	91.432(3)
Cell volume (Å ³)	3942.7(13)	8 903(3)	2177.60(10)	2486.22(14)
D_{calc} (Mg/m ³)	1.539	1.578	1.648	1.602
Temperature (K)	160(2)	120(2)	218(2)	140(2)
Absorption coefficient (mm ⁻¹)	3.757	3.463	3.922	3.497
θ Range (°)	1.69–27.00	1.69–26.00	1.74–29.00	2.15–28.00
No. of reflections collected	74333	117885	47545	55566
No. of independent reflections	8602	17491	11218	11864
Abs. corr.	Semi-empirical from equivalents	Empirical	Semi-empirical from equivalents	Semi-empirical from equivalents
No. of parameters refined	451	1012	489	581
$R(F)$, $R_w(F^2)$ ($F^2 > 2.0\sigma(F^2)$)	0.0749, 0.1013	0.0569, 0.0992	0.0345, 0.0829	0.0489, 0.1104
$R(F)$, $R_w(F^2)$ (all data)	0.1087, 0.1092	0.1405, 0.1222	0.0514, 0.0893	0.0957, 0.1264
Goodness of fit on F^2	1.167	0.990	1.038	1.043
Largest difference peak and hole (e Å ⁻³)	1.322, -2.898	1.118, -1.008	1.154, -1.011	1.904, -1.811

determined with a set of 45 narrow frames (0.3° in ϖ) scans. Typical data sets consisted of 3636 frames of intensity data collected with a frame width of 0.3° in ϖ and counting time of 15–30 s/frame at a crystal to detector distance of 4.950 cm. The double pass method of scanning was used to exclude any noise. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. SMART and SAINT software packages (Bruker Analytical X-ray, Madison, WI, 2003) were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of xyz centroids of thresholded reflections from the complete data set. Collected data were corrected for systematic errors using SADABS (Sheldrick, G. M., Bruker Analytical X-ray, Madison, WI, 2003) based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table 5. Structure solution and refinement were carried out using the SHELXTL-PLUS software package (Sheldrick, G. M., Bruker Analytical X-ray Division, Madison, WI, 2002). The structures were solved by direct methods and refined successfully in the space groups, $P\bar{1}$, $P2_1/n$, $P\bar{1}$ and $P2_1/c$, respectively. Full matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The final residual values and structure refinement parameters are listed in Table 5.

Both the triclinic structures (**11** and **14**) show disorder and they contain solvent molecules in the lattice. The disorder could be resolved in both cases. In the case of **11**, the Pt and Pd atoms, and the ligands attached to them (Me and Cl), are disordered over both sites. This disorder was modeled using partial occupancies. The acetone solvate is disordered due to the presence of an inversion center. Again the disorder was resolved by using partial occupancy for the disordered atoms. One of the phenyl groups attached to the P atom is disordered in case of **14**. The two disordered C-atoms of the phenyl group were modeled over two sites with partial occupancies. The solvent acetone exhibits the same type of disorder as in the previous structure.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC Nos. 283864–283867 for **1a**, **11**, **14**, and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax (int code) +44 (1223) 336 033, or deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.09.021.

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