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Coordination Studies of a New Nonsymmetric Ditertiary Phosphane Bearing a Single Phosphaadamantane Cage

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The new nonsymmetric ditertiary phosphane, $Ph_2P(CH_2)_2$-PAd (**1**), was prepared in one-step from $Ph_2PCH{=}CH_2$ and H-PAd (H-PAd = 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane) by a hydrophosphination reaction using 2,2′-azo-bisisobutyronitrile (AIBN) as free radical initiator. The sterically encumbered phosphaadamantane cage in **1** was found to influence the coordination capabilities of this ligand. The reaction of **1** with $[PdCl_2(cod)]$ or $[Pt(CH_3)_2(cod)]$ (cod = cycloocta-1,5-diene) gave the corresponding κ^2-*P,P′*-chelate complexes *cis*-$[PdCl_2(\mathbf{1})]$ (**2**) and *cis*-$[Pt(CH_3)_2(\mathbf{1})]$ (**3**), respectively. The dinuclear gold(I) complex $[Ph_2P(AuCl)(CH_2)_2PAd(AuCl)]$ (**4**) was prepared from **1** and 2 equiv. of [AuCl(tht)] (tht = tetrahydrothiophene). In contrast, the cleavage of the chloro-bridged dimers $\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2$ or $\{MCl_2(\eta^5\text{-Cp}^\star)\}_2$ (M = Rh, Ir) with **1** gave the κ^1-*P*-monodentate complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})(\mathbf{1})]$ (**5**), $[RhCl_2(\eta^5\text{-Cp}^\star)(\mathbf{1})]$ (**6**) and $[IrCl_2(\eta^5\text{-Cp}^\star)(\mathbf{1})]$ (**7**), respectively, in which the -PAd group is non-coordinating. Chloride abstraction from **6** (or **7**) can be accomplished upon addition of $Na[SbF_6]$ to generate the cationic κ^2-*P,P′*-chelate complexes **8b** (and **9b**). Alternatively **8a** (or **9a**) could be observed, as their chloride salts, by $^{31}P\{^1H\}$ NMR spectroscopy upon addition of several drops of CH_3OH to $CDCl_3$ solutions of **6** (or **7**). The reaction of **5**–**7** with [AuCl(tht)] gave the dinuclear complexes $[\kappa^2$-*P,P′*-μ-$RuCl_2(\eta^6\text{-}p\text{-cymene})\{Ph_2P(CH_2)_2PAd(AuCl)\}]$ (**10**), $[\kappa^2$-*P,P′*-μ-$RhCl_2(\eta^5\text{-Cp}^\star)\{Ph_2P(CH_2)_2PAd(AuCl)\}]$ (**11**) and $[\kappa^2$-*P,P′*-μ-$IrCl_2(\eta^5\text{-Cp}^\star)\{Ph_2P(CH_2)_2PAd(AuCl)\}]$ (**12**). Reaction of two equiv. of **5** with the labile precursors $[PdCl_2(CH_3CN)_2]$ or $[PtCl_2(PhCN)_2]$ gave instead the novel trinuclear Ru_2Pd and Ru_2Pt complexes *trans*-$[\{\kappa^2$-*P,P′*-μ-$RuCl_2(\eta^6\text{-}p\text{-cymene})\{Ph_2P(CH_2)_2PAd\}\}_2PdCl_2]$ (**13**) and *trans*-$[\{\kappa^2$-*P,P′*-μ-$RuCl_2(\eta^6\text{-}p\text{-cymene})\{Ph_2P(CH_2)_2PAd\}\}_2PtCl_2]$ (**14**), respectively. All new compounds have been fully characterised by spectroscopic and analytical methods. Furthermore the structures of $\mathbf{3}\cdot CHCl_3$, **4**, **5**, $\mathbf{7}\cdot CHCl_3$, $\mathbf{10}\cdot CH_2Cl_2\cdot 0.5C_2H_{10}O$ and $\mathbf{13}\cdot 2CH_2Cl_2$ have been elucidated by single-crystal X-ray crystallography. The X-ray structures of $\mathbf{10}\cdot CH_2Cl_2\cdot 0.5C_4H_{10}O$ and $\mathbf{13}\cdot 2CH_2Cl_2$ demonstrate how nonsymmetric ditertiary phosphane complexes bearing one pendant phosphaadamantane moiety can be used as metalloligands in the controlled syntheses of novel bi- and trimetallic complexes.

Introduction

As part of continuing studies[1–6] in our group we are interested in developing new tertiary and symmetric ditertiary phosphane ligands using simple condensation reactions. We, and others, have found that ditertiary phosphanes such as those of general formula $(R_2PCH_2)_2N(R)$ have interesting coordination properties[7,8] including their use in self-assembly reactions through covalent bonds or H-bonding contacts.[2–5,9] The tetraphenyl-substituted phosphane $(Ph_2PCH_2)_2N(R)$, closely related to the three-carbon spacer $(Ph_2PCH_2)_2CH_2$ [1,3-bis(diphenylphosphanyl)propane, dppp], has been widely utilised in several metal-catalysed reactions.[10–12]

Phosphaadamantane ligands containing one or more trioxa- or carbon-only-based cages have been shown to form complexes with Ru, Pd and Au metal centres[13,14] and in several cases, been investigated in a range of catalytic metal-mediated transformations.[15–23] We recently reported the synthesis and coordination studies of a new nonsymmetric ditertiary phosphane containing a P–C–N(*R*)–C–P skeletal backbone in which one of the P-based moieties was a phosphaadamantane cage.[24] The presence of a bulky adamantane cage imposed on this ligand the ability to adopt a range of ligating modes including κ^1-*P*-monodentate coordination upon complexation to $[RuCl_2(\eta^6\text{-}p\text{-cymene})]$ or $[IrCl_2(\eta^5\text{-Cp}^*)]$ metal fragments.[24] In an effort to promote other coordinating capabilities employing the unique steric properties of the phosphaadamantane group we report here a simple one-step hydrophosphination procedure by which a new saturated two-carbon spacer ditertiary phosphane bearing non-equivalent groups ($-PPh_2$ and -PAd) can be prepared. Pringle and co-workers[25] recently reported the synthesis of nonsymmetric diphosphanes based on a rigid ethene backbone and furthermore, upon coordination, the disposition of the phosphorus groups gave exclusive κ^2-che-

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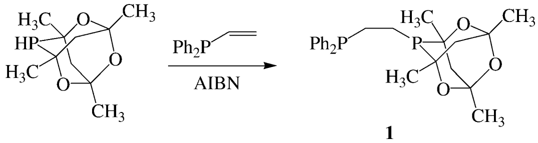
lation to square-planar metal centres. We demonstrate that our new, more flexible, ligand akin to the ubiquitous dppe [1,2-bis(diphenylphosphanyl)ethane] exhibits diverse coordination behaviour towards a range of late transition-metals and can function in a κ^1-*P*-monodentate manner in which the –PAd fragment remains non-coordinating. This has allowed us to use these intermediates as metalloligands for the construction of heterobimetallic and, for the first time, heterotrimetallic compounds as exemplified by our syntheses of complexes containing Ru/Au, Ir/Au, Ru_2Pd and Ru_2Pt metal centre combinations. The single-crystal X-ray structures of six compounds are reported here and discussed.

Results and Discussion

Ligand Synthesis

Free radical, base or transition metal catalysed hydrophosphination reactions have previously been used to prepare tertiary phosphane ligands.[26] The new ligand $Ph_2P(CH_2)_2PAd$ (**1**) was prepared in a single-step, by a AIBN free radical initiated hydrophosphination reaction of H-PAd (H-PAd = 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane) with $Ph_2PCH=CH_2$ and could be obtained in high yield (ca. 80%) as a transparent colourless oil [Equation (1)]. Ligand **1** was of sufficient purity to be used directly in further complexation studies. Because the nonsymmetric diphosphane contains two dissimilar phosphorus centres we observed, in the $^{31}P\{^1H\}$ NMR spectrum of **1**, two doublets at δ(P) –25.1 ppm and δ(P) –12.6 ppm ($^3J_{PP}$ 35.6 Hz) assigned to the –PAd and $–PPh_2$ groups, respectively. The ^1H NMR spectrum of **1** was in accord with the chemical structure proposed and showed no indication of a methine CH resonance that would be expected if the branched regioisomer $Ph_2P(AdP)C(H)CH_3$ had been formed instead via a Markovnikov addition. Exposing **1**, either as an oil or in solution, to air at ambient temperature gave very little oxidation products demonstrating the air stable nature of this new diphosphane. Other characterising data for **1** are given in the Exp. Sect.



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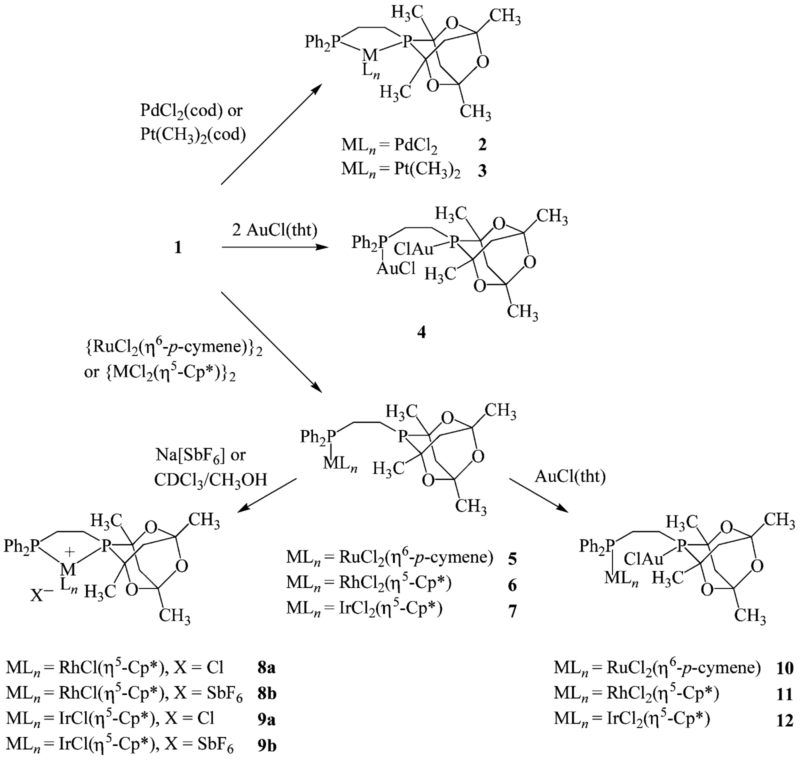
Coordination Studies

Transition-metal complexes of trioxa- or carbon-only-based phosphaadamantanes have been relatively poorly documented in the literature yet have started to show promise in various aspects relating to homogeneous catalysis.[13–23] The goal of these studies was to probe the ligating modes of this new ligand for the preparation of homobimetallic and hetereometallic complexes. Diphosphanes with



Scheme 1.

Table 1. Selected spectroscopic data for compounds **1**–**14**.[a]

	δ(P) /-PPh$_2$	δ(P) /-PAd	^3J(PP)	J(PtPPh$_2$)	J(PtPAd)	J(RhPPh$_2$)	J(RhPAd)	^2J(PP)	ν_{PdCl}	ν_{AuCl}
1	–12.6	–25.1	35.6							
2	65.8	60.9						8.1	285	
3	49.5	38.2		1749	1688			8.9		
4	29.9[b]	31.1[b]	47							329
5	25.4	–26.5	35.6							
6	30.4	–25.7	38			143				
7	–1.7	–24.8	40.5							
8	63.0[c]	55.9				128	134	15.4		
	61.4	47.7				131	134	25.2		
9	31.7[c]	28.5						13		
	30.7	19.2						3		
10	30.7	22.3	46							322
11	28.5	31.0	48.1			147				330
12	–2.0	31.6	48.6							324
13	24.3[d]	10.0							296	
	23.9	9.6								
14	24.0[d]	2.5			2590				296[e]	
	23.6	3.1			2585					

[a] Chemical shifts in ppm, coupling constants in Hz. [b] The assignments are tentative due to the close appearance of both phosphorus resonances. [c] Recorded as the SbF_6^- salt. The two sets of ^{31}P resonances correspond to two diastereomers present in solution. For **8**, ca. 73:27 ratio respectively. For **9**, ca. 74:26 ratio respectively. [d] For **13**, ca. 50:50 ratio; **14**, ca. 57:43 ratio respectively. [e] ν_{PtCl} vibration.

a two-carbon backbone are known to chelate metal centres[25] and are observed here for the synthesis of the dichloropalladium(II) and dimethylplatinum(II) complexes *cis*-[PdCl$_2${κ^2-*P,P′*-Ph$_2$P(CH$_2$)$_2$PAd}] (**2**) and *cis*-[Pt(CH$_3$)$_2$-{κ^2-*P,P′*-Ph$_2$P(CH$_2$)$_2$PAd}] (**3**), respectively. Both compounds were prepared by displacement of cod from either [PdCl$_2$(cod)] or [Pt(CH$_3$)$_2$(cod)] as shown in Scheme 1. The ^{31}P{^{1}H} NMR spectra of **2** and **3** showed two doublet resonances shifted considerably downfield as a consequence of five-membered chelate ring formation (Table 1). In **3** the ^{31}P resonance at δ(P) 49.5 ppm can be assigned the –PPh$_2$ group by close analogy with the ^{31}P chemical shift found for [Pt(CH$_3$)$_2$(dppe)].[27] Furthermore, in the case of **3**, the observed ^1J(PtP) coupling constants of 1688 Hz and 1749 Hz indicate similar stereoelectronic properties between both –PAd and –PPh$_2$ groups. These coupling constants are in good agreement with those of other platinum(II) complexes containing chelating diphosphanes *trans* to methyl ligands.[27,28] The ^{1}H NMR spectrum of **3** showed Pt-CH$_3$ signals as two distinct phosphorus coupled multiplets with ^{195}Pt satellites ($^2J_{PtH}$ ca. 71 Hz for both Pt-CH$_3$ groups). In an attempt to explore the stability of the five-membered chelate ring formed in **3** we repeated the reaction of [Pt(CH$_3$)$_2$(cod)] with two equiv. of **1** instead and monitored the reaction by ^{31}P{^{1}H} NMR spectroscopy. However, the only species observed were **3** and unreacted **1** with no ^{31}P{^{1}H} NMR evidence for κ^1-monodentate species of the type *cis*-[Pt(CH$_3$)$_2${κ^1-*P*-Ph$_2$P(CH$_2$)$_2$PAd}$_2$]. Further characterising details for **2** and **3** are given in Table 1 and the Exp. Sect.

The X-ray structure of **3**·CHCl$_3$ has been determined (Figure 1 and Table 2). Suitable crystals of **3**·CHCl$_3$ were obtained by slow diffusion of petroleum ether (b.p. 60–80 °C) into a CHCl$_3$ solution. The X-ray structure confirms that **1** adopts a κ^2-*P,P′*-chelating coordination mode and the environment about the platinum(II) metal centre is approximately square planar. Clear differences are seen in the P–Pt–C bond angles as a consequence of the different steric sizes between the –PAd [P(1)–Pt(1)–C(1) 97.25(18)°] and

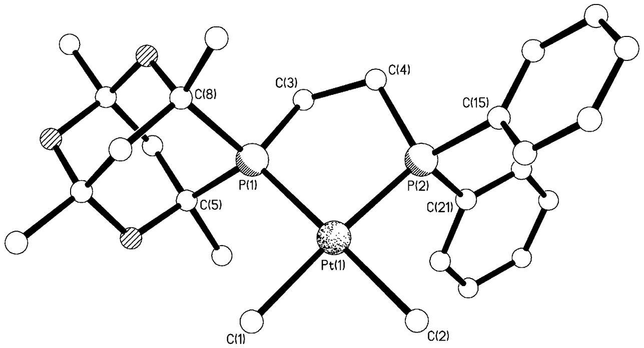


Figure 1. Molecular structure of **3**. All hydrogen atoms and chloroform solvent molecule have been removed for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for compound **3**.

Pt(1)–P(1)	2.2765(17)
Pt(1)–P(2)	2.2706(19)
Pt(1)–C(1)	2.136(6)
Pt(1)–C(2)	2.109(7)
P(1)–C(3)	1.845(7)
C(3)–C(4)	1.518(10)
C(4)–P(2)	1.845(7)
P(1)–Pt(1)–P(2)	85.73(7)
P(1)–Pt(1)–C(1)	97.25(18)
P(1)–Pt(1)–C(2)	172.4(3)
P(2)–Pt(1)–C(1)	176.42(18)
P(2)–Pt(1)–C(2)	92.9(2)
C(1)–Pt(1)–C(2)	83.9(3)
Pt(1)–P(1)–C(3)	108.7(2)
P(1)–C(3)–C(4)	110.9(5)
C(3)–C(4)–P(2)	110.7(5)
C(4)–P(2)–Pt(1)	109.1(2)
C(5)–P(1)–C(8)	93.6(3)

–PPh$_2$ groups [P(2)–Pt(1)–C(2) 92.9(2)°]. The Pt–P and Pt–C bond lengths and angles are comparable with those of [Pt(CH$_3$)$_2$(Ph$_2$PCH=CHPPh$_2$)] and [Pt(CH$_3$)$_2$(Et$_2$dppp)].[28] Hence in the case of [Pt(CH$_3$)$_2$(Ph$_2$PCH=CHPPh$_2$)] the Pt–P distances are 2.246(2) and 2.254(2) Å whereas the Pt–C bond lengths are 2.108(7) and 2.112(6) Å. The Pt(1)–P(1)–C(3)–C(4)–P(2) backbone in **3** is twisted as expected for a saturated two carbon linker. The C(3) and C(4) deviations of the ethyl backbone from the P(1)–Pt(1)–P(2) plane in **3** are 0.33 Å and 0.29 Å, respectively. The small P···P separation in **3** of 3.093 Å is as expected for a chelating ligand of this general type.

To further explore the versatility of this ligand to accommodate different bonding modes we treated **1** with two equiv. of [AuCl(tht)] and isolated the digold(I) compound **4** in high yield (83%). A downfield δ(P) shift for both inequivalent phosphorus nuclei and the observation of a ν_{AuCl} vibration at 329 cm^{-1} in the FT-IR spectrum support linear, two-coordinate gold(I) metal centres. Suitable crystals of **4** were obtained by slow diffusion of CH$_3$OH into a CH$_2$Cl$_2$ solution followed by slow evaporation. The X-ray structure of **4** (Figure 2, Table 3) showed an essentially linear arrangement about each gold(I) centre [P(1)–Au(1)–Cl(1) 175.55(7)° and P(2)–Au(2)–Cl(2) 176.78(7)°] with typical Au–Cl and Au–P bond lengths.[5] The P(1)–Au(1)···Au(2)–P(2) torsion angle in **4** is –65.98(6)°. A strong intramolecular aurophilic interaction is evident in **4** [Au(1)···Au(2) 2.9811(4) Å] and contrasts that of (AuCl)$_2$(μ-dppe) in which only large intramolecular Au···Au separations (> 6 Å for all polymorphic forms) are present.[29,30] There are no significant intermolecular Au···Au separations observed in **4**, again different from the previously reported X-ray structures for (AuCl)$_2$(μ-dppe) which display short intermolecular Au···Au contacts.[29,30] As would be expected for **1** adopting a bridging mode, the P···P separation in **4** of 3.796 Å is enlarged with respect to that found in **3**.

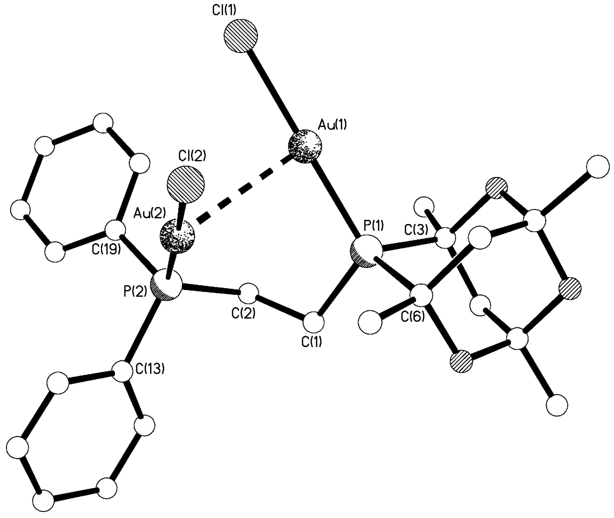


Figure 2. Molecular structure of **4**. All hydrogen atoms have been removed for clarity.

Table 3. Selected bond lengths [Å] and angles [°] for compound **4**.

Au(1)–P(1)	2.2328(16)
Au(1)–Cl(1)	2.2919(16)
Au(2)–P(2)	2.2357(16)
Au(2)–Cl(2)	2.2996(17)
P(1)–C(1)	1.828(6)
C(1)–C(2)	1.550(9)
C(2)–P(2)	1.822(6)
Cl(1)–Au(1)–P(1)	175.55(7)
Cl(2)–Au(1)–P(2)	176.78(7)
Au(1)–P(1)–C(1)	115.2(2)
P(1)–C(1)–C(2)	112.9(5)
C(1)–C(2)–P(2)	115.0(5)
C(2)–P(2)–Au(2)	114.8(2)

We next sought to explore whether some kind of steric control on the outcome of a complexation reaction using ligand **1** could be imposed. This could be achieved through appropriate choice of metal precursors with bulky ancillary ligands present. In this manner it may be anticipated that κ^1-*P*-monodentate coordination could be favoured leaving a pendant phosphorus group available for further complexation. Cleavage reactions of chloro-bridged Ru^{II}, Rh^{III} and Ir^{III} metal dimers are well known.[3,6] Recent work by independent groups have shown that half-sandwich complexes containing Fe^{II} or Ru^{II} centres bearing a single dppm [dppm = 1,1-bis(diphenylphosphanyl)methane] ligand can function in a κ^1-*P*-monodentate fashion.[31,32] Reaction of [RuCl$_2$(η^6-*p*-cymene)]$_2$ or [MCl$_2$(η^5-Cp*)]$_2$ (M = Rh, Ir) with **1** in dichloromethane gave the κ^1-*P*-monodentate complexes **5**–**7** in high yields. The ^{31}P{^{1}H} NMR spectra (Table 1) are especially informative showing downfield shifts for the –PPh$_2$ group whilst the "dangling" –PAd arm is observed at similar phosphorus chemical shifts to that of free ligand **1**. Additionally, for **6** and **7** the ^{31}P resonances for the –PPh$_2$ groups [δ(P) 30.4 ppm for **6**; –1.7 ppm for **7**] are similar to those observed previously for κ^2-*P*,*P*′-μ-{MCl$_2$(η^5-Cp*)}$_2$(dppe) [M = Rh, δ(P) 29.5 ppm; M = Ir, δ(P) –1.0 ppm][33] and [κ^1-*P*-IrCl$_2$(η^5-Cp*)(Ph$_2$PCH$_2$-NHC$_6$H$_4$PPh$_2$)] [δ(P) 0.10 ppm].[34] The rhodium(III) and iridium(III) complexes are solvent dependant and undergo smooth isomerism to cationic κ^2-*P*,*P*′-chelate complexes in solution. Hence addition of several drops of CH$_3$OH to CDCl$_3$ solutions of **6** (or **7**) and monitoring by ^{31}P{^{1}H} NMR spectroscopy showed the disappearance of signals attributed to the κ^1-*P*-monodentate complexes and new downfield shifted signals ($^1J_{RhP}$ couplings in the range 128–134 Hz) assigned to the cationic *P*,*P*′-chelate half-sandwich complexes [RhCl(η^5-Cp*){κ^2-*P*,*P*′-Ph$_2$P(CH$_2$)$_2$PAd}]Cl (**8a**) and [IrCl(η^5-Cp*){κ^2-*P*,*P*′-Ph$_2$P(CH$_2$)$_2$PAd}]Cl (**9a**). In both cases the presence of two well-resolved sets of ^{31}P resonances infer two diastereomers are present [73:27 ratio (for **8a**) and 74:26 ratio (for **9a**)] because the resulting cationic complexes are now chiral-at-metal.[35] The compounds **8b** and **9b** were isolated, albeit in low to moderate yields, as the hexafluoroantimonate salts and have been characterised (see Exp. Sect. for details).

The X-ray structures of the piano-stool complexes **5** and **7**·CHCl$_3$ have been established by X-ray crystallography

(Figure 3 and Figure 4, Table 4). Suitable crystals of **5** were obtained by slow diffusion of hexanes into a $CHCl_3$ solution followed by slow evaporation whilst crystals of **7**·$CHCl_3$ were obtained by allowing a $CHCl_3/Et_2O$/petroleum ether (b.p 60–80 °C) filtrate to stand for several days. Within the coordination sphere of **5** the Ru–P, Ru–Cl and Ru–C_{arene} bond lengths are comparable to those of the half-sandwich ruthenium(II) complex $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{\kappa^1\text{-}P\text{-}Ph_2PCH_2N(Ph)CH_2PAd\}]$ recently described by us.[24] Similarly the Ir–P, Ir–Cl and Ir–$C_{centroid}$ metric parameters are comparable to those of other iridium(III) half-sandwich compounds.[24,36] The P···P separations within **5** and **7**·$CHCl_3$ are 4.514 Å and 4.545 Å respectively and larger than in **4**. Presumably the strong aurophilic interaction seen in **4** may account for this shorter P···P separation.

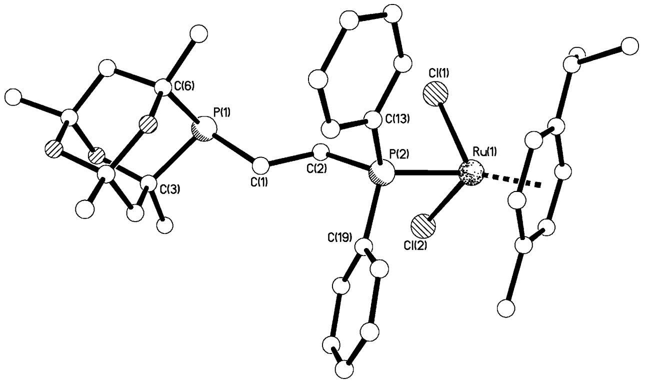


Figure 3. Molecular structure of **5**. Hydrogen atoms are not shown for clarity.

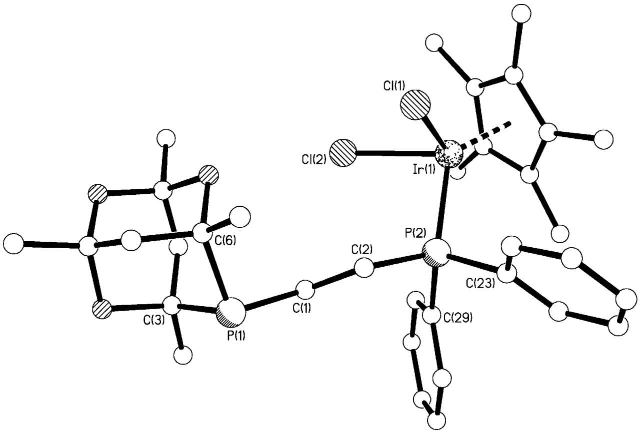
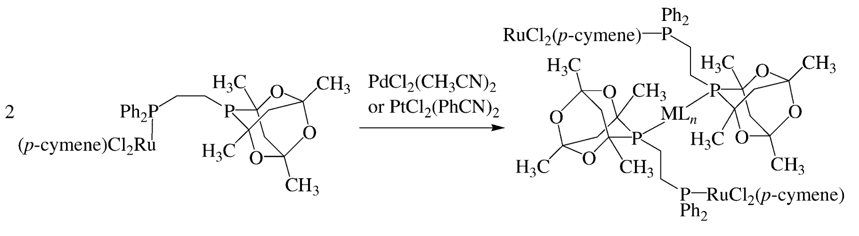


Figure 4. Molecular structure of **7**. Hydrogen atoms and solvent molecules are not shown for clarity.

Reaction of **5**–**7** with one equiv. of [AuCl(tht)] in CH_2Cl_2 gave the Ru/Au, Rh/Au and Ir/Au bimetallic complexes **10**–**12** in good yields. For all three compounds significant downfield shifts for the –PAd group were observed upon gold(I) complexation [δ(P) 22.3–31.6 ppm] and furthermore, in the FT-IR spectra of **10**–**12**, ν_{AuCl} vibrations in the range 322–330 cm^{-1} were observed. Crystals of **10**·CH_2Cl_2·$0.5C_4H_{10}O$ suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with diethyl ether and petroleum ether (b.p. 60–80 °C) with selected bond lengths and angles given in Table 4. The Ru^{II} centre (Figure 5) remains coordinated to the –PPh_2 group of **1** and the other coordination sites are occupied by two chlorides and

Table 4. Selected bond lengths [Å] and angles [°] for compounds **5**, **7**·$CHCl_3$, **10**·CH_2Cl_2·$0.5C_4H_{10}O$ and **13**·$2CH_2Cl_2$.

	5 M = Ru	**7**·$CHCl_3$ M = Ir	**10**·CH_2Cl_2·$0.5C_4H_{10}O$ M = Ru	**13**·$2CH_2Cl_2$ M = Ru
M(1)–P(2)	2.3347(6)	2.303(2)	2.3545(17)	2.3570(14)
M(1)–Cl(1)	2.4110(6)	2.407(3)	2.4068(18)	2.4162(16)
M(1)–Cl(2)	2.4085(6)	2.412(2)	2.4059(19)	2.4147(16)
M(1)–$C_{centroid}$	1.7014(10)	1.817(4)	1.707(3)	1.709(2)
P(1)–C(1)	1.856(3)	1.853(8)	1.814(7)	1.833(5)
C(1)–C(2)	1.523(4)	1.525(11)	1.515(10)	1.524(7)
C(2)–P(2)	1.839(3)	1.847(8)	1.829(7)	1.852(5)
Au(1)–P(1)			2.2316(19)	
Au(1)–Cl(3)			2.280(2)	
Pd(1)–P(1)				2.3406(15)
Pd(1)–Cl(3)				2.282(2)
Pd(1)–Cl(4)				2.304(2)
Cl(1)–M(1)–Cl(2)	85.54(2)	87.46(9)	86.15(6)	89.61(6)
Cl(1)–M(1)–P(2)	86.42(2)	87.55(8)	87.86(6)	88.92(5)
Cl(2)–M(1)–P(2)	85.48(2)	91.13(8)	86.84(6)	82.46(5)
M(1)–P(2)–C(2)	116.18(8)	117.8(3)	118.1(2)	119.85(19)
P(2)–C(2)–C(1)	114.70(19)	114.9(6)	114.0(5)	116.7(4)
C(2)–C(1)–P(1)	113.6(2)	113.8(6)	115.6(5)	111.1(4)
C(3)–P(1)–C(6)	92.23(14)	93.0(5)	95.2(3)	94.2(3)
Cl(3)–Au(1)–P(1)			177.11(10)	
C(1)–P(1)–Au(1)			112.9(2)	
Cl(3)–Pd(1)–Cl(4)				180.0
Cl(3)–Pd(1)–P(1)				93.91(4)
Cl(4)–Pd(1)–P(1)				86.09(4)
P(1)–Pd(1)–P(1′)				172.18(7)
C(1)–P(1)–Pd(1)				112.3(2)



5

ML_n = *trans*-$PdCl_2$ **13**
ML_n = *trans*-$PtCl_2$ **14**

(2)

an η^6-*p*-cymene arene ligand. The Ru–P, Ru–Cl, Au–Cl and Au–P lengths are all similar and as anticipated. The Au^I metal centre is essentially linear in geometry [Cl(1)–Au(1)–P(1) 177.11(10)°]. The P···P separation in **10** is 4.487 Å whilst the Ru···Au separation is 7.162 Å. Both are smaller than those previously documented[24] and is a consequence of the longer P–C–N–C–P backbone between the two different phosphorus centres than observed here with **1** (P–C–C–P). The intermolecular Au···Au separation [5.594 Å] infers no significant aurophilic interactions between neighbouring P–Au–Cl units.

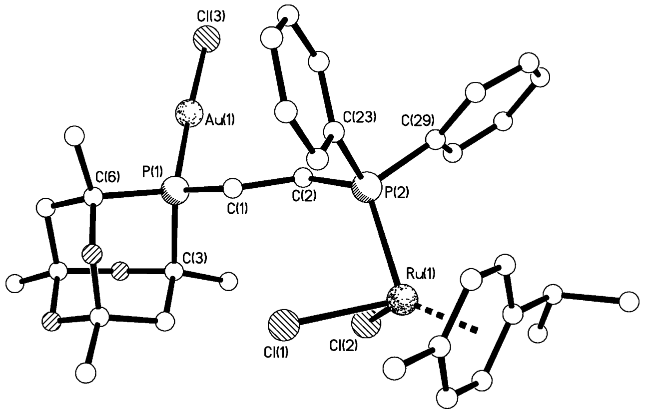


Figure 5. Molecular structure of **10**. Hydrogen atoms and solvent molecules are not shown for clarity.

Reaction of two equiv. of **5** with either [$PdCl_2(CH_3CN)_2$] or [$PtCl_2(PhCN)_2$] in CH_2Cl_2 gave the trinuclear complexes *trans*-[{κ^2-*P,P′*-μ-$RuCl_2(\eta^6$-*p*-cymene)}{$Ph_2P(CH_2)_2PAd$}}$_2$-$PdCl_2$] (**13**) and *trans*-[{κ^2-*P,P′*-μ-$RuCl_2(\eta^6$-*p*-cymene)-{$Ph_2P(CH_2)_2PAd$}}$_2PtCl_2$] (**14**), as orange solids, in 83% and 74% yield respectively [Equation (2)]. The $^{31}P\{^1H\}$ NMR spectra (Table 1, Figure 6 for **13**) were informative and confirmed, in both cases, coordination of the –PAd group by the new downfield phosphorus signals with respect to **5**. Furthermore, the $^{31}P\{^1H\}$ NMR spectra of **13** and **14** showed pairs of closely spaced "triplets" for the –PAd and –PPh_2 groups consistent with the presence of two diastereomers (in approx. equal ratios). Compound **14** showed additional ^{195}Pt coupling to –PAd ($^1J_{PtP}$ ca. 2500 Hz) in accord with a *trans* disposition of phosphane ligands about the platinum(II) centre.[17b]

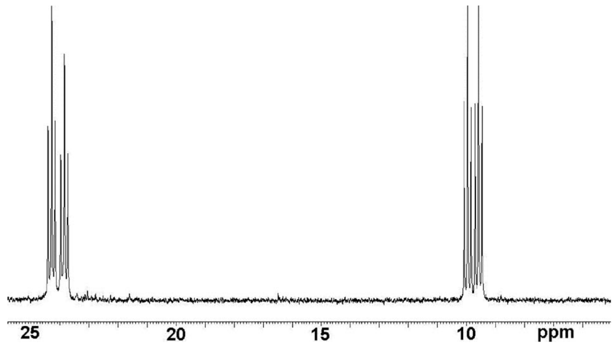


Figure 6. $^{31}P\{^1H\}$ NMR spectrum of **13** recorded in $CDCl_3$ at 298 K.

In the case of **13** suitable crystals were obtained for X-ray crystallography and the structure is shown in Figure 7 (Table 4 for selected metric parameters). Crystals of **13**·$2CH_2Cl_2$ suitable for X-ray diffraction were grown by

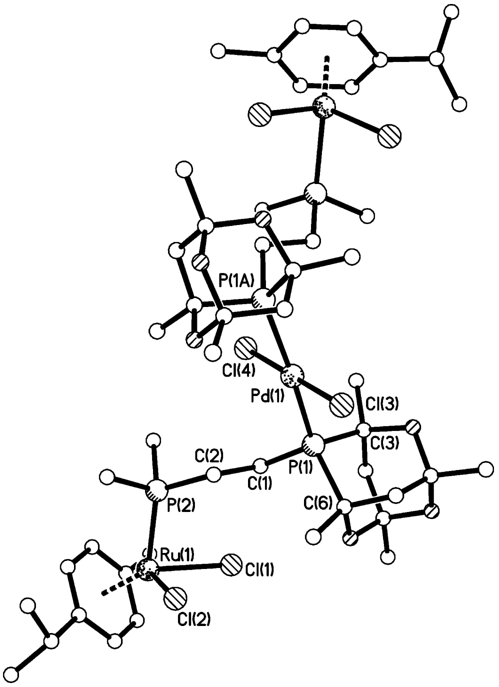


Figure 7. Molecular structure of **13**. Hydrogen atoms and solvent molecules are not shown for clarity. Only the *ipso* carbon atoms of the phenyl rings bound to P(2) are shown.

diffusion of diethyl ether into a CH_2Cl_2 solution. The coordination sphere of the palladium(II) metal centre comprises two *trans* disposed metalloligands **5** and two chlorides.[17b] The geometry of the two *trans* phosphane ligands is slightly distorted from 180° [P(2A)–Pd(1)–P(2) 172.18(7)°]. The Ru^{II} centre is pseudotetrahedral in geometry with typical Ru–Cl and Ru–P bond lengths.[37] The P···P separation in **13**·$2CH_2Cl_2$ is 4.516 Å and similar to that found in **10**·CH_2Cl_2·$0.5C_4H_{10}O$. Balakrishna and co-workers recently reported the synthesis of heterotrinuclear Pd/Au_2, Pt/Au_2 and Cu/Au_2 complexes using a cyclodiphosphazane ligand.[38]

Conclusions

A simple procedure to a new nonsymmetric diphosphane, akin to dppe, has been developed and its coordination chemistry investigated. Whilst κ^2-*P,P′*-chelation is observed upon complexation to square planar metal centres such as Pd^{II} and Pt^{II} we have found that **1** can efficiently function as a κ^1-*P*-monodentate tertiary phosphane. Facile coordination to one or two additional metal precursors afford new examples of late transition metal hetero-bimetallic and trimetallic compounds bridged by phosphane **1**. Our work has shown that, not only can the phosphadamantane cage impart good solubility and crystallisation properties on its resulting compounds but furthermore, the steric size of the cage can be utilised in controlling the ligating modes of this ligand. Our work should be contrasted, for example, with that of Keim and co-workers[33] who showed that Ru^{II}, Rh^{III} and Ir^{III} complexes of dppe readily bridge two metal fragments affording symmetric dinuclear compounds. The use of bidentate and polyphosphane ligands in the construction of heterometallic species remains an interesting area of coordination chemistry.[39,40] Further studies are ongoing and will be reported later.

Experimental Section

Materials: Standard Schlenk techniques were used for the synthesis of **1** whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. The metal complexes [AuCl(tht)] (tht = tetrahydrothiophene),[41] [$RuCl_2$(η^6-*p*-cymene)]$_2$,[42] [MCl_2(η^5-Cp*)]$_2$ (M = Rh, Ir; Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl)[43] and [Pt(CH_3)$_2$(cod)][44] were prepared according to known procedures. All other chemicals were obtained from commercial suppliers and used directly without further purification.

Instrumentation: Infrared spectra were recorded as KBr pellets in the range 4000–200 cm^{-1} with a Perkin–Elmer System 2000 Fourier-transform spectrometer, ^1H NMR spectra (400 MHz) with a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of $SiMe_4$ and coupling constants (J) in Hz, $^{31}P\{^1H\}$ NMR spectra (162 MHz) were recorded with a Bruker DPX-400 FT spectrometer with chemical shifts (δ) in ppm to high frequency of 85% H_3PO_4. All NMR spectra were measured in $CDCl_3$. Elemental analyses (Perkin–Elmer 2400 CHN or Exeter Analytical, Inc. CE-440 Elemental Analyzers) were performed by the Loughborough University Analytical Service within the Department of Chemistry.

Preparation of $Ph_2P(CH_2)_2PAd$ (1): Vinyldiphenylphosphane (0.515 g, 2.42 mmol) was heated to 110 °C and 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane (0.521 g, 2.42 mmol) added in several portions with stirring. 2,2′-azobis(isobutyronitrile) (0.02 g) was added and the reaction mixture stirred for 6 h. The temperature was reduced to 80 °C and the system placed under vacuum to remove any volatile components giving the product as a colourless oil which was used directly in all coordination studies. Yield 0.769 g, 74%. Selected spectroscopic data: ^1H NMR ($CDCl_3$): δ = 7.45–7.30 (m, arom. H), 2.21 (m, CH_2), 1.95–1.21 (m, CH_2, Ad cage) ppm. ES-MS: *m*/*z* = 428 [M^+]. $C_{24}H_{30}O_3P_2$ (428.47): calcd. C 67.28, H 7.06; found C 66.74, H 7.12.

Preparation of *cis*-[$PdCl_2\{Ph_2P(CH_2)_2PAd\}$] (2): Compound **1** (0.060 g, 0.14 mmol) was dissolved in CH_2Cl_2 (10 mL) and added dropwise to a solution of [$PdCl_2(PhCN)_2$] (0.055 g, 0.14 mmol) dissolved separately in CH_2Cl_2 (10 mL). After stirring for 3 h, the volume of the solution was reduced to ca. 2–3 mL and Et_2O (60 mL) added. The resulting yellow precipitate was filtered and dried in vacuo. Yield 0.112 g, 76%. ^1H NMR ($CDCl_3$): δ = 7.99 (dd, arom. H), 7.57–7.35 (m, arom. H), 3.63 (dd, CH_2), 2.81–2.17 (m, CH_2), 1.83–1.19 (m, Ad cage) ppm. FAB-MS: *m*/*z* = 570 [M – Cl]$^+$. $C_{24}H_{30}Cl_2O_3P_2Pd$ (605.79): calcd. C 47.59, H 4.99; found C 47.78, H 4.94.

Preparation of *cis*-[$Pt(CH_3)_2\{Ph_2P(CH_2)_2PAd\}$] (3): Compound **1** (0.095 g, 0.234 mmol) was dissolved in CH_2Cl_2 (5 mL) and added dropwise to a separate solution of [$Pt(CH_3)_2$(cod)] (0.078 g, 0.234 mmol) in CH_2Cl_2 (10 mL) with stirring. The colourless solution was stirred for 3 h after which the volume of solution was reduced to ca. 2–3 mL. Addition of petroleum ether (60–80 °C, 40 mL) gave a white solid which was filtered and dried in vacuo. Yield 0.051 g, 32%. ^1H NMR ($CDCl_3$): δ = 7.69–7.26 (m, arom. H), 2.54 (dd, CH_2), 2.23–1.11 (m, CH_2, Ad cage), 0.83 (tt, $^2J_{PtH}$ = 71, $^3J_{PH}$ = 14 Hz, Pt-CH_3), 0.51 (tt, $^2J_{PtH}$ = 71, $^3J_{PH}$ = 15 Hz, Pt-CH_3) ppm. FAB-MS: *m*/*z* = 653 [M^+]. $C_{26}H_{36}O_3P_2Pt$·Et_2O (727.76): calcd. C 49.52, H 6.37; found C 49.55, H 5.69.

Preparation of [$(AuCl)_2\{\mu$-$Ph_2P(CH_2)_2PAd\}$] (4): To a CH_2Cl_2 (10 mL) solution of AuCl(tht) (0.154 g, 0.480 mmol) was added **1** (0.112 g, 0.261 mmol) in CH_2Cl_2 (5 mL) dropwise. The colourless solution was stirred for 30 min and the volume concentrated under reduced pressure to ca. 1–2 mL. Addition of diethyl ether (15 mL) and hexanes (15 mL) gave solid **1** which was collected and dried in vacuo. Yield 0.178 g, 83%. ^1H NMR ($CDCl_3$): δ = 7.76–7.53 (m, arom. H), 2.80 (br, CH_2), 2.35–1.26 (m, CH_2, Ad cage) ppm. FAB-MS: *m*/*z* = 857 [M – Cl]$^+$. $C_{24}H_{30}Au_2Cl_2O_3P_2$·$0.25Et_2O$ (911.84): calcd. C 32.93, H 3.60; found C 33.55, H 3.46.

Preparation of [$RuCl_2(\eta^6$-*p*-cymene)$\{Ph_2P(CH_2)_2PAd\}$] (5): [$RuCl(\mu$-Cl)(η^6-*p*-cymene)]$_2$ (0.131 g, 0.021 mmol) was dissolved in CH_2Cl_2 (10 mL). Separately, **1** (0.184 g, 0.043 mmol) was dissolved in CH_2Cl_2 (15 mL) and added dropwise to the stirred solution of [$RuCl(\mu$-Cl)(η^6-*p*-cymene)]$_2$. The mixture was stirred for ca. 3 h after which the solution was concentrated to 2–3 mL and Et_2O (50 mL) added to afford a bright orange solid which was filtered and dried in vacuo. Yield 0.104 g, 66%. ^1H NMR ($CDCl_3$): δ = 7.86–7.39 (m, arom. H), 5.20–4.89 (m, *p*-cymene arom. H), 2.77 (m, CH_2), 2.52 (m, CH_2), 2.47 (sept, *p*-cymene CH), 1.83 (s, *p*-cymene CH_3), 1.75–0.74 (m, Ad cage, *p*-cymene $C(CH_3)_2$) ppm. FAB-MS: *m*/*z* = 735 [M^+]. $C_{34}H_{44}Cl_2O_3P_2Ru$ (734.68): calcd. C 55.59, H 6.05; found C 55.25, H 6.02. A similar procedure was also used for the preparation of the rhodium(III) and iridium(III) complexes **6** (97%) and **7** (73%). **6:** ^1H NMR ($CDCl_3$): δ = 7.86–

7.42 (m, arom. H), 3.00 (m, CH_2), 2.68 (m, CH_2), 1.76–0.97 (m, Ad cage), 1.28 (d, $^4J_{PH}$ = 2 Hz, Cp*) ppm. FAB-MS: *m/z* = 702 [M – Cl]$^+$. $C_{34}H_{45}Cl_2O_3P_2Rh{\cdot}CH_2Cl_2$ (822.45): calcd. C 51.11, H 5.77; found C 51.20, H 5.83. **7:** ^{1}H NMR ($CDCl_3$): δ = 7.76–7.37 (m, arom. H), 3.08 (m, CH_2), 2.78 (m, CH_2), 1.74–0.81 (m, Ad cage), 1.28 (d, $^4J_{PH}$ = 2 Hz, Cp*) ppm. FAB-MS: *m/z* = 791 [M – Cl]$^+$. $C_{34}H_{45}Cl_2IrO_3P_2{\cdot}CHCl_3$ (946.19): calcd. C 44.43, H 4.90; found C 45.04, H 5.13.

Preparation of [RhCl(η^5-Cp*){$Ph_2P(CH_2)_2PAd$}]SbF_6 (8b): A suspension of complex **6** (0.041 g, 0.056 mmol) and Na[SbF_6] (0.016 g, 0.062 mmol) in CH_2Cl_2 (10 mL) was stirred at ambient temperature for 5 d. The mixture was passed through a small Celite plug and the solvent evaporated to dryness. The residue was taken up in the minimum volume of CH_2Cl_2 (0.5 mL) and diethyl ether (15 mL) added to give an orange solid. The solid was collected by suction filtration and dried. Yield 0.018 g, 34%. ^{1}H NMR ($CDCl_3$): δ = 7.58–7.30 (m, arom. H), 3.21 (m, CH_2), 2.51 (m, CH_2), 2.20 (m, CH_2), 1.99–0.56 (m, Ad cage, Cp*) ppm. FAB-MS: *m/z* = 701 [M – SbF_6]$^+$. $C_{34}H_{45}ClF_6O_3P_2RhSb$ (931.77): calcd. C 43.82, H 4.88; found C 43.38, H 4.85. The iridium complex [IrCl(η^5-Cp*){$Ph_2P(CH_2)_2PAd$}]SbF_6 (**9b**) was isolated as a yellow solid (50%). ^{1}H NMR ($CDCl_3$): δ = 7.64–7.34 (m, arom. H), 3.18 (m, CH_2), 2.51 (m, CH_2), 2.38 (m, CH_2), 2.17 (m, CH_2), 2.05–0.63 (m, Ad cage, Cp*) ppm. $C_{34}H_{45}ClF_6IrO_3P_2Sb$ (1021.07): calcd. C 39.99, H 4.45; found C 39.87, H 4.36.

Preparation of [$RuCl_2$(η^6-*p*-cymene){$Ph_2P(CH_2)_2PAd(AuCl)$}] (10): [AuCl(tht)] (0.035 g, 0.11 mmol) was dissolved in CH_2Cl_2 (5 mL) and a separate solution of **5** (0.081 g, 0.11 mmol) in CH_2Cl_2 (10 mL) added dropwise. After stirring for 3 h the volume of the solution was reduced to ca. 3 mL and Et_2O (50 mL) added. The resulting orange solid was filtered and dried in vacuo. Yield 0.053 g, 50%. ^{1}H NMR ($CDCl_3$): δ = 7.82–7.43 (m, arom. H), 5.29–4.69 (m, *p*-cymene arom. H), 3.10 (m, CH_2), 2.48 (sept, *p*-cymene CH), 2.34 (m, CH_2), 1.87 (s, CH_3), 1.82–1.04 (m, Ad cage), 1.01 [d, *p*-cymene $C(CH_3)_2$], 0.85 [d, *p*-cymene $C(CH_3)_2$] ppm. $C_{34}H_{44}AuCl_3O_3P_2Ru$ (967.09): calcd. C 42.20, H 4.59; found C 41.66, H 4.41. A similar procedure was also used for the preparation of the rhodium(III) and iridium(III) complexes **11** (78%) and **12** (35%) respectively. For **11:** ^{1}H NMR ($CDCl_3$): δ = 7.81–7.45 (m, arom. H), 3.13 (m, CH_2), 2.64 (m, CH_2), 2.37 (m, CH_2), 2.18–1.04 (m, Ad cage), 1.29 (d, $^4J_{PH}$ = 1.5 Hz, Cp*) ppm. FAB-MS: *m/z* = 970 [M$^+$]. $C_{34}H_{45}AuCl_3O_3P_2Rh{\cdot}CH_2Cl_2$ (1054.87): calcd. C 39.85, H 4.50; found C 40.10, H 4.56. For **12:** ^{1}H NMR ($CDCl_3$): δ = 7.73–7.37 (m, arom. H), 3.26 (m, CH_2), 2.82 (m, CH_2), 2.40 (m, CH_2), 2.19–1.02 (m, Ad cage), 1.28 (d, $^4J_{PH}$ = 1.6 Hz, Cp*) ppm. FAB-MS: *m/z* 1059 [M$^+$]. $C_{34}H_{45}AuCl_3IrO_3P_2{\cdot}CH_2Cl_2$ (1144.16): calcd. C 36.74, H 4.15; found C 37.05, H 4.18.

Preparation of *trans*-[{$RuCl_2$(η^6-*p*-cymene){$Ph_2P(CH_2)_2PAd$}}$_2$-$PdCl_2$] (13): To a CH_2Cl_2 (5 mL) solution of [$PdCl_2(CH_3CN)_2$] (0.011 g, 0.042 mmol) was added **5** (0.060 g, 0.082 mmol) in CH_2Cl_2 (5 mL). The orange solution was stirred for 18 h and concentrated to ca. 1–2 mL under reduced pressure. Addition of diethyl ether (40 mL) afforded solid **13** which was collected by suction filtration and dried in vacuo. Yield 0.058 g, 83%. ^{1}H NMR ($CDCl_3$): δ = 7.92–7.41 (m, arom. H), 5.31–4.90 (m, *p*-cymene arom. H), 3.24 (m, CH_2), 3.00 (m, CH_2), 2.70 (m, CH_2), 2.50 (sept, *p*-cymene CH), 2.03 (m, CH_2), 1.90 (s, CH_3), 1.89 (s, CH_3), 1.65–1.19 (m, Ad cage), 0.98 [dd, *p*-cymene $C(CH_3)_2$], 0.87 [dd, *p*-cymene $C(CH_3)_2$] ppm. FAB-MS: *m/z* 1645 [M$^+$]. $C_{68}H_{88}Cl_6O_6P_4PdRu_2{\cdot}CH_2Cl_2$ (1646.54): calcd. C 47.86, H 5.25; found C 47.85, H 5.17.

Preparation of *trans*-[{$RuCl_2$(η^6-*p*-cymene){$Ph_2P(CH_2)_2PAd$}}$_2$-$PtCl_2$] (14): To a CH_2Cl_2 (5 mL) solution of [$PtCl_2(PhCN)_2$] (0.019 g, 0.040 mmol) was added **5** (0.060 g, 0.082 mmol) in CH_2Cl_2 (5 mL). The orange solution was stirred for 22 h and concentrated to ca. 1–2 mL under reduced pressure. Addition of diethyl ether (40 mL) afforded solid **14** which was collected by suction filtration and dried in vacuo. Yield 0.052 g, 74%. ^{1}H NMR ($CDCl_3$): δ = 7.87–7.37 (m, arom. H), 5.25–4.77 (m, *p*-cymene arom. H), 3.16 (m, CH_2), 2.91 (m, CH_2), 2.53 (dt, CH_2), 2.44 (sept, *p*-cymene CH), 2.00 (m, CH_2), 1.85 (s, CH_3), 1.82 (s, CH_3), 1.66–1.11 (m, Ad cage), 0.94 [t, *p*-cymene $C(CH_3)_2$], 0.76 [dd, *p*-cymene $C(CH_3)_2$] ppm. FAB-MS: *m/z* 1735 [M$^+$]. $C_{68}H_{88}Cl_6O_6P_4PtRu_2{\cdot}0.25CH_2Cl_2$ (1756.4): calcd. C 46.67, H 5.09; found C 46.46, H 5.03.

Table 5. Crystallographic data for **3**·$CHCl_3$, **4** and **5**.

Compound	**3**·$CHCl_3$	**4**	**5**
Empirical formula	$C_{27}H_{37}Cl_3O_3P_2Pt$	$C_{24}H_{30}Au_2Cl_2O_3P_2$	$C_{34}H_{44}Cl_2O_3P_2Ru$
Formula weight	772.95	893.25	734.60
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	11.5096(7)	12.2059(4)	7.4877(2)
b [Å]	11.4565(7)	12.5859(3)	13.4870(4)
c [Å]	23.1932(14)	17.7503(5)	33.2358(9)
α [°]			
β [°]	98.545(2)	103.9388(12)	92.3280(4)
γ [°]			
Volume [Å^3]	3024.3(3)	2646.54(13)	3353.60(16)
Z	4	4	4
T [K]	150(2)	120(2)	150(2)
Density (calcd.) [Mg /m^3]	1.698	2.242	1.455
Absorption coeff. [mm^{-1}]	5.037	11.421	0.755
Crystal	block, colourless	plate, colourless	block, dark red
Crystal size [mm^3]	0.26 × 0.21 × 0.10	0.14 × 0.08 × 0.02	0.49 × 0.32 × 0.23
θ Range [°]	1.78–29.07	3.03–27.48	1.63–30.55
Reflections collected	25066	27475	38615
Independent reflections	7322 [R_{int} = 0.058]	6041 [R_{int} = 0.041]	10239 [R_{int} = 0.041]
Final *R*, R_w	0.047, 0.113	0.036, 0.076	0.043, 0.100

Table 6. Crystallographic data for **7**·$CHCl_3$, **10**·CH_2Cl_2·$0.5C_4H_{10}O$ and **13**·$2CH_2Cl_2$.

Compound	**7**·$CHCl_3$	**10**·CH_2Cl_2·$0.5C_4H_{10}O$	**13**·$2CH_2Cl_2$
Empirical formula	$C_{35}H_{46}Cl_5IrO_3P_2$	$C_{37}H_{51}AuCl_5O_3P_2Ru$	$C_{70}H_{92}Cl_{10}O_6P_4PdRu_2$
Formula weight	946.11	1081.00	1816.36
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	P-1	$C2/c$
a [Å]	14.437(3)	12.2147(12)	29.148(2)
b [Å]	12.105(2)	12.2872(12)	11.8624(9)
c [Å]	22.147(4)	14.1978(14)	22.5109(16)
α [°]		84.6310(16)	
β [°]	98.023(3)	80.5268(17)	98.431(2)
γ [°]		88.1919(16)	
Volume [$Å^3$]	3832.6(11)	2092.3(4)	7699.4(10)
Z	4	2	4
T [K]	150(2)	150(2)	150(2)
Density (calcd.) [Mg/m^3]	1.640	1.729	1.567
Absorption coeff. [mm^{-1}]	3.949	4.292	1.097
Crystal	plate, yellow	plate, orange	needle, orange
Crystal size [mm^3]	0.34 × 0.22 × 0.05	0.34 × 0.25 × 0.02	0.49 × 0.08 × 0.06
θ Range [°]	1.86–25.00	1.66–25.00	1.83–29.02
Reflections collected	27462	15122	33403
Independent reflections	6755 [R_{int} = 0.038]	7338 [R_{int} = 0.038]	9320 [R_{int} = 0.072]
Final R, R_w[a]	0.049, 0.144	0.048, 0.121	0.052, 0.137

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for "observed" reflections having $F^2 > 2\sigma(F^2)$. $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2]^{1/2}$ for all data.

X-ray Crystallography: Measurements were made with either a Bruker AXS SMART 1000 CCD area-detector diffractometer[45] for **3**·$CHCl_3$, **4**, **5**, **7**·$CHCl_3$, **10**·CH_2Cl_2·$0.5C_4H_{10}O$ and **13**·$2CH_2Cl_2$ using sealed-tube graphite-monochromated Mo-K_α radiation and narrow frame exposures (0.3°) in ω or a Bruker-Nonius 95 mm CCD kappa diffractometer[46,47] equipped with a rotating anode generator for **4**. Cell parameters were refined from the observed (ω) angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. All structures were solved by direct methods and refined on F^2 values for all unique data by full-matrix least-squares.[48] Table 5 and Table 6 give further details. All non-hydrogen atoms were refined anisotropically. For **10**·CH_2Cl_2·$0.5C_4H_{10}O$ a molecule of CH_2Cl_2 and an Et_2O on an inversion centre, both disordered, were modelled by the Platon Squeeze procedure.[49] In **13**·$2CH_2Cl_2$ the dichloromethane molecule was modelled with one chlorine atom split over two sets of positions. This disorder was modelled with restraints on anisotropic displacement parameters.

CCDC-664025 (for **3**·$CHCl_3$), -664026 (for **4**), -664027 (for **5**), -664028 (for **7**·$CHCl_3$), -664029 (for **10**·CH_2Cl_2·$0.5C_4H_{10}O$) and -664030 (for **13**·$2CH_2Cl_2$) contain the complete set of X-ray crystallographic structural data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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