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Mononuclear and Heterodinuclear Metal Complexes of Nonsymmetric Ditertiary Phosphanes Derived from R_2PCH_2OH

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The new nonsymmetric ditertiary phosphanes, $Ph_2PCH_2N(R)CH_2PAd$ [**3a**: R = C_6H_5, **3b**: R = $C_6H_4(4\text{-}CH_3)$] were prepared using a three-step sequence of condensation reactions. Hence treatment of AdP-H (AdP-H = 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane) with $(CH_2O)_n$ at 110 °C gave the adamantane-derived hydroxymethylphosphane **1**, which upon condensation with $C_6H_5NH_2$ or $C_6H_4(4\text{-}CH_3)NH_2$ gave the secondary aminophosphanes $HN(R)CH_2PAd$ [**2a**: R = C_6H_5, **2b**: R = $C_6H_4(4\text{-}CH_3)$]. Further condensation of **2a** or **2b** with Ph_2PCH_2OH gave **3a** or **3b** in high yields (ca. 85 %) containing the sterically encumbered adamantane cage. The coordination capabilities of **2a**, **3a** and **3b** have been explored with various Pd^{II}, Pt^{II}, Ru^{II}, Ir^{III} and Au^{I} metal centres. Bridge cleavage of $\{Pd(\kappa^2\text{-}C,N\text{-}C_{16}H_{16}N)Br\}_2$ with 2 equiv. of **2a** gave the neutral, mononuclear complex $Pd(\kappa^2\text{-}C,N\text{-}C_{16}H_{16}N)Br$(**2a**) (**4**). Reaction of **3a/3b** with MCl_2(cod) (M = Pt, Pd) gave the corresponding κ^2-*P,P′*-chelate complexes *cis*-MCl_2(**3**) [**5a**: M = Pt, R = C_6H_5, **5b**: Pt, R = $C_6H_4(4\text{-}CH_3)$, **5c**: Pd, R = C_6H_5, **5d**: Pd, R = $C_6H_4(4\text{-}CH_3)$]. In contrast, bridge cleavage of the dimers $\{RuCl_2(\eta^6\text{-}p\text{-cym})\}_2$ or $\{IrCl_2(\eta^5\text{-}Cp^*)\}_2$ with **3a** gave the κ^1-*P*-monodentate complexes $RuCl_2(\eta^6\text{-}p\text{-cym})$(**3a**) (**6**) and $IrCl_2(\eta^5\text{-}Cp^*)$(**3a**) (**7**), respectively, in which the –PAd group is noncoordinating. Reaction of **6** or **7** with AuCl(tht) (tht = tetrahydrothiophene) gave the mixed-metal complexes κ^2-*P,P′*-μ-$RuCl_2(\eta^6\text{-}p\text{-cym})\{Ph_2PCH_2N(Ph)CH_2PAd(AuCl)\}$ (**8**) and κ^2-*P,P′*-μ-$IrCl_2(\eta^5\text{-}Cp^*)\{Ph_2PCH_2N(Ph)CH_2PAd(AuCl)\}$ (**9**). All new compounds have been fully characterised by spectroscopic and analytical methods. Furthermore, the structures of **2a**, **4**, **5a**, **5b** and **6**–**9** have been elucidated by single-crystal X-ray crystallography. The X-ray structures of **5a**, **5b** and **6**–**9** represent the first examples of crystallographically characterised nonsymmetric ditertiary phosphane complexes bearing one adamantane moiety.

Introduction

As part of ongoing studies[1–5] in our group we have been interested in developing new tertiary and symmetric ditertiary phosphanes using Mannich-based condensation reactions. Compounds of the formula $(R_2PCH_2)_2N(R)$ and $\{(R_2PCH_2)_2N\}_2(R)$ are two such examples[6–10] which have interesting coordination properties, catalytic applications and, more recently, are important ligands for self-assembly reactions using covalent bonds or H-bonding interactions.[1,2,4,11] 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 successfully utilised in several metal-catalysed reactions.[12–14] Furthermore, a related C_3 backbone diphosphane structurally comparable to dppp, is the bulky electron-rich diphosphane $(AdPCH_2)_2CH_2$ (bpap) recently reported by Pringle and co-workers.[15,16] Both bpap and related diphospha-adamantane ligands have been shown to form complexes with Ru, Pd and Au metal centres.[15,16] There has also been interest in these adamantane-based phosphane ligands for their important uses in a range of catalytic metal-mediated transformations such as aminations, hydroformylation, hydrogenations, methoxycarbonylation of internal alkenes and Suzuki and Sonogashira couplings.[17–25]

Nonsymmetric ditertiary phosphanes have seldom been studied in relation to their symmetric counterparts possibly reflecting the necessity to perform multistep syntheses.[26–31] When considering possible coordination modes for nonsymmetric diphosphanes of the type $R_2PCH_2XCH_2PR'_2$ various coordination modes are plausible some of which are shown in Figure 1. Hence κ^1-*P*-monodentate coordination is possible at either $–PR_2$ or $–PR'_2$ centres (structures **I** and **II**) and μ-*PP′* bridging between similar/disparate metal centres (structures **III**–**V**; the presence of a metal–metal interaction is illustrated by a dashed line). Alternatively such mixed ligands may adopt a more classic κ^2-*PP′*-chelating mode to a single metal centre (structure **VI**). Finally, depending on the nature of the X spacer group [e.g. N-

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$(CH_2)_4$] separating the two phosphorus donor atoms, κ^3-*PNP′*-tridentate coordination is possible utilising all three group-15 donor atoms (structure **VII**).[8]

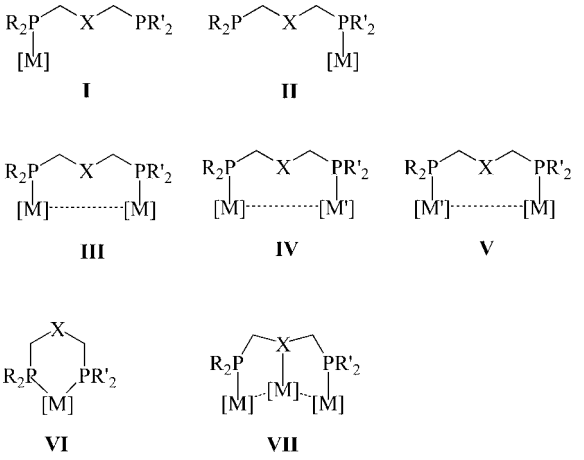
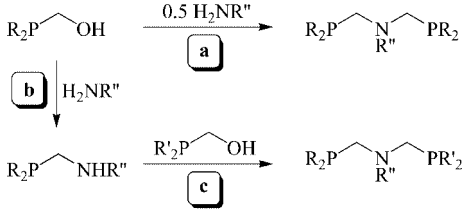


Figure 1. Schematic representation of the possible coordination modes for $R_2PCH_2XCH_2PR'_2$.

Herein we report a simple two-step condensation procedure (Scheme 1, pathway **b/c**) by which ditertiary phosphanes bearing non-equivalent groups (–PPh_2 and –PAd) can be obtained. In contrast, while pathway **a** generally affords symmetric diphosphanes, pathway **b** gives initially a secondary aminophosphane that can undergo further reaction with a second different hydroxymethylphosphane precursor (pathway **c**) to yield the desired nonsymmetric diphosphane. We demonstrate that these ligands exhibit 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 (structure **I**). This has allowed us to use these intermediates as "metalloligands" for the construction of heterobimetallic species as exemplified by our syntheses of complexes containing Ru/Au and Ir/Au metal centre combinations. The single-crystal X-ray structures of eight compounds are reported.

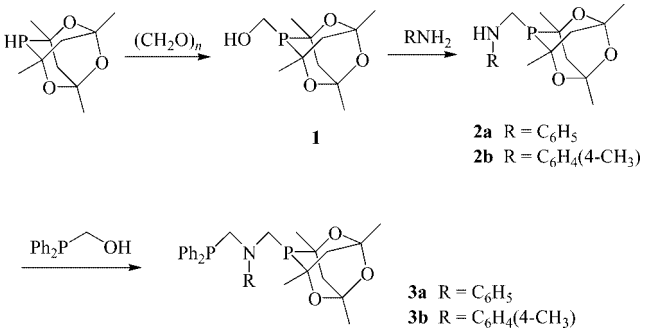


Scheme 1.

Results and Discussion

Ligand Syntheses

Previous studies using Ph_2PCH_2OH have shown that condensation with primary amines (RNH_2) can be used to access either singly substituted products [of the type $Ph_2PCH_2N(H)R$] or symmetric ditertiary phosphanes [of the type $(Ph_2PCH_2)_2N(R)$] depending on the R group.[1–5] We have found that by using two consecutive Mannich based condensation reactions, nonsymmetric ditertiary phosphanes such as **3a** and **3b** can be realised. Accordingly, insertion of paraformaldehyde into the P–H bond of AdP-H (1:1 ratio) at 110 °C for 90 min affords the hydroxymethyl-functionalised phosphane **1**. Mannich condensation of **1** with $H_2NC_6H_5$ (1:1 ratio) in CH_3OH at room temperature, under anaerobic conditions, gave the secondary aminophosphane **2a** as a racemic mixture of enantiomers. Similarly, **2b** could be prepared from $H_2NC_6H_4(4\text{-}CH_3)$ employing a similar method (Scheme 2). Further treatment of **2a** (or **2b**) with Ph_2PCH_2OH in CH_3OH at room temperature gave the desired nonsymmetric ditertiary phosphanes **3a** (or **3b**) in good yields (ca. 85%). The formulation of these compounds were confirmed by a combination of spectroscopic and analytical methods.



Scheme 2.

The $^{31}P\{^1H\}$ NMR chemical shifts for **1**, **2a** and **2b** are all similar [δ(P) –31.2, –32.2 and –32.4 ppm, respectively], but differ from the starting secondary phosphane AdP-H, by ca. 20 ppm [δ(P) –49.7 ppm, $CDCl_3$].[32] Furthermore, the $^{31}P\{^1H\}$ NMR chemical shifts for **1**, **2a** and **2b** differ by ca. 10 ppm with respect to the phenyl-modified phosphaadamantanes, AdP-Ph, previously reported.[19] Upon second condensation the ^{31}P resonance for the –PAd group is shifted upfield by ca. 10 ppm to –41.5 ppm (for **3a**) and –42.0 ppm (for **3b**). The –PPh_2 resonance is observed at δ(P) –27.4 ppm (for **3a**) and –27.6 ppm (for **3b**), which differs by ca. 10 ppm with respect to dppp [δ(P) –17.3 ppm, $CDCl_3$]. In the ^1H NMR spectra of **2a** and **2b** the CH_2 hydrogen atoms are diastereotopic as two separate doublet of doublets are observed at ca. 3.4 and 2.9 ppm. On the basis of FT-IR spectroscopy (KBr pellets), characteristic ν_{O-H} and ν_{N-H} stretches were observed at 3470 cm^{-1}, 3367 cm^{-1} and 3319 cm^{-1} for **1**, **2a** and **2b**, respectively, yet these frequencies were absent in either **3a** or **3b** as would be expected. Other characterising data are given in Table 1 and the Exp. Sect.

The X-ray structure of **2a** has been determined (Figure 2, Table 2) and confirms the presence of the phospha-adamantane cage. While a few crystallographic examples of sterically hindered phosphanes containing this cage have been reported in the literature[15–19,21,25] this structure represents

Table 1. Selected spectroscopic data for compounds **1**–**10**.[a]

	δ(P) / –PPh_2	δ(P) / –PAd	^4J(PP)	J(PtPPh_2)	J(PtPAd)	^2J(PP)	ν(OH)/ ν(NH)	ν(MCl)
1		–31.2					3470	
2a		–32.2					3367	
2b		–32.4					3319	
3a	–27.4	–41.5	5					
3b	–27.6	–42.0	4					
4		18.7					3297	
5a	–8.0	–19.0		3233	3489	19		315, 293
5b	–8.0	–18.9		3230	3489	19		315, 292
5c	9.6	–4.0				8		304, 291
5d	9.6	–3.9				10		304, 291
6	23.6	–39.0	n.r.					
7	–5.1	–38.7	5					
8	28.4	24.1	11					331
9	17.5	–3.2	9					336
10[b]	14	10	n.r.					329

[a] Chemical shifts in ppm, coupling constants in Hz. [b] Recorded at –50 °C in $CDCl_3$. n.r. = not resolved.

the first example of such a compound bearing a remote, secondary amine functional group. The P(1)–C(11) [1.8591(19) Å] and C(11)–N(1) [1.456(2) Å] distances are similar to other documented tertiary phosphanes bearing phenyl substituents on phosphorus [P–C 1.8208(19), 1.8515(18) Å; C–N 1.456(2), 1.454(2) Å] illustrating that the adamantane cage has negligible electronic/steric effects on these structural parameters.[1,33]

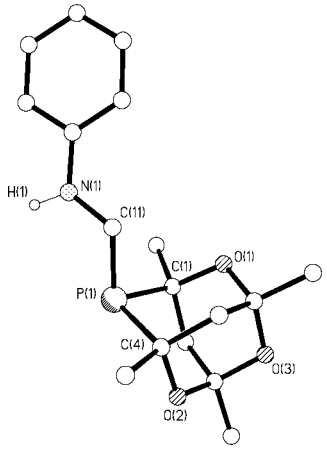


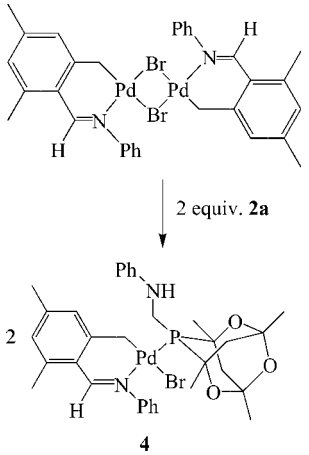
Figure 2. Molecular structure of **2a**; all hydrogen atoms except on N(1) have been removed for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for compounds **2a** and **4**.

	2a	**4**
Pd(1)–Br(1)		2.5676(3)
Pd(1)–P(1)		2.2522(6)
Pd(1)–N(2)		2.1291(18)
Pd(1)–C(33)		2.050(2)
N(2)–C(24)		1.282(3)
P(1)–C(11)	1.8591(19)	1.872(2)
C(11)–N(1)	1.456(2)	1.444(3)
Br(1)–Pd(1)–P(1)		94.067(16)
Br(1)–Pd(1)–C(33)		167.48(7)
Br(1)–Pd(1)–N(2)		89.01(5)
P(1)–Pd(1)–C(33)		95.42(7)
P(1)–Pd(1)–N(2)		173.14(5)
C(33)–Pd(1)–N(2)		82.47(8)
Pd(1)–P(1)–C(11)		111.02(2)
P(1)–C(11)–N(1)	108.35(13)	117.08(16)

Coordination Studies

Given the paucity of palladium complexes with adamantane-based phosphorus ligands documented in the literature[17,19,25] we prepared the palladium(II) complex **4** by bridge cleavage of the known[34] dimeric compound {Pd(κ^2-*C,N*-$C_{16}H_{16}N$)Br}$_2$ with **2a** in refluxing acetone [Equation (1)]. Compound **4** displayed a singlet at δ(P) 18.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum (Table 1) and furthermore was characterised by single-crystal X-ray crystallography.



(1)

The X-ray structure (Figure 3, Table 2) confirmed a near square-planar arrangement about palladium with angles in the range 82.47(8)–95.42(7) Å. The Pd(1)–P(1) distance in **4** [2.2522(6) Å] is as expected. As previously observed for

other cyclometallated complexes of palladium the phosphane **2a** is *trans* to the imine nitrogen N(2).[35] Within the κ^2-*C*,*N*-metallated ligand an *E* configuration is adopted by the two arene groups located about the C(24)=N(2) imine double bond. The six-membered PdC_4N metallacycle adopts a nonplanar conformation hinged about C(24)/C(33). The Pd deviates from the P(1)/Br(1)/N(2)/C(33) mean plane by 0.0242 Å. Within the bonded P ligand the intra-cage C–P–C angle is 94.05(10)° which is slightly enlarged with respect to **2a** [92.90(8)°] but similar in magnitude to other coordinated phospha-adamantane ligands.[16,19] The amine group forms an intramolecular hydrogen bond to the coordinated bromide ligand [N(1)···Br(1) 3.265(2) Å, H(1)···Br(1) 2.61(3) Å; N(1)–H(1)···Br(1) 137(2)°].

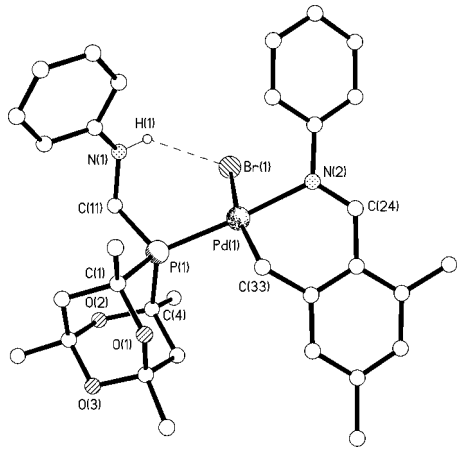


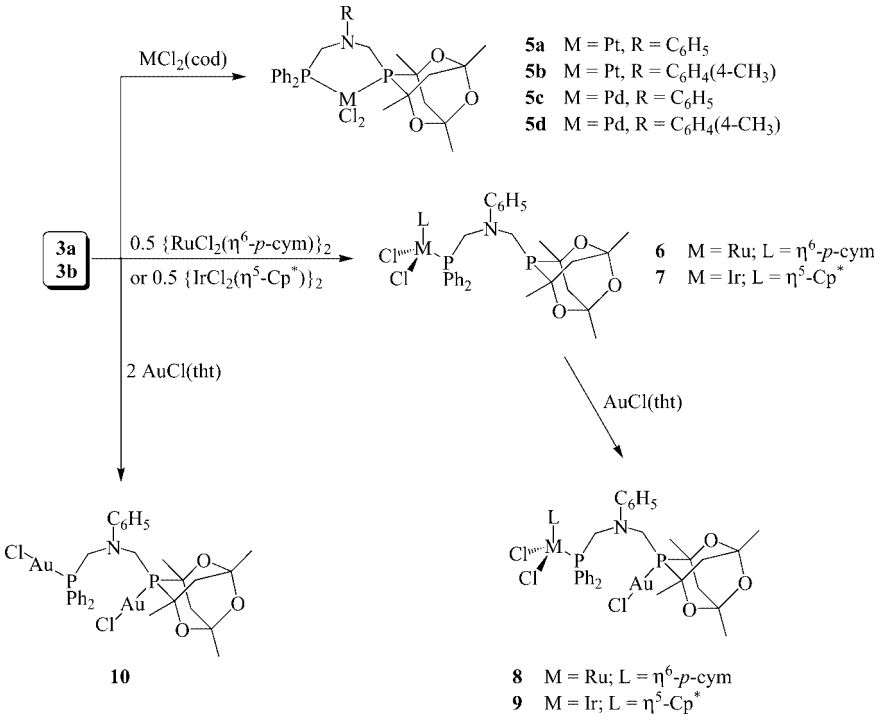
Figure 3. Molecular structure of **4**. All hydrogen atoms except on N(1) have been removed for clarity.

Reaction of **3a** (and **3b**) with MCl_2(cod) (M = Pt, Pd) gave the dichloro κ^2-*P*,*P*′-chelate compounds MCl_2(**3a**) [M = Pt **5a**; Pd **5c**] and MCl_2(**3b**) [M = Pt **5b**; Pd **5d**] in high yields (Scheme 3). By virtue of the different substituents on each phosphorus the $^{31}P\{^1H\}$ NMR spectra of the chelate complexes **5a**–**5d** are particularly diagnostic showing a classical AX pattern (Table 1). The ^{31}P chemical shifts between the two phosphorus nuclei differ by ca. 10 ppm whilst the *J*(PtP) couplings differ by ca. 250 Hz with the *J*(PtP) coupling to the –PAd group being the larger of the two. These variations can presumably be ascribed to the difference in stereoelectronic properties between the two phosphorus centres.

The X-ray structures of the nonsymmetric diphosphane platinum(II) complexes **5a** and **5b** have been determined (Figure 4, Figure 5 and Table 3). Suitable crystals of **5a** and **5b** were obtained by slow diffusion of diethyl ether into a $CDCl_3$ solution. The X-ray structures show that both **5a** and **5b** adopt a chelating coordination mode and furthermore, the coordination environment around platinum is ostensibly square-planar. In **5a** the P(2)–Pt(1)–Cl(2) [83.07(5)°] bond angle is contracted by some 10° with respect to P(1)–Pt(1)–Cl(1) [93.87(6)°] clearly reflecting the different steric effects of phenyl vs. adamantane groups. The P(1)–Pt(1)–P(2) hinge angle is 96.33(5)° which compares favourably with the previously reported angle for the symmetric, bulky diphosphane palladium(II) complex $PdCl_2$(bpap), previously reported by Pringle and coworkers.[15] The Pt–P [2.2362(16), 2.2373(14) Å] and Pt–Cl [2.3545(14), 2.3499(14) Å] bond lengths are similar and illustrate the negligible effect the different substituents on P have on these distances. The Pt is out of the mean plane [defined by the donor atoms P(1), P(2), Cl(1) and Cl(2)] by 0.0139 Å (for **5a**) and 0.0451 Å (for **5b**). The six-membered Pt–P–C–N–C–P′ rings in **5a** and **5b** adopt a conformation in which the Pt(1), P(1), P(2), C(11) and C(18) atoms are essentially flat (to within ±0.07 Å for **5a**; ±0.19 Å for **5b**) and N(1) is out of this plane by 0.74 Å (for **5a**) and 0.66 Å (for **5b**). Furthermore the N–arene torsion angles, defined by the C(11)/N(1)/C(18) and C(12)>C(17) mean planes, are 37° and 76° for **5a** and **5b** respectively. Analysis of the packing in the two crystal structures shows the orientations of the N–arene rings are determined by weak C–H(Me or Ph)···π(N–arene) interactions to neighbouring molecules.

Having established these nonsymmetric ligands successfully *P*,*P*′-chelate to platinum(II) and palladium(II) metal centres we next sought to establish whether the sterically demanding adamantane group could impose a *P*-monodentate mode of binding through the sterically less encumbered $-PPh_2$ group. This sort of *P*-monodentate behaviour, whilst known for flexible small bite angle diphosphanes such as dppm,[36] dppa [bis(phenylphosphanyl)amine][37] and others,[28] is less prevalent with dppp bearing an extended C_3 spacer. Gratifyingly when we reacted **3a** with $\{RuCl_2(\eta^6\text{-}p\text{-cym})\}_2$ or $\{IrCl_2(\eta^5\text{-Cp*})\}_2$ in dichloromethane we obtained the κ^1-*P*-monodentate complexes **6** and **7** in high yields. Presumably under these experimental conditions the –PAd group is too bulky to coordinate to the $RuCl_2(\eta^6\text{-}p\text{-cym})$ or $IrCl_2(\eta^5\text{-Cp*})$ fragments [vide infra for reactions with AuCl(tht)]. The $^{31}P\{^1H\}$ NMR spectra (Table 1) are particularly informative showing new downfield δ(P) resonances for the coordinated $-PPh_2$ group at δ(P) 23.6 ppm (for **6**) and –5.1 ppm (for **7**) whilst the pendant –PAd group is observed at δ(P) ca. –39 ppm (cf. –41.5 ppm for **3a**).

The X-ray structures of the piano-stool complexes **6** and **7** have both been established by X-ray crystallography (see Figures 6 and 7, Table 3). Within the coordination sphere of **6** the Ru–P, Ru–Cl or $Ru-C_{arene}$ bond lengths are comparable to other half-sandwich compounds e. g. $RuCl_2$(*p*-cym)PTA (PTA = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]-decane), $RuCl_2$(*p*-cym)$Ph_2P(2\text{-}C_5H_4N)$ and $RuCl_2$(*p*-cym)Ph_2PCH_2Y [Y = $-NHC_6H_4(2\text{-}CO_2H)$, $-NHC_6H_4(2\text{-OH})$, $-NHC_6H_4(2\text{-}CH_2OH)$].[1,38] As a consequence of κ^1-*P*-monodentate coordination the C(11)–N(1)–C(18) bond angle has marginally increased by ca. 3° for **6** (and 4° for **7**) with respect to that observed in the κ^2-*P*,*P*′-chelate complexes **5a** and **5b**. The P···P separations within **6** and **7** are 4.868 Å and 5.319 Å, respectively.



Scheme 3.

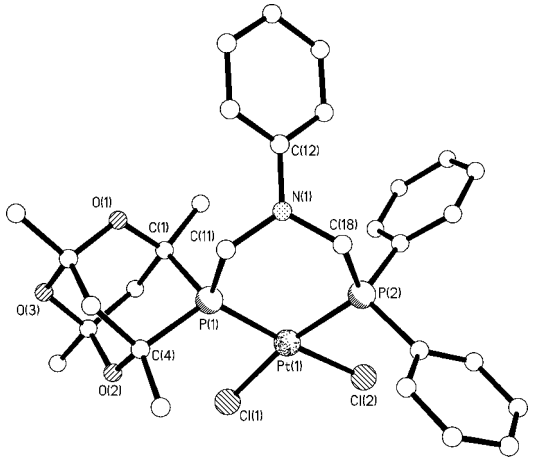


Figure 4. Molecular structure of **5a**. All hydrogen atoms and solvent have been removed for clarity.

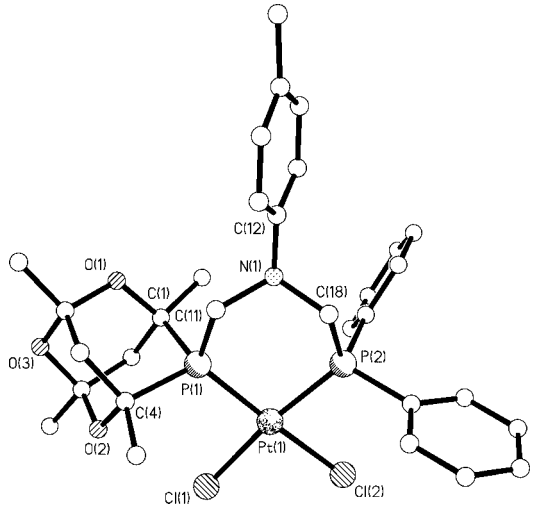


Figure 5. Molecular structure of **5b**. All hydrogen atoms and solvent have been removed for clarity.

In order to pursue the possibility of introducing a second metal centre we elected to react both **6** and **7** with 1 equiv. of AuCl(tht) in dichloromethane at room temperature. After work up the red/orange solids κ^2-*P*,*P*′-μ-$RuCl_2(\eta^6$-*p*-cym){$Ph_2PCH_2N(Ph)CH_2PAd(AuCl)$} **8** and κ^2-*P*,*P*′-μ-$IrCl_2(\eta^5$-Cp*){$Ph_2PCH_2N(Ph)CH_2PAd(AuCl)$} **9** were isolated in 93% and 77% yields respectively. The $^{31}P\{^1H\}$ NMR spectra were particularly informative showing a downfield shift for –PAd to δ(P) 24.1 ppm (for **8**) and δ(P) –3.2 ppm (for **9**) with respect to the noncomplexed –PAd group in **6** and **7** (Table 1). Further indication for gold(I) coordination was evident from the IR spectra which clearly showed ν_{AuCl} vibrations at 331 cm^{-1} and 336 cm^{-1} for **8** and **9**, respectively.

Upon complexation the gold(I) chloride fragment is approximately linear with respect to the coordinated –PAd moiety (see Figures 8 and 9, Table 4). The Au–Cl and Au–P bond lengths are normal and in the region previously observed for phosphane gold(I) complexes.[4,39–41] No significant changes are observed for the M–Cl and M–P (M = Ru or Ir) distances/bond angles upon gold complexation. In addition the Cl(1)–Au(1)–P(1) angles [177.18(4)° for **8**; 174.42(8)° for **9**] suggest very minimal steric congestion between the adamantane cage or neighbouring N–Ph group. Furthermore, the C(11)–N(1)–C(18) angles for **8** and **9** are 115.9(2)° and 115.5(6)°, respectively, whilst the N–arene

Table 3. Selected bond lengths [Å] and angles [°] for compounds **5a** and **5b**.

	5a	5b
Pt(1)–Cl(1)	2.3545(14)	2.3544(15)
Pt(1)–Cl(2)	2.3499(14)	2.3553(14)
Pt(1)–P(1)	2.2362(16)	2.2436(14)
Pt(1)–P(2)	2.2373(14)	2.2330(14)
P(1)–C(11)	1.852(6)	1.833(5)
C(11)–N(1)	1.456(8)	1.468(7)
N(1)–C(18)	1.462(7)	1.469(7)
C(18)–P(2)	1.834(6)	1.830(5)
Cl(1)–Pt(1)–P(1)	93.87(6)	94.67(5)
Cl(1)–Pt(1)–P(2)	169.29(5)	171.83(5)
Cl(1)–Pt(1)–Cl(2)	87.05(5)	85.97(5)
Cl(2)–Pt(1)–P(2)	83.07(5)	85.91(5)
Cl(2)–Pt(1)–P(1)	174.86(5)	176.54(5)
P(1)–Pt(1)–P(2)	96.33(5)	93.38(5)
Pt(1)–P(1)–C(11)	116.9(2)	118.12(18)
P(1)–C(11)–N(1)	110.7(4)	113.4(3)
C(11)–N(1)–C(18)	112.4(5)	112.0(4)
N(1)–C(18)–P(2)	111.6(4)	110.3(3)
C(18)–P(2)–Pt(1)	117.53(19)	117.22(19)

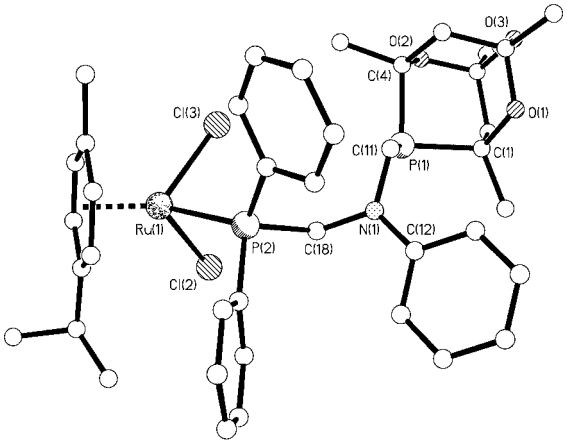


Figure 6. Molecular structure of **6**; all hydrogen atoms and solvent have been removed for clarity.

torsion angles for **6**–**9**, defined by the C(11)/N(1)/C(18) and C(12)>C(17) mean planes, are all in the range 7.6–17.3°. The P···P distances in both heterobimetallic complexes are 5.238 Å and 5.283 Å for **8** and **9**, which also dictate large Ru···Au [8.304 Å] and Ir···Au [8.481 Å] separations. The shortest intermolecular Au···Au separations are 7.628 Å and 5.987 Å, respectively, indicating the absence of any significant aurophilic interactions between neighbouring P–Au–Cl units.[42]

We next sought to demonstrate whether **3a** could bridge two identical metal centres and accordingly prepared the digold(I) compound **10** from 2 AuCl(tht) and 1 equiv. of **3a** in CH_2Cl_2. The ambient temperature $^{31}P\{^1H\}$ NMR spectrum of **10** in $CDCl_3$ revealed two broad resonances around δ(P) 15 ppm which sharpened upon cooling to –50 °C (Figure 10). The close similarity of both phosphorus signals makes assignment of these somewhat speculative. The

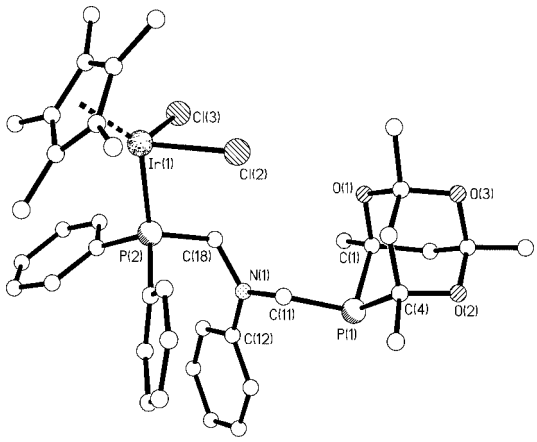


Figure 7. Molecular structure of **7**; all hydrogen atoms and solvent have been removed for clarity.

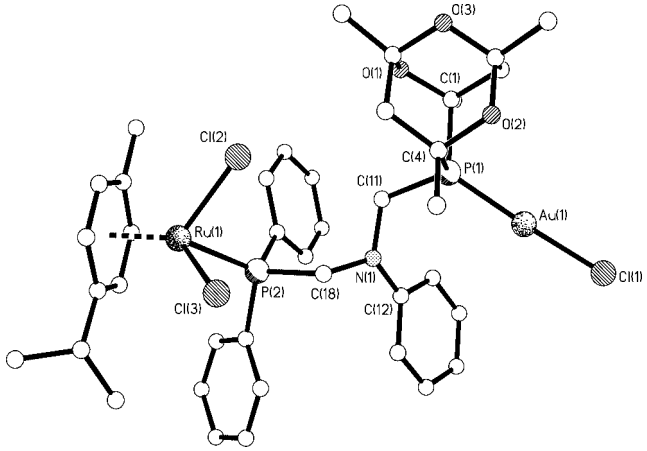


Figure 8. Molecular structure of **8**; all hydrogen atoms and solvent have been removed for clarity.

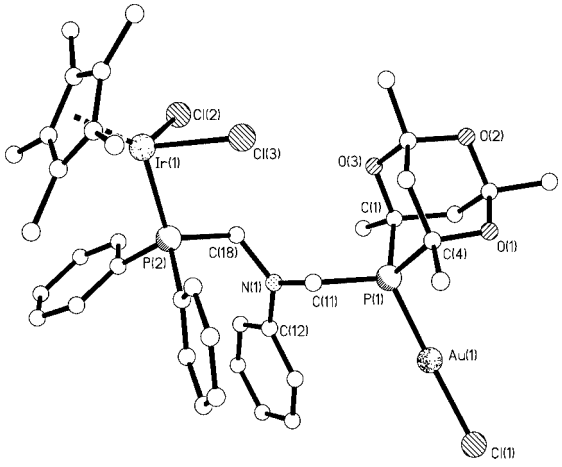


Figure 9. Molecular structure of **9**; all hydrogen atoms have been removed for clarity.

downfield resonance at δ(P) 14 ppm is tentatively assigned to the $-PPh_2(AuCl)$ bonded metal centre by analogy with $PhN(CH_2PPh_2AuCl)_2$ which has recently been reported.[4]

Table 4. Selected bond lengths [Å] and angles [°] for compounds **6**–**9**.

	6 M = Ru	**7** M = Ir	**8** M = Ru	**9** M = Ir
M(1)–Cl(2)	2.4039(17)	2.408(2)	2.4160(8)	2.4010(19)
M(1)–Cl(3)	2.4063(17)	2.398(2)	2.4090(3)	2.424(2)
M(1)–P(2)	2.3391(18)	2.3091(19)	2.3420(8)	2.3047(19)
M(1)–$C_{centroid}$	1.698	1.814	1.709	1.805
P(2)–C(18)	1.894(6)	1.900(7)	1.888(3)	1.881(8)
C(18)–N(1)	1.435(8)	1.451(9)	1.454(4)	1.452(9)
N(1)–C(11)	1.459(8)	1.474(10)	1.449(4)	1.444(9)
C(11)–P(1)	1.885(7)	1.869(8)	1.851(3)	1.869(8)
P(1)–Au(1)			2.2227(8)	2.223(2)
Au(1)–Cl(1)			2.2804(9)	2.280(2)
Cl(2)–M(1)–Cl(3)	88.63(6)	89.24(8)	87.45(3)	89.02(7)
Cl(2)–M(1)–P(2)	83.64(6)	88.64(7)	85.55(3)	85.05(7)
Cl(3)–M(1)–P(2)	84.40(6)	85.18(7)	84.49(3)	88.29(7)
M(1)–P(2)–C(18)	113.3(2)	112.4(2)	113.49(10)	112.0(2)
P(2)–C(18)–N(1)	118.4(4)	114.4(5)	116.9(2)	116.4(5)
C(18)–N(1)–C(11)	115.0(5)	115.9(6)	115.9(2)	115.5(6)
N(1)–C(11)–P(1)	112.5(4)	113.4(5)	113.2(2)	115.1(5)
C(11)–P(1)–Au(1)			118.16(10)	115.6(3)
P(1)–Au(1)–Cl(1)			177.18(4)	174.42(8)

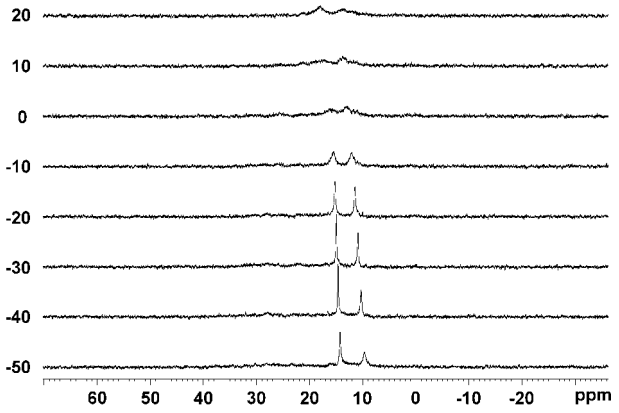


Figure 10. Variable temperature $^{31}P\{^1H\}$ NMR spectra for **10** recorded in the range 20 to –50 °C.

Conclusions

In summary, we have developed a facile method for the synthesis of two nonsymmetric ditertiary phosphanes bearing one bulky substituent on phosphorus. This procedure is potentially a valuable synthetic route to highly modular nonsymmetric diphosphanes with tuneable stereoelectronic properties. Whilst κ^2-*P,P′*-chelation is observed upon complexation to square-planar metal centres we have shown the ability of one of these ligands to function as a κ^1-*P*-monodentate tertiary phosphane. Coordination to a second, different metal, affords new examples of late transition metal heterobimetallic compounds bridged by the phosphane **3a**. This clearly illustrates the importance of steric effects on phosphorus and how this can be implemented in directing variable ligating modes. Our work should be contrasted with that of others who have shown that dppp can readily act as a bridging ligand affording symmetric dinuclear complexes based on e. g. Mo,[43] Ru,[44] Ir,[45] Ni,[46] Pd[47] and Au[48] metal fragments. However, crystallographic examples where dppp bridges two different metal sites are extremely scarce.[45b] Dinuclear Rh/Au complexes[49] have recently been reported using κ^3-*PN*$_2$-bridged pyridylphosphanes whilst $\{Ph_2PCH_2\}_2PPh$ has been used to generate, amongst others, cationic Ru/Rh and Ru/Ag heteronuclear complexes.[50,51] Further studies are in progress and will be reported in due course.

Experimental Section

Materials: Standard Schlenk techniques were used for the synthesis of **1**, **2a**, **2b**, **3a** and **3b** whilst all other reactions were carried out in air using previously distilled solvents unless otherwise stated. (Diphenylphosphanyl)methanol[52] and the metal complexes AuCl(tht) (tht = tetrahydrothiophene),[53] $\{RuCl_2(\eta^6\text{-}p\text{-cym})\}_2$,[54] $\{IrCl_2(\eta^5\text{-Cp*})\}_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl),[55] MCl_2(cod) (M = Pd, Pt)[56] and $\{Pd(\kappa^2\text{-}C,N\text{-}C_{16}H_{16}N)Br\}_2$[34] 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 $CDCl_3$ unless otherwise stated. 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 1: 1,3,5,7-Tetramethyl-2,4,8-trioxa-6-phosphaadamantane (0.649 g, 2.91 mmol) and $(CH_2O)_n$ (0.096 g, 3.20 mmol) were heated at 110 °C for 90 min affording a yellow oil which was used directly in subsequent condensation reactions. Compound **1** slowly crystallises upon standing in a freezer. Routinely the purity of **1** was shown, by $^{31}P\{^1H\}$ NMR, to be ca. 85%. ^1H NMR ($CDCl_3$): δ = 4.06 (m, CH_2), 2.45 (s, OH), 1.97–1.35 (m, Ad cage) ppm.

Preparation of 2a: A solution of $C_6H_5NH_2$ (5.561 g, 59.7 mmol) in methanol (HPLC grade, 35 mL) was added to a methanol (HPLC grade, 35 mL) solution of **1** (2.714 g, 9.37 mmol) by cannula. The resulting mixture was stirred for 17 h and then concentrated under reduced pressure to ca. 10 mL. The solid was collected by suction filtration and dried in vacuo. Yield: 2.455 g, 84%. ^1H NMR ($CDCl_3$): δ = 7.16–6.58 (m, arom. H), 3.85 (NH), 3.43 (dd, J = 12 Hz, 1.6 Hz, CH_2), 2.91 (dd, J = 13 Hz, 3.2 Hz, CH_2), 1.92–1.30 (m, Ad cage) ppm. $C_{17}H_{24}NO_3P$ (321.37): calcd. C 63.54, H 7.53, N 4.36; found C 63.05, H 7.52, N 4.30. This procedure was also used for the preparation of **2b** albeit in lower yield (53%). For **2b:** ^1H NMR ($CDCl_3$): δ = 7.01 (d, J = 8 Hz, arom. H), 6.60 (d, J = 8.4 Hz, arom. H), 3.90 (NH), 3.48 (dd, J = 13 Hz, 1.4 Hz, CH_2), 2.96 (dd, J = 13.2 Hz, 3.2 Hz, CH_2), 2.25 (CH_3), 1.98–1.33 (m, Ad cage) ppm. $C_{18}H_{26}NO_3P$ (335.4): calcd. C 64.46, H 7.81, N 4.18; found C 64.37, H 7.79, N 4.26.

Preparation of 3a: A solution of Ph_2PCH_2OH (0.245 g, 0.906 mmol) in methanol (HPLC grade, 5 mL) was added to a

methanol (HPLC grade, 5 mL) suspension of **2** (0.327 g, 0.906 mmol) by cannula. The mixture was stirred for 24 h and the solid **3a** collected by suction filtration and dried in vacuo. Yield: 0.412 g, 87%. For **3a**, ^{1}H NMR ($CDCl_3$): δ = 7.38–6.72 (m, arom. H), 4.33–4.11 (m, CH_2), 3.56 (d, J = 14.4 Hz, CH_2), 3.10 (dd, J = 14.4 Hz, 5.2 Hz, CH_2), 1.88–1.08 (m, Ad cage) ppm. This procedure was also used for the preparation of **3b** (85%). The purity of **3a** (and **3b**) were shown, by $^{31}P\{^1H\}$ NMR, to be ca. 75–80%. For **3b**, ^{1}H NMR ($CDCl_3$): δ = 7.44–7.24 (m, arom. H), 6.97 (d, J = 8.4 Hz, arom. H), 6.76 (d, J = 8.8 Hz, arom. H), 4.26–4.13 (m, CH_2), 3.53 (d, J = 14.4 Hz, CH_2), 3.10 (dd, J = 14.6 Hz, 5 Hz, CH_2), 2.19 (CH_3), 1.83–1.02 (m, Ad cage) ppm. All efforts to obtain analytical samples of **3a** (and **3b**) have so far been unsuccessful.

Preparation of 4: A mixture of **2a** (0.071 g, 0.221 mmol) and $\{Pd(\kappa^2\text{-}C,N\text{-}C_{16}H_{16}N)Br\}_2$ (0.090 g, 0.110 mmol) in HPLC grade acetone (10 mL) were refluxed for 75 min. After cooling the solution was concentrated under reduced pressure to ca. 2–3 mL and diethyl ether (10 mL)/hexanes (10 mL) added. The solid was collected by suction filtration and dried in vacuo. Yield: 0.113 g, 70%. ^{1}H NMR ($CDCl_3$): δ = 8.22 (d, J = 12.4 Hz, CH=N), 7.67–6.43 (arom. H), 4.70 (NH), 4.23 (d, J = 12.8 Hz, CH_2), 3.77–3.63 (m, CH_2), 2.43 and 2.24 (CH_3), 2.41–1.46 (m, Ad cage) ppm. $C_{33}H_{37}BrN_2O_3PPd$ (726.99): calcd. C 54.52, H 5.13, N 3.85; found C 54.09, H 5.47, N 3.77.

Preparation of 5a: 3a (0.119 g, 0.192 mmol) was added as a solid to a CH_2Cl_2 (10 mL) solution of $PtCl_2$(cod) (0.072 g, 0.192 mmol). The solution was stirred for 2.5 h and then concentrated to ca. 1–2 mL under reduced pressure. Addition of diethyl ether (20 mL) afforded a solid which was collected by suction filtration and dried in vacuo. Yield: 0.129 g, 85%. $C_{30}H_{35}Cl_2NO_3P_2Pt\cdot 0.5CH_2Cl_2$ (828.04): calcd. C 44.24, H 4.38, N 1.69; found C 43.94, H 3.89, N 2.04. A similar procedure was also used for the preparation of **5b** (92%). ^{1}H NMR ($CDCl_3$): δ = 8.02–7.31 (m, arom. H), 7.04 (d, J = 8.4 Hz, arom. H), 6.80 (d, J = 8.8 Hz, arom. H), 4.27–4.09 (m, CH_2), 3.47–3.23 (m, CH_2), 2.23 (CH_3), 1.76–1.19 (m, Ad cage) ppm. $C_{31}H_{37}Cl_2NO_3P_2Pt\cdot CH_2Cl_2$ (884.53): calcd. C 43.44, H 4.44, N 1.58; found C 42.94, H 4.03, N 1.49. The dichloropalladium(II) complexes **5c** (from **3a**) and **5d** (from **3b**) were prepared in 98% and 92% yields respectively. For **5c:** $C_{30}H_{35}Cl_2NO_3P_2Pd\cdot 0.75CH_2Cl_2$ (760.61): calcd. C 48.56, H 4.84, N 1.84; found C 48.84, H 4.48, N 1.57. For **5d**, ^{1}H NMR ($CDCl_3$): δ = 7.97–7.33 (m, arom. H), 7.04 (d, J = 8 Hz, arom. H), 6.76 (d, J = 8 Hz, arom. H), 4.11–4.03 and 3.52–3.22 (m, CH_2), 2.23 (CH_3), 1.81–1.27 (m, Ad cage) ppm. $C_{31}H_{37}Cl_2NO_3P_2Pd\cdot 2.5CH_2Cl_2$ (923.27): calcd. C 43.58, H 4.59, N 1.52; found C 43.09, H 4.24, N 1.71.

Preparation of 6: 3a (0.098 g, 0.151 mmol) was added as a solid to a CH_2Cl_2 (10 mL) solution of $\{RuCl_2(\eta^6\text{-}p\text{-cym})\}_2$ (0.046 g, 0.075 mmol). The solution was stirred for 45 min and then concentrated to ca. 1–2 mL under reduced pressure. Addition of diethyl ether (25 mL) and hexane (25 mL) afforded a red/orange solid which was collected by suction filtration and dried in vacuo. Yield: 0.078 g, 63%. $C_{40}H_{49}Cl_2NO_3P_2Ru\cdot 0.25CH_2Cl_2$ (847.03): calcd. C 57.07, H 5.89, N 1.65; found C 56.97, H 6.27, N 1.66. A similar procedure was also used for the preparation of the iridium(III) complex **7** (96%). For **7**, ^{1}H NMR ($CDCl_3$): δ = 7.86–6.36 (m, arom. H), 5.26 (d, J = 4 Hz, CH_2) and 5.08 (d, J = 16 Hz, CH_2), 2.98 (dd, J = 15.2 Hz, 4.4 Hz, CH_2) and 2.71 (d, J = 15.2 Hz, CH_2), 1.79–1.11 (m, Ad cage), 1.28 (d, J = 2 Hz, Cp*) ppm. $C_{40}H_{50}Cl_2IrNO_3P_2\cdot 4.5CH_2Cl_2$ (1300.26): calcd. C 41.11, H 4.57, N 1.08; found C 40.78, H 4.41, N 1.02.

Preparation of 8: AuCl(tht) (0.016 g, 0.050 mmol) was added as a solid to a CH_2Cl_2 (10 mL) solution of **6** (0.055 g, 0.050 mmol). The solution was stirred for 45 min and then concentrated to ca. 1–2 mL under reduced pressure. Addition of diethyl ether (25 mL) and hexane (25 mL) afforded a red/orange solid which was collected by suction filtration and dried in vacuo. Yield: 0.049 g, 93%. For **8**, $C_{40}H_{49}AuCl_3NO_3P_2Ru$ (1058.22): calcd. C 45.40, H 4.67, N 1.32; found C 46.26, H 4.48, N 1.06. A similar procedure was also used for the preparation of the iridium(III) complex **9** (77%). For **9**, ^{1}H NMR ($CDCl_3$): δ = 7.89–6.45 (m, arom. H), 5.26 (d, J = 16.8 Hz, CH_2) and 4.95 (d, J = 16 Hz, CH_2), 3.56 (d, J = 16 Hz, CH_2) and 3.30 (dd, J = 15.8 Hz, 4.2 Hz, CH_2), 2.19–1.10 (m, Ad cage), 1.28 (d, J = 2 Hz, Cp*) ppm. $C_{40}H_{50}AuCl_3IrNO_3P_2$ (1150.36): calcd. C 41.77, H 4.38, N 1.22; found C 41.69, H 4.17, N 1.20.

Preparation of 10: 3a (75% purity, 0.117 g, 0.164 mmol) was added as a solid to a CH_2Cl_2 (10 mL) solution of AuCl(tht) (0.105 g, 0.328 mmol). The solution was stirred for 45 min in the dark and then concentrated to ca. 1–2 mL under reduced pressure. Addition of diethyl ether (25 mL) and hexane (25 mL) afforded solid **10** which was collected by suction filtration and dried in vacuo. Yield: 0.135 g, 84%. $C_{30}H_{35}Au_2Cl_2NO_3P_2\cdot 0.75C_6H_{14}$ (1049.08): calcd. C 39.50, H 4.37, N 1.34; found C 39.25, H 3.76, N 1.55.

X-ray Crystallography: Vapour diffusion of diethyl ether into an acetone solution (for **4**) or $CDCl_3$ solutions (for **5a** or **5b**) over several days afforded suitable X-ray quality crystals. Compound **9** was obtained by slow diffusion of petroleum ether (b.p. 60–80 °C) into a $CDCl_3$ solution whereas slow diffusion of hexane into a CH_2Cl_2 solution gave suitable crystals of compound **6**. Compound **2a** was obtained upon allowing a CH_3OH filtrate to stand for several days. Compounds **7** and **8** were obtained by slow evaporation to dryness of a CH_2Cl_2/petroleum ether (b.p. 60–80 °C) or $CHCl_3$/hexane solution respectively. Details for the crystal data of **2a** and **4**–**9** and a summary of data collection parameters are given in Table 5 and Table 6.

Measurements were made with either a Bruker AXS SMART 1000 CCD area-detector diffractometer[57] for **2a**, **4**, **5a**, **5b** and **8** 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[58,59] equipped with a rotating anode generator for **6**, **7** and **9**. Cell parameters were refined from the observed ω angles of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, on the basis of symmetry-equivalent and repeated reflections. The structures were solved by direct methods (Patterson synthesis for **5a**, **5b**, **8** and **9**), and refined on F^2 values for all unique data by full-matrix least-squares.[60] Tables 5 and 6 give further details. All non-hydrogen atoms were refined anisotropically. For **5b** a molecule of Et_2O is badly disordered over an inversion centre while in **7** there is a disordered molecule of CH_2Cl_2 in a general position; these were modelled by the Platon Squeeze procedure.[61] In **6** a molecule of CH_2Cl_2 is disordered over an inversion centre. In **8** a molecule of $CHCl_3$ was disordered with the three Cl atoms split over two sets of positions, the major sites occupied 72.1(3)%. The disorder in **6** and **8** was modelled with restraints applied to assist geometry and anisotropic displacement parameters.

CCDC-629342 to -629349 (for compounds **2a**, **4** and **5a**–**9**) contain the 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. at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.ac.uk) on request, quoting the deposition numbers.

Table 5. Crystallographic data for **2a**, **4**, **5a** and **5b**.

Compound	**2a**	**4**	**5a**·$CHCl_3$	**5b**·$CHCl_3$·1/2OEt_2
Empirical formula	$C_{17}H_{24}NO_3P$	$C_{33}H_{40}BrN_2O_3PPd$	$C_{31}H_{36}Cl_5NO_3P_2Pt$	$C_{34}H_{43}Cl_5NO_{3.5}P_2Pt$
Formula weight	321.34	729.95	904.89	955.97
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	*C*2/*c*	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a [Å]	21.6340(12)	10.0874(5)	14.8165(10)	15.6828(7)
b [Å]	8.0270(4)	12.1965(7)	16.6937(11)	12.8162(6)
c [Å]	21.0236(12)	14.4382(8)	14.3993(10)	18.2303(8)
α [°]		70.580(2)		
β [°]	116.317(2)	80.716(2)	90.655(2)	93.261(2)
γ [°]		75.021(2)		
Volume [Å^3]	3272.5(3)	1612.81(15)	3561.3(4)	3658.2(3)
Z	8	2	4	4
T [K]	150(2)	200(2)	150(2)	150(2)
Density (calcd.) [Mg/m^3]	1.304	1.503	1.688	1.736
Absorption coeff. [mm^{-1}]	0.180	1.899	4.437	4.326
Crystal habit	colourless tablet	colourless block	colourless plate	colourless needle
Crystal size [mm^3]	0.25 × 0.19 × 0.07	0.60 × 0.30 × 0.25	0.31 × 0.22 × 0.05	0.36 × 0.04 × 0.02
θ range [°]	2.10–29.00	1.81–28.88	1.84–29.03	1.67–29.09
Reflections collected	14145	14148	31031	31911
Independent reflections	3988 [R_{int} = 0.030]	7379 [R_{int} = 0.019]	8608 [R_{int} = 0.048]	8854 [R_{int} = 0.039]
Final *R*, R_w	0.041, 0.100	0.027, 0.069	0.040, 0.101	0.040, 0.117

Table 6. Crystallographic data for **6**–**9**.

Compound	**6**·1/2CH_2Cl_2	**7**·CH_2Cl_2	**8**·$CHCl_3$	**9**
Empirical formula	$C_{40.50}H_{50}Cl_3NO_3P_2Ru$	$C_{41}H_{52}Cl_4IrNO_3P_2$	$C_{41}H_{50}AuCl_6NO_3P_2Ru$	$C_{40}H_{50}AuCl_3IrNO_3P_2$
Formula weight	868.17	1002.78	1177.50	1150.27
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	*C*2/*c*	$P\bar{1}$	*C*2/*c*
a [Å]	12.7297(12)	27.2637(13)	12.5894(6)	27.5062(17)
b [Å]	13.6693(12)	11.6769(6)	14.1427(6)	11.7458(6)
c [Å]	13.9918(14)	27.5628(14)	15.2006(7)	27.3935(17)
α [°]	65.609(5)		64.547(2)	
β [°]	68.646(4)	112.943(2)	80.820(2)	111.376(2)
γ [°]	66.295(6)		68.287(2)	
Volume [Å^3]	1972.2(3)	8080.6(7)	2270.36(18)	8241.5(8)
Z	2	8	2	8
T [K]	120(2)	120(2)	150(2)	120(2)
Density (calcd.) [Mg/m^3]	1.462	1.649	1.722	1.854
Absorption coeff. [mm^{-1}]	0.721	3.688	4.021	7.092
Crystal habit	orange plate	yellow plate	red block	orange lath
Crystal size [mm^3]	0.17 × 0.14 × 0.04	0.34 × 0.30 × 0.02	0.37 × 0.24 × 0.16	0.22 × 0.06 × 0.02
θ range [°]	2.97–25.00	1.60–27.59	1.69–28.99	2.91–27.60
Reflections collected	32530	29404	20226	37377
Independent reflections	6917 [R_{int} = 0.105]	8118 [R_{int} = 0.069]	10522 [R_{int} = 0.020]	9397 [R_{int} = 0.057]
Final *R*, R_w	0.075, 0.156	0.057, 0.177	0.028, 0.060	0.051, 0.103

Acknowledgments

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