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Synthesis and characterization of Ru^{II}/Au^{I}, Pd^{II}/Au^{I}, $Pd^{II}/2Au^{I}$, $Pt^{II}/2Au^{I}$ and $Cu^{I}/2Au^{I}$ heterometallic complexes of cyclodiphosphazane *cis*-$\{(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)\}_2$

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Abstract

Mononuclear complexes of cyclodiphosphazane with an uncoordinated phosphorus centre $[RuCl_2(\eta^6\text{-cymene})\{L\text{-}\kappa P\}]$ (**1a**) (L = *cis*-$\{(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)\}_2$) and $[PdCl_2(PEt_3)\{L\text{-}\kappa P\}]$ (**1b**) react with 1 equiv. of $[AuCl(SMe_2)]$ to afford Ru^{II}/Au^{I} and Pd^{II}/Au^{I} heterodinuclear complexes $[RuCl_2(\eta^6\text{-cymene})\{\mu\text{-}L\text{-}\kappa P,\kappa P\}AuCl]$ (**2**) and $[PdCl_2(PEt_3)\{\mu\text{-}L\text{-}\kappa P,\kappa P\}AuCl]$ (**3**), respectively. Heterotrinuclear complexes $[PdCl_2\{\mu\text{-}L\text{-}\kappa P,\kappa P\}_2(AuCl)_2]$ (**4**), $[PtCl_2\{\mu\text{-}L\text{-}\kappa P,\kappa P\}_2(AuCl)_2]$ (**5**) and $[CuI\{\mu\text{-}L\text{-}\kappa P,\kappa P\}_2(AuCl)_2]$ (**6**) containing $Pd^{II}/2Au^{I}$, $Pt^{II}/2Au^{I}$ and $Cu^{I}/2Au^{I}$ metal centers have been synthesized from the reactions of *trans*-$[PdCl_2\{L\text{-}\kappa P\}_2]$ (**1c**), *cis*-$[PtCl_2\{L\text{-}\kappa P\}_2]$ (**1d**) and $[CuI\{\{L\text{-}\kappa P\}_2]$ (**1f**) respectively, with 2 equiv. of $[AuCl(SMe_2)]$. Molecular structures of complexes **2**, **3** and **4** were established by single crystal X-ray diffraction studies.

Keywords: Cyclodiphosphazanes; Heterometallic complexes; Mono- and bidentate coordination; Crystal structures

1. Introduction

Over the past decade cyclodiphosphazanes have been extensively used for the syntheses of several phosphorus–nitrogen macrocycles and cages [1]. Stahl and Chivers utilized amide substituted cyclodiphosphazanes of the type *cis*-$[(^tBuNH)P(E)(\mu\text{-}N^tBu)]_2$ (E = lone pair, O, S, Se) to stabilize various main group and transition metals [2]. Earlier reports on the coordination chemistry of cyclodiphosphazanes were limited to group-6 and 10 metals [3]. Recently we investigated [4] the coordination behavior of the cyclodiphosphazane *cis*-$[(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)]_2$ with various transition metal reagents and observed the *cis*-$[(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)]_2$ ligand selectively forming mononuclear complexes with metal reagents such as $[RuCl_2(\eta^6\text{-cymene})]_2$, $[MCl(COD)]_2$ (M = Rh, Ir), $[PdCl_2(PEt_3)]_2$, $[MCl_2(COD)]$ (M = Pd, Pt) and AgCN irrespective of the stoichiometry and the reaction conditions. In contrast, reactions with $[Rh(CO)_2Cl]_2$, $[PdCl(\eta^3\text{-}C_3H_5)]_2$, CuX (X = Cl, Br, I), AgOTf and $AuCl(SMe_2)$ afforded complexes with ligand exhibiting both monodentate and bridged bidentate coordination modes. The bridging coordination mode of the cyclodiphosphazane leads to the formation of novel metallamacrocycles (Rh^{I}, Au^{I}) and one dimensional coordination polymers (Cu^{I} and Ag^{I}). The monodentate coordination of the cyclodiphosphazane leads to the complex having a free P^{III} site for further coordination. This interesting coordination behavior of *cis*-$[(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)]_2$ can be utilized for the syntheses of numerous hetero-multinuclear complexes containing two or more different late transition metals. Heterometallic complexes containing two different early or late transition metals are difficult to synthesize due to the similar reactivity of late metals toward symmetrical ligands, whilst late-early heterometallic (LEHM) complexes can be conveniently prepared using amide or alkoxy functionalized phosphine ligands due to the preference of

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early metals for hard centers and late metals for soft metal centers [5]. Heterometallic complexes containing platinum metals which are far apart with out metal–metal interactions can be utilized as one pot catalysts to promote more than one type of catalytic reaction [6]. In this context, we report the syntheses of Ru^{II}/Au^{I}, Pd^{II}/Au^{I}, $Pd^{II}/2Au^{I}$, $Pt^{II}/2Au^{I}$ and $Cu^{I}/2Au^{I}$ heterometallic complexes anchored by the cyclodiphosphazane, *cis*-$[(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)]_2$ and also the molecular structures of Ru^{II}/Au^{I}, Pd^{II}/Au^{I}, $Pd^{II}/2Au^{I}$ heterometallic derivatives.

2. Experimental

All experimental manipulations were carried out under an atmosphere of dry nitrogen using Schlenk techniques. Solvents were dried and distilled prior to use by conventional methods [7]. The compounds $[RuCl_2(\eta^6\text{-cymene})\{\mu\text{-L-}\kappa P\}]$ (**1a**), $[PdCl_2(PEt_3)\{\mu\text{-L-}\kappa P\}]$ (**1b**), *trans*-$[PdCl_2\{\mu\text{-L-}\kappa P\}_2]$ (**1c**), *cis*-$[PtCl_2\{\mu\text{-L-}\kappa P\}_2]$ (**1d**) [4b], $[CuI\{\mu\text{-L-}\kappa P\}_2]$ (**1e**) [4c] (**L** = *cis*-$\{(o\text{-}MeOC_6H_4O)P(\mu\text{-}N^tBu)\}_2$) and $[AuCl(SMe_2)]$ [8] were prepared according to the published procedures.

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded using Varian Mercury Plus spectrometer operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. Microanalyses were performed on a Carlo Erba Model 1112 elemental analyzer. Mass spectrometry experiments were carried out using Waters Q-Tof micro-YA-105. Melting points were recorded in capillary tubes and are uncorrected.

2.1. Synthesis of $[RuCl_2(\eta^6\text{-cymene})\{\mu\text{-L-}\kappa P,\kappa P\}AuCl]$ (2)

A dichloromethane (7 mL) solution of $[AuCl(SMe_2)]$ (20.2 mg, 0.069 mmol) was added dropwise to $[RuCl_2(\eta^6\text{-cymene})\{\mu\text{-L-}\kappa P\}]$(**1a**) (52.3 mg, 0.069 mmol) in CH_2Cl_2 (5 mL) at room temperature with stirring. Stirring was continued for 6 h with minimum light exposure. The reaction mixture was concentrated to 5 mL under reduced pressure and to this was added 3 mL of hexane. Storage at −30 °C for one day afforded the product as dark orange crystals (52.5 mg, 77%). M.p.: 170–172 °C (dec). *Anal.* Calc. for $C_{32}H_{46}N_2P_2O_4Cl_3RuAu$: C, 38.85; H, 4.68; N, 2.83. Found: C, 38.59; H, 4.71; N, 3.05%. ^1H NMR (400 MHz; $CDCl_3$, 25 °C): $\delta_H = 7.26–6.90$ (m, 8H, Ph), 5.47 (d, $J_{HH} = 6$ Hz, 2H, $MeC_6H_4{}^iPr\text{-}p$), 5.34 (d, 2H, $MeC_6H_4{}^iPr\text{-}p$), 3.85 (s, 3H, OMe), 3.86 (s, 3H, OMe), 2.92 (sep, 1H, CH), 2.16 (s, 3H, Me), 1.54 (s, 18H, ^tBu), 1.28 (d, $J_{HH} = 6.8$ Hz, 6H, CMe_2) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 25 °C): $\delta_P = 129.3$ (s, 1P, PRu), 105.3 (s, 1P, PAu) ppm.

2.2. Synthesis of $[PdCl_2(PEt_3)\{\mu\text{-L-}\kappa P,\kappa P\}AuCl]$ (3)

$[AuCl(SMe_2)]$ (19.2 mg, 0.065 mmol) dissolved in 5 mL of dichloromethane was added to $[PdCl_2(PEt_3)\{\mu\text{-L-}\kappa P\}]$ (**1b**) (48.7 mg, 0.065 mmol) also in dichloromethane at room temperature. The resulting reaction mixture was stirred for 4 h, concentrated to 5 mL and diluted with 5 mL CH_3CN. Slow evaporation of CH_2Cl_2 from this solution at room temperature yielded the product as yellow crystals (58.6 mg, 92%). M.p.: 218–220 °C (dec). *Anal.* Calc. for $C_{28}H_{47}N_2O_4P_3PdAuCl_3$: C, 34.37; H, 4.84; N, 2.86. Found: C, 34.56; H, 4.98; N, 2.79%. ^1H NMR (400 MHz; $CDCl_3$, 25 °C): $\delta_H = 7.05–6.84$ (m, 8H, Ph), 3.87 (s, 3H, OMe), 3.79 (s, 3 H, OMe), 2.27 (m, 2H, CH_2), 1.55 (s, 18H, ^tBu), 1.26 (m, 3H, CH_3) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 25 °C): $\delta_P = 108.9$ (d, $^2J_{PP} = 39$ Hz, 1P, AuP), 83.8 (dd, 1P, PdP), 30.2 (d, $^2J_{PP} = 16$ Hz, 1P, $PdPEt_3$) ppm. MS(EI, *m*/*z*): 942.76 (M–Cl).

2.3. Synthesis of $[PdCl_2\{\mu\text{-L-}\kappa P,\kappa P\}_2(AuCl)_2]$ (4)

A dichloromethane solution (7 mL) of $[AuCl(SMe_2)]$ (48.1 mg, 0.164 mmol) was added dropwise to a well-stirred dichloromethane solution (10 mL) of *trans*-$[PdCl_2\{\mu\text{-L-}\kappa P\}_2]$ (**1c**) (88.3 mg, 0.082 mmol) at room temperature. The yellow reaction mixture was stirred at room temperature for 4 h, concentrated to 10 mL under reduced pressure and diluted with 5 mL of CH_3CN. Storage at room temperature for 3 days afforded the product as yellow crystals (110 mg, 87%). M.p.: 206–208 °C (dec). *Anal.* Calc. for $C_{44}H_{64}N_4P_4O_8PdAu_2Cl_4$: C, 34.24; H, 4.18; N, 3.63. Found: C, 34.48; H, 4.27; N, 3.44%. ^1H NMR (400 MHz; $CDCl_3$, 25 °C): $\delta_H = 8.04–6.83$ (m, 16 H, Ph), 3.88 (s, 6H, OMe), 3.86 (s, 6H, OMe), 1.63 (s, 36H, ^tBu) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 25 °C): $\delta_P = 105.0$ (d, $^2J_{PP} = 40$ Hz, 1P, PAu), 70.5 (d, 1P, PPd) ppm.

2.4. Synthesis of $[PtCl_2\{\mu\text{-L-}\kappa P,\kappa P\}_2(AuCl)_2]$ (5)

A dichloromethane solution (7 mL) of $[AuCl(SMe_2)]$ (22.1 mg, 0.079 mmol) was added dropwise to a well-stirred dichloromethane solution (5 mL) of *cis*-$[PtCl_2\{\mu\text{-L-}\kappa P\}_2]$ (**1d**) (43.7 mg, 0.037 mmol) at room temperature. The reaction mixture was stirred for 4 h, concentrated to 5 mL and diluted with 3 mL of hexane. Storage at −30 °C for one day afforded a white crystalline product (41.1 mg, 68%). M.p.: 224–226 °C (dec). *Anal.* Calc. for $C_{44}H_{64}N_4O_8P_4Au_2PtCl_4$: C, 32.38; H, 3.95; N, 3.43. Found: C, 32.55; H, 4.12; N, 3.77%. ^1H NMR (400 MHz; $CDCl_3$, 25 °C): $\delta_H = 7.74–6.82$ (m, 16 H, Ph), 3.87 (s, 6H, OMe), 3.83 (s, 6H, OMe), 1.45 (s, 36 H, ^tBu) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 25 °C): $\delta_P = 109.4$ (d, $^3J_{PtP} = 81$ Hz, 2P, AuP), 47.0 (d, $^1J_{PtP} = 5738$ Hz, $^2J_{PP} = 36$ Hz, 2P, PtP) ppm.

2.5. Synthesis of $[CuI\{\mu\text{-L-}\kappa P,\kappa P\}_2(AuCl)_2]$ (6)

A solution of $[AuCl(SMe_2)]$ (46.3 mg, 0.157 mmol) in 7 mL of CH_2Cl_2 was added dropwise to a well-stirred CH_2Cl_2 (5 mL) solution of $[CuI\{\mu\text{-L-}\kappa P\}_2]$ (**1e**) (85.3 mg, 0.078 mmol) at room temperature. The colorless reaction mixture was stirred for 4 h, concentrated to 5 mL under reduced pressure and diluted with 3 mL of hexane. Storage at −30 °C for one day afforded the product as a white crystalline solid (84.9 mg, 70%). M.p.: 194–196 °C (dec). *Anal.* Calc. for $C_{44}H_{64}N_4O_8P_4CuAu_2ICl_2$: C, 33.95; H, 4.14; N, 3.60. Found: C, 33.74; H, 4.06; N, 3.72%. ^1H NMR (400 MHz; $CDCl_3$, 25 °C): $\delta_H = 7.89–6.73$ (m, 16H, Ph), 3.85 (s, 6H, OMe), 3.77 (s, 6H, OMe), 1.52 (s, 36H, ^{t}Bu) ppm. $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$, 25 °C): $\delta_P = 120.9$ (br s, 2P, CuP), 105.9 (s, 2P, AuP) ppm.

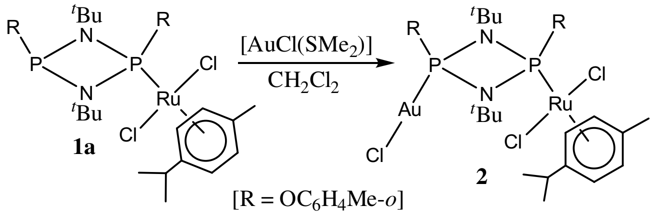
2.6. X-ray crystallography

Crystals of **2**, **3** and **4** were mounted in a CryoLoop with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex attachment of the Bruker APEX CCD diffractometer. Full spheres of intensity data were collected for each crystals as three sets of 400 scans in ω (0.5° per scan at $\phi = 0°$, 90° and 180°) and two sets of 800 scans in ϕ (0.45° per scan at $\omega = -30°$ and 210°). Intensity data were collected using the SMART software package [9] and these were reduced to F^2 values with the SAINT+ software [10] which also performed a global refinement of unit cell parameters using 9217 (for **2**), 9275 (for **3**) and 8300 (for **4**) reflections chosen from the full data set. Crystals of **2** and **3** proved to be twinned and the integration of the raw data was carried out with the two-component version of SAINT+ using the two-component orientation file prepared by CELL_NOW [11] and with the cell parameters of the second domain of the twin constrained to be identical to those of the first domain. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (TWINABS [12] for **2** and **3** and SADABS [13] for **4**). The structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package [14]. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å (aromatic rings) or 0.98 Å (methyl groups)) and included as riding contributions with isotropic displacement parameters 1.2 (aromatic rings) or 1.5 (methyl groups) times those of the attached non-hydrogen atoms.

3. Results and discussion

3.1. Synthesis of heterometallic complexes

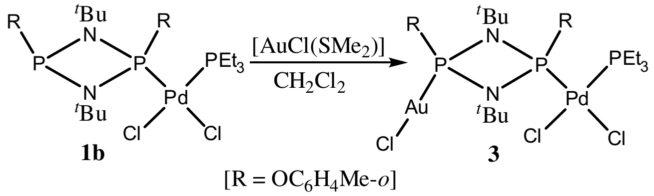
Mononuclear Ru^{II} and Pd^{II} complexes $[RuCl_2(\eta^6\text{-cymene})\{\mu\text{-L-}\kappa P\}]$ (**1a**) and $[PdCl_2(PEt_3)\{\mu\text{-L-}\kappa P\}]$ (**1b**) containing one uncoordinated P^{III} site were prepared from the reaction of *cis*-$\{(o\text{-MeOC}_6H_4O)P(\mu\text{-N}^tBu)\}_2$ (**L**) with $[RuCl_2(\eta^6\text{-cymene})]_2$ and $[PdCl_2(PEt_3)]$, respectively [4b]. Interestingly, the cyclodiphosphazane *cis*-$\{(o\text{-MeO-}C_6H_4O)P(\mu\text{-N}^tBu)\}_2$ afforded exclusively the mononuclear derivatives **1a** and **1b**, irrespective of the reaction conditions and stoichiometry. The Ru^{II}/Au^I heterobimetallic complex $[RuCl_2(\eta^6\text{-cymene})\{\mu\text{-L-}\kappa P,P\}AuCl]$ (**2**) was synthesized by treating **1a** with 1 equiv. of $[AuCl(SMe_2)]$ in dichloromethane as shown in Scheme 1. The ^{31}P NMR spectrum of **2** exhibits two single resonances at 129.3 and 105.3 ppm, respectively, for ruthenium and gold coordinated phosphorus centers of the cyclodiphosphazane. Surprisingly, no $^2J_{PP}$ coupling was observed although complex **1a** shows a $^2J_{PP}$ coupling of 8.7 Hz.



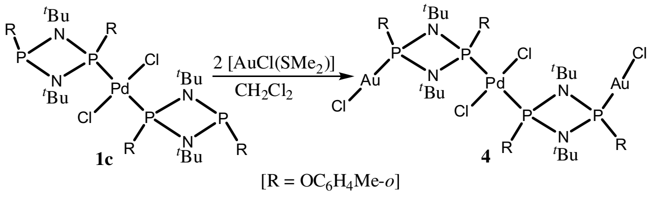
Scheme 1. Synthesis of Ru^{II}/Au^I complex.

Addition of 1 equiv. of $[AuCl(SMe_2)]$ to a dichloromethane solution of $[PdCl_2(PEt_3)\{\mu\text{-L-}\kappa P\}]$ (**1b**) results in the formation of a Pd^{II}/Au^I heterobimetallic complex $[PdCl_2(PEt_3)\{\mu\text{-L-}\kappa P,\kappa P\}AuCl]$ (**3**) in quantitative yield (Scheme 2). The ^{31}P NMR spectrum of **3** exhibits three signals due to the presence of three P-centers. The phosphorus-31 resonance corresponding to the Au-coordinated centre appears as a doublet at 108.9 ppm, with a $^2J_{PP}$ coupling of 39 Hz, whereas the Pd-bound phosphorus of the cyclodiphosphazane appears as a doublet of doublets centered at 83.8 ppm due to the coupling with two different neighboring phosphorus centers. The signal corresponding to PEt_3 appears as a doublet at 30.2 ppm with a $^2J_{pp}$ coupling of 16 Hz.

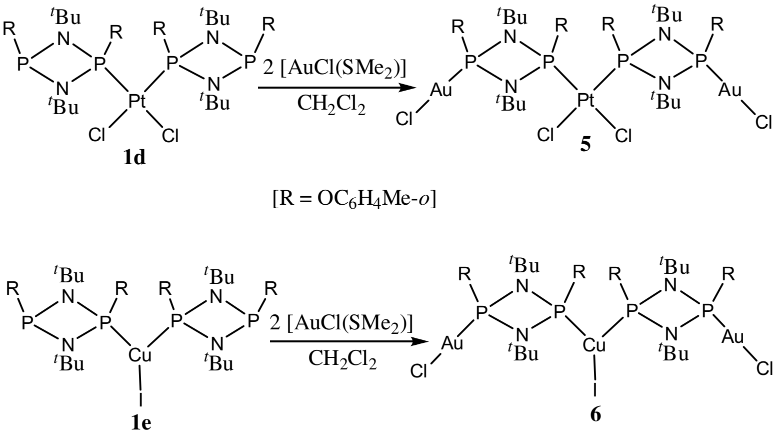
The reaction of 2 equiv. of *cis*-$\{(o\text{-MeOC}_6H_4O)P\text{-}(\mu\text{-N}^tBu)\}_2$ with $[PdCl_2(NCPh)_2]$ or $[PdCl_2(SMe_2)_2]$ afforded *trans*-$[PdCl_2\{\mu\text{-L-}\kappa P\}_2]$ (**1c**) exclusively [4b]. The molecular structure of **1c** reveals the *trans* arrangement of two cyclodiphosphazanes with two uncoordinated P^{III} centers



Scheme 2. Synthesis of Pd^{II}/Au^I complex.



Scheme 3. Synthesis of $Pd^{II}/2Au^I$ complex.



Scheme 4. Synthesis of $Pt^{II}/2Au^{I}$ and $Cu^{I}/2Au^{I}$ complexes.

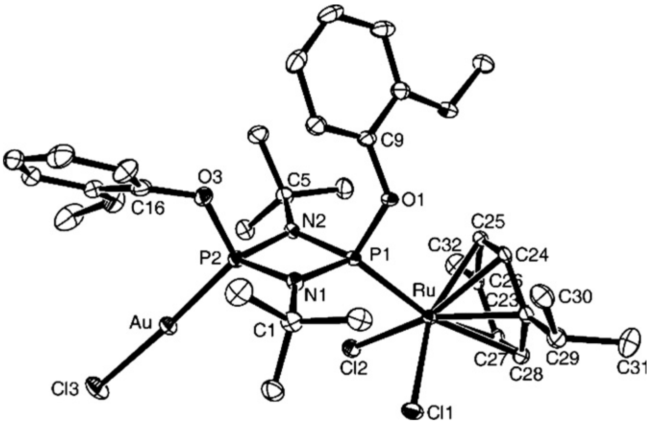


Fig. 1. ORTEP drawing of compound **2**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

projecting in an anti-parallel manner so this compound can serve as an excellent metalloligand for designing hetero polynuclear complexes. The 1:2 reaction between *trans*-[PdCl$_2${μ-L-κP}$_2$] (**1c**) and [AuCl(SMe$_2$)] in dichloromethane affords a $Pd^{II}/2Au^{I}$ hetero-trinuclear complex [PdCl$_2${μ-L-κP,κP}$_2$(AuCl)$_2$] (**4**) as shown in Scheme 3. The ^{31}P NMR spectrum of **4** exhibits two doublets centered at 105 and 70.5 ppm, respectively, for Au and Pd coordinated centers with a $^2J_{PP}$ coupling of 40 Hz. Again, the $^2J_{PP}$ coupling is not observed in *trans*-[PdCl$_2${μ-L-κP}$_2$] (**1c**) which exhibited single resonances for coordinated and uncoordinated P-centers.

Heterotrinuclear complexes [PtCl$_2${μ-L-κP,κP}$_2$(AuCl)$_2$] (**5**) and [CuI{μ-L-κP,κP}$_2$(AuCl)$_2$] (**6**) containing $Pt^{II}/2Au^{I}$ and $Cu^{I}/2Au^{I}$ metal centers were synthesized from

Table 1
Crystallographic information for **2**, **3** and **4**

	2	**3**	**4**
Formula	$C_{32}H_{46}AuCl_3N_2O_4P_2Ru$	$C_{28}H_{47}AuCl_3N_2O_4P_3Pd$	$C_{44}H_{64}Au_2Cl_4N_4O_8P_4Pd$
Formula weight	989.03	978.30	1543.03
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	13.453(1)	10.973(1)	10.723(3)
b (Å)	13.589(1)	15.218(2)	19.685(1)
c (Å)	20.634(2)	21.589(3)	13.700(1)
α (°)	90	90	90
β (°)	97.982(1)	98.630(2)	107.307(1)
γ (°)	90	90	90
V (Å^3)	3735.7(6)	3564.3(8)	2760.8(3)
Z	4	4	2
ρ_{calc} (g cm^{-3})	1.759	1.823	1.856
μ (Mo Kα) (mm^{-1})	4.664	5.010	5.984
$F(000)$	1952	1928	1504
Crystal size (mm)	$0.12 \times 0.18 \times 0.23$	$0.15 \times 0.17 \times 0.26$	$0.16 \times 0.19 \times 0.25$
T (K)	100	100	100
2θ range (°)	2.1–28.4	2.2–28.3	2.2–28.3
Total number of reflections	23530	23926	48400
Number of independent reflections [R_{int}]	9361 [0.074]	8888 [0.042]	6846 [0.032]
R_1^a	0.0351	0.0341	0.0252
wR_2^b	0.0776	0.0845	0.0681
Goodness-of-fit (F^2)	0.95	1.01	1.07

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $wR_2 = \{[\sum w(F_o{}^2 - F_c{}^2)/\sum w(F_o{}^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (xP)^2]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

the reaction of *cis*-[PtCl$_2${μ-L-κP}$_2$] (**1d**) and [CuI{μ-L-κP}$_2$] (**1e**) with 2 equiv. of [AuCl(SMe$_2$)] in dichloromethane at room temperature (Scheme 4). The ^{31}P NMR spectrum of **5** exhibits a doublet centered at 109.4 ppm for the gold coordinated center with a $^2J_{PP}$ coupling of 36 Hz along with a $^3J_{PtP}$ coupling of 81 Hz. The platinum bound phosphorus center exhibits a doublet at 47.0 ppm along with very large $^1J_{PtP}$ coupling of 5738 Hz, which confirms the *cis* arrangement of the two cyclodiphosphazanes [15]. The ^{31}P NMR spectrum of complex **6** exhibits two singlets at 120.9 and 105.9 ppm, respectively, for copper and gold coordinated phosphorus centers of the cyclodiphosphazane.

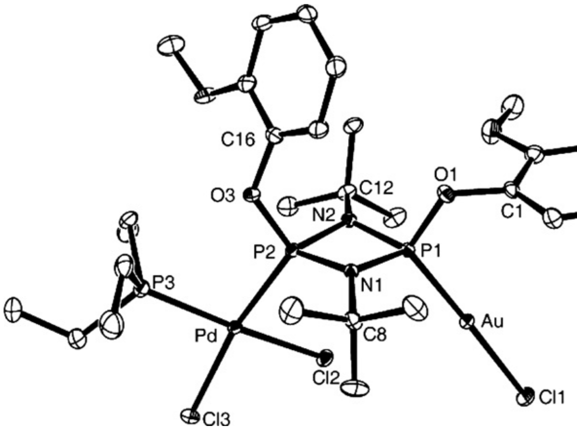


Fig. 2. ORTEP drawing of compound **3**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

3.2. Molecular structures of 2, 3 and 4

The molecular structure of complex **2** is shown in Fig. 1. Crystal data and details of the structure determination are presented in Table 1 while selected bond parameters are listed in Table 2. The X-ray quality crystals of **2** were obtained by slow diffusion of Et$_2$O into a dichloromethane solution of **2** at room temperature. In molecule **2**, the cyclodiphosphazane bridges {AuCl} and {RuCl$_2$(η^6-cymene)} fragments through P-coordination with the metals arranged in a *cis* orientation. The gold center is dicoordinated with a P2–Au–Cl3 angle of 176.51(2)°. The coordination geometry around the ruthenium center in **2** is the typical pseudo octahedral mode with a three-legged piano-stool arrangement commonly observed for half-sandwich phosphine complexes [16]. The Ru–P1 and Au–P2 bond distances are 2.348(1) and 2.205(1) Å, respectively, and agree well with reported values for similar complexes of the type [Cp(PPh$_3$)RuCl-{μ-PPh$_2$(CH$_2$)$_n$PPh$_2$}AuCl] [17].

Perspective views of the molecular structures of **3** and **4** are depicted in Figs. 2 and 3, respectively, with important bond parameters listed in Table 3. Single crystals of **3** and **4** suitable for X-ray diffraction studies were obtained by slow evaporation of dichloromethane from CH$_3$CN/CH$_2$Cl$_2$ solutions of the respective compounds at room temperature. In complexes **3** and **4** the cyclodiphosphazane ligand *cis*-{^{t}BuNP(OC$_6$H$_4$OMe-*o*)}$_2$ (L) bridges the gold and palladium centers to furnish Pd^{II}/Au^I, Pd^{II}/2Au^I heterometallic complexes. The palladium atoms occupy the center of square planar ligand set with the corners occupied by two chlorides and two phosphorus atoms. As complex **4** has crystallographically-imposed centrosymmetry, the P1–Pd–P1^i and Cl1–Pd–Cl1^i bond angles in **4** are exactly linear and similar to the parent compound **1c** [4b]. The gold centers are linear in geometry with P–Au–Cl angles of 176.25(4)° and 179.27(3)°, respectively, for **3** and **4**. The Pd–P bond lengths in **3** and **4** are, respectively the same and slightly shorter than the corresponding bonds in the respective mononuclear complexes **1b** and **1c** [4b]. The exocyclic phenyl substituents on the phosphorus atoms are present in *exo,endo* orientations with respect to the planar P$_2$N$_2$ ring.

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

Bond distances (Å)		Bond angles (°)	
Ru–P1	2.348(1)	P1–Ru–Cl1	96.51(2)
Ru–Cl1	2.406(1)	P1–Ru–Cl2	84.87(2)
Ru–Cl2	2.391(1)	C25–Ru–P1	94.34(7)
Ru–C23	2.236(3)	P2–Au–Cl3	176.51(2)
Ru–C24	2.207(3)	C24–Ru–P1	93.83(7)
Ru–C25	2.211(3)	C25–Ru–P1	94.34(7)
Ru–C26	2.249(3)	C28–Ru–P1	156.07(7)
Ru–C27	2.236(3)	C25–Ru–Cl2	116.06(7)
Ru–C28	2.221(3)	C28–Ru–Cl2	118.94(7)
Au–P2	2.205(1)	P1–N1–P2	96.77(11)
Au–Cl3	2.281(1)	P1–N2–P2	96.70(11)
P1–N1	1.706(2)	N1–P1–N2	81.96(11)
P1–N2	1.709(2)	N1–P2–N2	84.12(11)
P2–N1	1.672(2)	C1–N1–P1	134.85(18)
P2–N2	1.670(2)	C1–N1–P2	127.65(18)
P1–O1	1.616(2)	C9–O1–P1	128.52(15)
P2–O3	1.608(2)	C16–O3–P2	128.38(18)

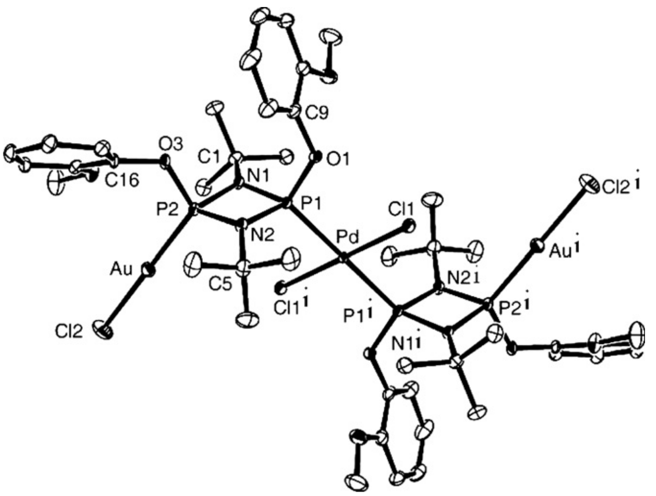


Fig. 3. ORTEP drawing of compound **4**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity.

Table 3
Selected bond distances (Å) and bond angles (°) for **3** and **4**

Bond distances (Å)		Bond angles (°)	
Complex 3			
Au–P1	2.199(1)	P1–Au–Cl1	176.25(4)
Pd–P2	2.233(2)	P2–Pd–P3	96.88(4)
Pd–P3	2.281(2)	P2–Pd–Cl2	83.71(3)
Au–Cl1	2.277(1)	Cl2–Pd–Cl3	89.23(3)
Pd–Cl2	2.346(1)	P3–Pd–Cl3	91.21(3)
Pd–Cl3	2.334(2)	P1–N1–P2	95.31(16)
P1–N1	1.686(3)	P1–N2–P2	95.61(16)
P1–N2	1.687(4)	N1–P1–N2	83.81(16)
P2–N1	1.688(4)	N1–P2–N2	83.99(15)
P2–N2	1.679(3)	P1–O1–C1	121.7(2)
P1–O1	1.606(3)	P2–O3–C16	126.4(2)
P2–O3	1.603(3)	P1–N1–C8	129.4(2)
		P2–N1–C8	130.1(2)
Complex 4			
Pd–P1	2.287(1)	P1–Pd–Cl1	93.65(3)
Pd–Cl1	2.296(1)	P1–Pd–P1^{i}	180.00
Au–P2	2.208(1)	Cl1–Pd–Cl1^{i}	180.00
Au–Cl2	2.281(1)	Cl1–Pd–P1^{i}	86.35(3)
P1–N1	1.689(3)	P2–Au–Cl2	179.27(3)
P1–N2	1.684(3)	P2–N1–P1	95.74(13)
P2–N1	1.673(2)	P2–N2–P1	95.60(15)
P2–N2	1.682(3)	N2–P1–N1	83.83(12)
P1–O1	1.592(2)	N1–P2–N2	84.37(14)
P2–O3	1.607(2)	P1–N1–C1	133.3(2)
		P2–N1–C1	130.2(2)

4. Conclusions

Variable coordination modes exhibited by the cyclodiphosphazane *cis*-$\{(o\text{-MeOC}_6\text{H}_4\text{O})\text{P}(\mu\text{-N}^t\text{Bu})\}_2$ with different transition metal precursors offer straightforward synthetic routes to make a variety of heterometallic complexes in excellent yield. We are investigating the catalytic reactions of these heterometallic complexes for various organic transformations.

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Appendix A. Supplementary material

CCDC 652466, 652467 and 652468 contain the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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