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Coordination Chemistry of the *cyclo*-(P_5tBu_4)$^-$ Ion: Monomeric and Oligomeric Copper(I), Silver(I) and Gold(I) Complexes

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Abstract: [Na{*cyclo*-(P_5tBu_4)}] (**1**) reacts with [CuCl($PCyp_3$)$_2$] (Cyp = *cyclo*-C_5H_9) and [CuCl(PPh_3)$_3$] (1:1) to give the corresponding copper(I) complexes with a tetra-*tert*-butylcyclopentaphosphanide ligand, [Cu{*cyclo*-(P_5tBu_4)}($PCyp_3$)$_2$] (**2**) and [Cu{*cyclo*-(P_5tBu_4)}(PPh_3)$_2$] (**3**). The CuCl adduct of **2**, [Cu_2(μ-Cl){*cyclo*-(P_5tBu_4)}($PCyp_3$)$_2$] (**4**), was obtained from the reaction of **1** with [CuCl($PCyp_3$)$_2$] (1:2). Compounds **2** and **3** rearrange, even at −27 °C, to give [Cu_4{*cyclo*-(P_4tBu_3)P*t*Bu}$_4$] (**5**), in which ring contraction of the [*cyclo*-(P_5tBu_4)]$^-$ anion has occurred. The reaction of **1** with [AgCl($PCyp_3$)]$_4$ or [AgCl(PPh_3)$_2$] (1:1) leads to the formation of [Ag_4{*cyclo*-(P_4tBu_3)P*t*Bu}$_4$] (**6**). Intermediates, which are most probably mononuclear, "[Ag{*cyclo*-(P_5tBu_4)}(PR_3)$_2$]" (R = Cyp, Ph) could be detected in the reaction mixtures, but not isolated. Finally, the reaction of **1** with [AuCl($PCyp_3$)] (1:1) yielded [Au{*cyclo*-(P_5tBu_4)}($PCyp_3$)] (**7**), whereas an inseparable mixture of [Au_3{*cyclo*-(P_5tBu_4)}$_3$] (**8**) and [Au_4{*cyclo*-(P_4tBu_3)P*t*Bu}$_4$] (**9**) was obtained from the analogous reaction with [AuCl(PPh_3)]. Complexes **3**–**7** were characterised by ^{31}P NMR spectroscopy, and X-ray crystal structures were determined for **3**–**9**.

Keywords: copper • gold • P ligands • phosphorus • silver

Introduction

Linear and cyclic oligophosphanes such as *cyclo*-$(PR)_n$ and oligophosphanide anions such as *cyclo*-$(P_nR_{n-1})^-$ and $(P_nR_n)^{2-}$ are interesting objects of study, owing to their analogy to cycloalkanes[1] and because the presence of catenated $(PR)_x$ moieties results in versatile coordination chemistry. Although neutral oligophosphanes have been studied intensively for many decades,[2,3] related anions have been investigated to a lesser extent.[4,5] We recently embarked on a systematic study of the syntheses, structural properties and reactivities of oligophosphanide anions with the specific aim of exploring their utility as building blocks for phosphorus-rich metal complexes. The high-yield synthesis and full characterisation of the sodium salt [Na{*cyclo*-(P_5tBu_4)}] (**1**) and its use to prepare the unusual nickel cyclopentaphosphene complex [Ni(*cyclo*-P_5tBu_3)(PEt_3)$_2$] were early breakthroughs in this project.[6] Subsequent transmetallation reactions of **1** with various halides of the nickel triad revealed its ability to form a structurally diverse class of complexes with Ni, Pd and Pt.[7] We observed that such reactions are markedly dependent on the nature of the co-ligand and the transition metal. Thus, either straightforward salt elimination may occur, or the elimination of *t*BuCl may lead to cyclopentaphosphene complexes containing zero-valent metal atoms, and in some cases ring contraction yielded complexes containing the new {*cyclo*-(P_4tBu_3)P*t*Bu}$^-$ ligand. Interestingly, the reaction of **1** with [RhCl(PPh_3)$_3$] gave [Rh{*cyclo*-(P_5tBu_4)}(PPh_3)$_2$], in which the *cyclo*-(P_5tBu_4)$^-$ anion remained intact.[8] In contrast to the successful transmetallation of **1** with group 9 and group 10 metal halides, redox reactions were observed in attempts to prepare main group metal complexes by reaction of **1** with $SnCl_2$, $PbCl_2$ or $BiCl_3$.[9] Formation of the dimer (*cyclo*-P_5tBu_4)$_2$ as the major product was observed as well as precipitation of elemental Sb, Pb or Bi.[9] Nevertheless, the complex [$AlEt_2$(*cyclo*-P_5tBu_4)] was formed by reaction of **1** with $AlEt_2Cl$.[9] Thus, *cyclo*-(P_5tBu_4)$^-$ shows a fascinating variety of possibilities to form unusual phosphorus-rich metal compounds.

More recently, we have begun to investigate the coordination chemistry of linear oligophosphanediides $(P_nR_n)^{2-}$ ($n =$

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2–4)[10] and have reported the synthesis of the first copper(I) oligophosphanide complex $[Cu_4(P_4Ph_4)_2(PCyp_3)_3]$, which was obtained from the reaction of two equivalents of $[CuCl(PCyp_3)_2]$ with one equivalent of $[Na_2(thf)_5(P_4Ph_4)]$.[11] Inspired by this result, we have now studied the reactivity of [Na{*cyclo*-(P_5tBu$_4$)}] (**1**) with copper(I), silver(I) and gold(I) halides. Although, numerous oligonuclear copper(I) and silver(I) phosphanido complexes are known[12] oligonuclear gold(I) phosphanides with six-, eight- and twelve-membered Au_nP_n rings have been reported only recently.[13] To our knowledge, mononuclear oligophosphanides of copper and gold are unknown.

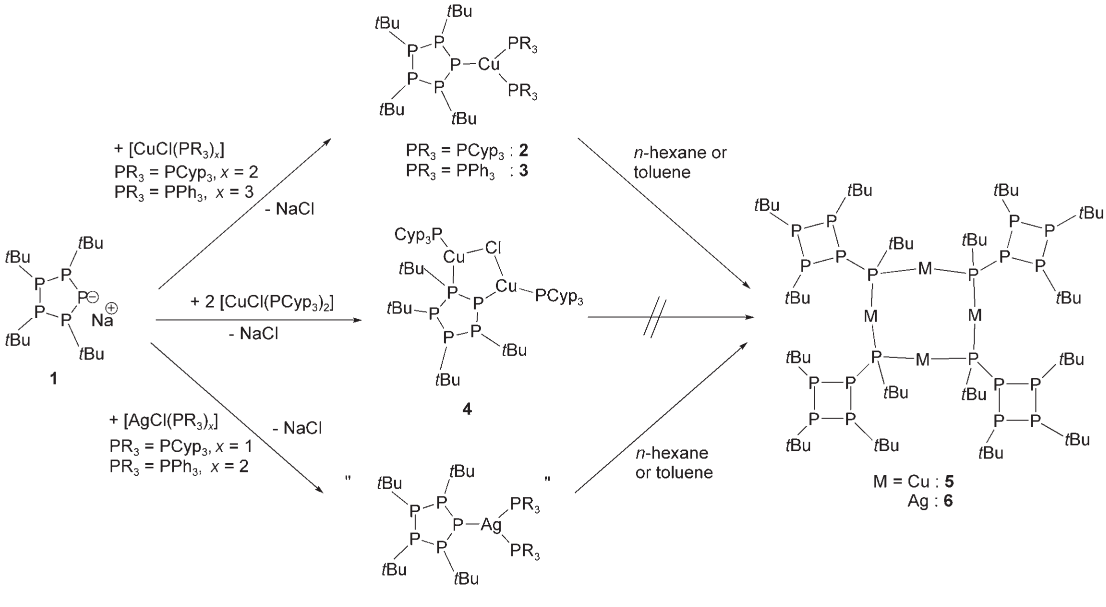
Here we present the synthesis and structural characterisation of unusual, monomeric Cu^I and Au^I oligophosphanido complexes, [Cu{*cyclo*-(P_5tBu$_4$)}($PCyp_3$)$_2$] (**2**), [Cu{*cyclo*-(P_5tBu$_4$)}(PPh_3)$_2$] (**3**) and [Au{*cyclo*-(P_5tBu$_4$)}($PCyp_3$)] (**7**), and rare examples of oligomeric coinage metal oligophosphanides, namely, dinuclear copper(I) chloride complex [Cu_2(μ-Cl){*cyclo*-(P_5tBu$_4$)}($PCyp_3$)$_2$] (**4**), unprecedented trinuclear Au complex [Au_3{*cyclo*-(P_5tBu$_4$)}$_3$] (**8**) and the tetranuclear compounds [M_4{*cyclo*-(P_4tBu$_3$)P*t*Bu}$_4$] (M = Cu, **5**; Ag, **6**; Au, **9**), in which the *cyclo*-(P_5tBu$_4$)$^-$ ligand has rearranged to a {*cyclo*-(P_4tBu$_3$)P*t*Bu}$^-$ group.

Results and Discussion

Syntheses of the complexes: The reaction of [Na{*cyclo*-(P_5tBu$_4$)}] (**1**) with phosphane complexes of group 11 metals is markedly dependent on the metal and the reaction conditions. Thus, $[CuCl(PCyp_3)_2]$ and $[CuCl(PPh_3)_3]$ react with **1** (1:1) to give [Cu{*cyclo*-(P_5tBu$_4$)}($PCyp_3$)$_2$] (**2**) and [Cu{*cyclo*-(P_5tBu$_4$)}(PPh_3)$_2$] (**3**), in which the *cyclo*-(P_5tBu$_4$)$^-$ ligand has remained intact (Scheme 1). A small amount of *cyclo*-(P_5tBu$_4$H)[14] is observed as a by-product. If the reaction of **1** with $[CuCl(PCyp_3)_2]$ is carried out in 1:2 molar ratio (Scheme 1), [Cu_2(μ-Cl){*cyclo*-(P_5tBu$_4$)}($PCyp_3$)$_2$] (**4**) is isolated as the main product. The structure of **4** can be viewed as a 1:1 adduct of **2** and CuCl. The copper(I) complexes **2** and **3** are unstable in *n*-hexane or toluene and rearrange to [Cu_4{*cyclo*-(P_4tBu$_3$)P*t*Bu}$_4$] (**5**) even at −27 °C. Interestingly, rearrangement of **4** to **5** is not observed even after prolonged storage at room temperature. Complex **5** is also obtained, albeit in very modest yield, by refluxing $[CuCl(PCyp_3)_2]$ or $[CuCl(PPh_3)_3]$ with **1** overnight in THF. Once complex **5** is isolated, it is very insoluble[15] and does not decompose easily in air.

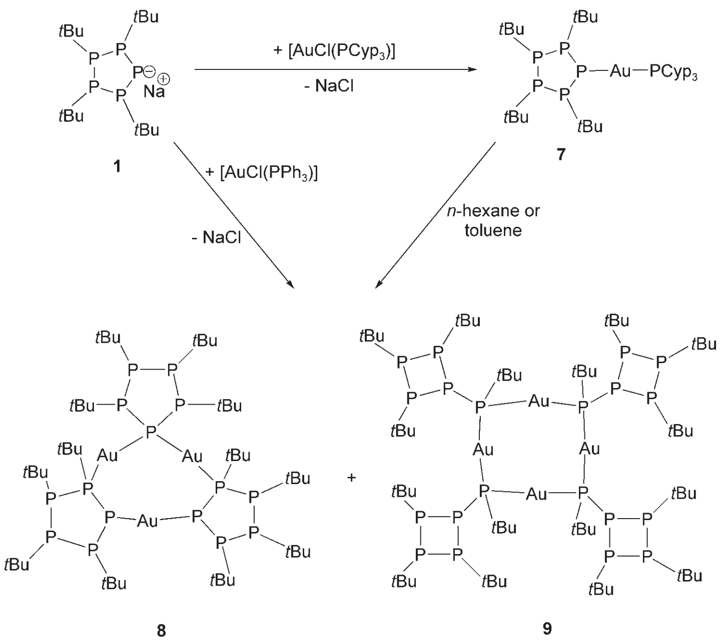
The silver compounds $[AgCl(PCyp_3)]_4$ (see the Supporting Information) and $[AgCl(PPh_3)_2]$ react with **1** (1:4 and 1:1) with formation of [Ag_4{*cyclo*-(P_4tBu$_3$)P*t*Bu}$_4$] (**6**) in moderate yield (Scheme 1). Complex **6** is presumably formed via the corresponding mononuclear silver(I) phosphanido complexes "[Ag{*cyclo*-(P_5tBu$_4$)}(PR_3)$_2$]" (R = Cyp, Ph), which were detected in the reaction mixtures,[16] but could not be isolated even if the reaction was worked up after short reaction times or carried out in the dark. Thus, it seems that the rearrangement of the postulated monomeric intermediates (which were isolated for copper) proceeds faster in the case of silver(I). As in the case of **5**, once **6** is isolated as a solid, it is very insoluble and moderately air stable.

The reaction of **1** with $[AuCl(PCyp_3)]$ (1:1) leads to the formation of [Au{*cyclo*-(P_5tBu$_4$)}($PCyp_3$)] (**7**) in high yield with some *cyclo*-(P_5tBu$_4$H) formed as a side product. Complex **7** decomposes slowly in *n*-hexane or toluene at room temperature over approximately six months to give a mixture of gold complexes. We presume the decomposition products to be **8** and **9**, but these investigations were hampered by the oligomeric nature of the products, which give very complex $^{31}P\{^1H\}$ NMR spectra and are poorly soluble once isolated. Fortunately, reactions of **1** with $[AuCl(PPh_3)]$



Scheme 1.

(1:1), which contains the more labile triphenylphosphane ligand, were more successful and led directly to formation of an inseparable product mixture from which [Au$_3${*cyclo*-(P$_5$*t*Bu$_4$)}$_3$] (**8**) and [Au$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**9**) could be obtained (Scheme 2) in the form of single crystals, which were characterised by X-ray structure determination.

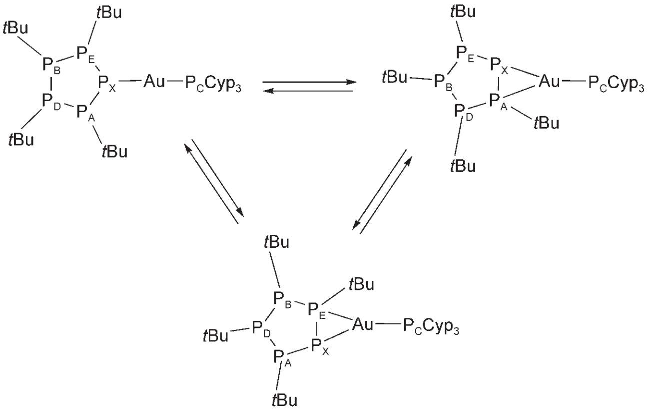


Scheme 2.

^{31}P NMR spectroscopy: ^{31}P NMR spectroscopy is a very powerful tool for characterizing phosphorus-rich compounds in solution. However, the detrimental influence of the quadrupolar moments of the metals employed and the low solubility of most of the isolated compounds even in polar solvents such as THF made full analysis of the ^{31}P NMR spectroscopic data only possible in specific cases.

The ^{31}P{^{1}H} NMR spectrum of [Cu{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)$_2$] (**2**) in THF is quite similar to that reported for **1** and shows a set of broad signals even at −80 °C, which corresponds to the expected AA′BB′CD spin system. A similar spectrum is also observed for [Cu{*cyclo*-(P$_5$*t*Bu$_4$)}(PPh$_3$)$_2$] (**3**) with even broader multiplets down to −80 °C, whereas the ^{31}P{^{1}H} NMR spectrum of [Cu$_2$(μ-Cl){*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)$_2$] (**4**) shows a set of four broad signals at $\delta = 64.0$, 11.6 (PCyp$_3$), 5.2 (PCyp$_3$) and −79.7 ppm (ratio 4:1:1:1). The anionic phosphorus atoms bound to copper give rise to the most shielded signals, at $\delta \approx -94$ (**2**), −97 (**3**) and −80 ppm (**4**). The severe line broadening, which precluded numerical analysis of the coupling patterns, may partly be attributable to the influence of the quadrupolar ^{63}Cu and ^{65}Cu nuclei as well as unidentified dynamic processes involving the *cyclo*-(P$_5$*t*Bu$_4$)$^-$ ligands. Nevertheless, the similarity of the spectra of **2** and **3** to that of **1** leaves little doubt that the *cyclo*-(P$_5$*t*Bu$_4$)$^-$ ligand also remains intact in solution, and the spectrum of **4** is also consistent with its solid-state structure.

Unfortunately, the ^{31}P NMR spectroscopic characterisation of [Cu$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**5**) and [Ag$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**6**) was prevented by their lack of solubility in any common solvents. The more soluble monomeric complex [Au{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)] (**7**) shows three broad multiplets at $\delta \approx 65$, 55 and −55 ppm (ratio 1:4:1) in the ^{31}P{^{1}H} NMR spectrum, which correspond to similar peaks in the spectrum of **2**. The signal at $\delta = 55$ ppm is very broad at room temperature, this suggests a dynamic behaviour for **7**. A variable-temperature ^{31}P{^{1}H} NMR experiment was carried out, and the spectrum recorded at $\delta = -80$ °C revealed a set of six different multiplets ($\delta = 65.4$, 64.6, 63.7, 42.3, 29.6 and −55.8 ppm), and the multiplicity of the high-field signal at $\delta = -55$ ppm, which corresponds to the anionic phosphorus atom of the ring, increased. The increased asymmetry of the spectrum at low temperatures seems to indicate that one of the phosphorus atoms (P$_E$) adjacent to the anionic phosphorus atom (P$_X$) may be involved in coordination, leading to a coordination number of three at the gold atom.[17] At higher temperatures, this structure may be in rapid equilibrium with the identical structure involving the other phosphorus atom (P$_A$) and/or with the linear, two-coordinate structure observed for **7** in the solid state (Scheme 3). The ^{31}P{^{1}H} NMR spectrum of **7** at −80 °C could be successfully simulated with the program SPINWORKS[18] (Figure 1). The observed and calculated coupling patterns are in very good agreement and indicate that the *cyclo*-(P$_5$*t*Bu$_4$) unit is retained. The fragment P$_X$-P$_E$-P$_B$-P$_D$ has the largest absolute values for the ^1J(P,P) coupling constants (^1J(P,P) = −305 to −408 Hz), which indicate some double-bond character,[19] whereas P$_A$ shows smaller ^1J(P,P) coupling constants (^1J(A,D) = −272 Hz, ^1J(A,X) = −199 Hz).



Scheme 3.

Spectra of the reaction mixture of [Na{*cyclo*-(P$_5$*t*Bu$_4$)}] (**1**) with [AuCl(PPh$_3$)] (1:1) show numerous complex, overlapping multiplets besides the by-product PPh$_3$. The complexity of the spectra precluded detailed analyses. Clearly, a mixture of compounds was formed in solution. As the products [Au$_3${*cyclo*-(P$_5$*t*Bu$_4$)}$_3$] (**8**) and [Au$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**9**) could not be separated by fractional crystallisation, and the

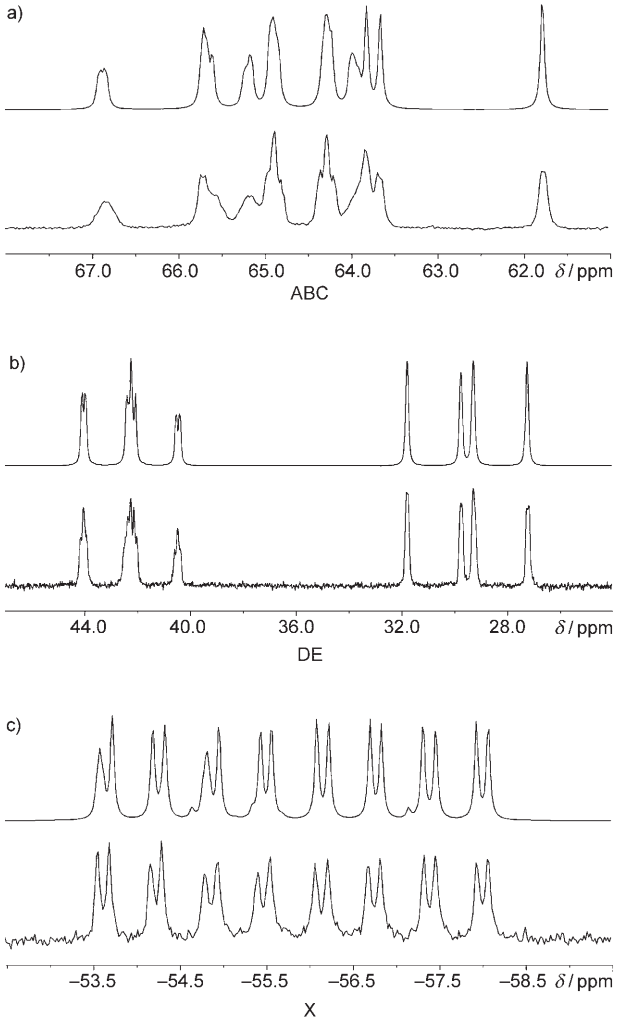


Figure 1. The $^{31}P\{^1H\}$ NMR spectrum of **7** at 193 K. a) $P_{A,B,C}$, b) $P_{D,E}$ and c) P_X. Simulated (top) and experimental (bottom).

compounds had only low solubility, their $^{31}P\{^1H\}$ NMR spectra could not be analysed satisfactorily.

Mass spectrometry: Observation of the molecular ions in the FAB or ESI mass spectra of **2**, **3**, **4** and **7** (see Experimental Section) provides additional support for the compositions obtained from the X-ray structure analyses. In addition, the presence of interesting organyl-free fragments such as $[CuP_6]^+$ and $[CuP_3]^+$ for [Cu{*cyclo*-($P_5t$$Bu_4$)}$(PCyp_3)_2$] (**2**) and [Cu{*cyclo*-($P_5t$$Bu_4$)}$(PPh_3)_2$] (**3**) indicates that these complexes could be suitable precursors for the formation of binary metal phosphides. No molecular ions were observed for oligomeric complexes **5**, **6**, **8** and **9**, although different techniques were employed (ESI-MS, FAB-MS, LDI-MS). However, the detection of characteristic fragments involving trinuclear (**8**) and tetranuclear moieties (**5**, **6**, **9**) further supports the identities established by X-ray crystallography (see Experimental Section).

X-Ray crystallography: Molecular structures of **3**–**9** were determined; selected bond lengths and angles are summarised in Table 1.

The structure of [Cu{*cyclo*-($P_5t$$Bu_4$)}$(PPh_3)_2$] (**3**) shows a mononuclear complex in which the copper atom is coordinated by the anionic phosphorus atom of the *cyclo*-$(P_5tBu_4)^-$ ligand and two triphenylphosphane molecules. To our knowledge, **3** is the first example of a monomeric copper phosphanide. The structure of [Cu_2(μ-Cl){*cyclo*-($P_5t$$Bu_4$)}$(PCyp_3)_2$] (**4**) differs from **3** in that one of the triphenylphosphane ligands has been replaced by a CuCl($PCyp_3$) moiety, which is coordinated by one of the P atoms adjacent to the anionic phosphorus atom of *cyclo*-$(P_5tBu_4)^-$ and displays a bridging chlorine atom. Both **3** and **4** (Figure 2 and Figure 3) show all-*trans* arrangements of the *t*Bu groups and

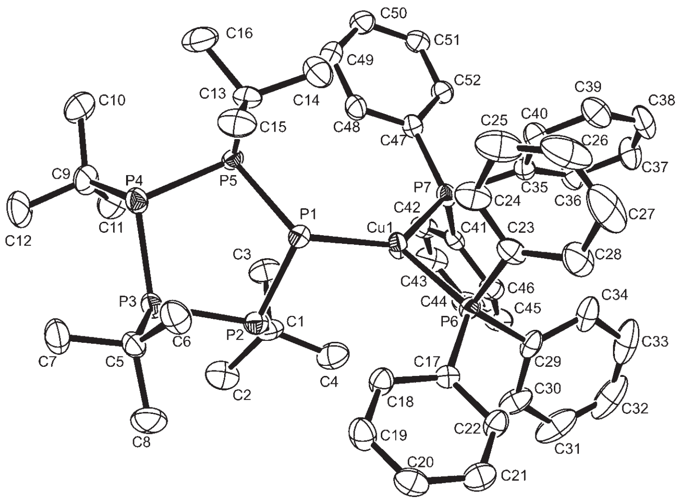


Figure 2. Molecular structure and atom-labelling scheme for **3** with thermal ellipsoids at 50 % probability (hydrogen atoms are omitted for clarity).

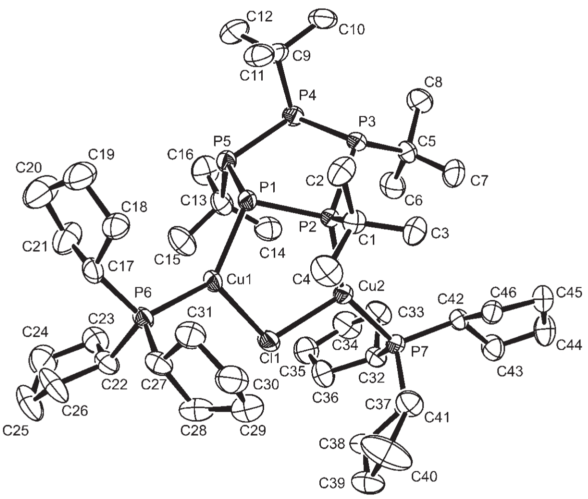


Figure 3. Molecular structure and atom-labelling scheme for **4** with thermal ellipsoids at 50 % probability (hydrogen atoms are omitted for clarity).

Table 1. Selected bond lengths [pm] and angles [°] for **3**–**9**.

	3	**4**	**5**	**6**	**7**	**8**	**9**
P1–P2	214.6(2)	220.0(2)	219.3(2)	218.69(8)	223.0(2)	221(1)	219.7(5)
P2–P3	221.0(2)	221.8(2)	222.5(2)	222.73(8)	222.5(2)	221(2)	221.3(5)
P3–P4	221.1(2)	221.5(2)	221.4(2)	221.89(9)	221.6(2)	221(2)	222.8(6)
P4–P5	221.9(2)	220.5(2)	222.2(1)	222.35(8)	220.7(2)	219(2)	222.9(6)
P1–P5	222.2(2)	214.6(2)			217.3(2)	219(2)	
P2–P5			221.7(1)	222.02(9)			221.2(5)
M1–P1	228.6(2)	225.6(1)	221.44(8)	238.26(5)	233.3(2)	231.7(7)	232.1(3)
M1–P6	231.3(2)	221.0(1)			230.1(2)	230.7(7)	
M1–P7	227.1(2)						
M2–P1			222.65(8)	240.19(6)			
M2–P2		227.3(1)					
M2–P7		223.3(1)				232.0(7)	
M2–P11						233.1(7)	
M3–P1						233.2(7)	
M3–P12						231.6(7)	
M1–Cl1		233.5(2)					
M2–Cl1		234.7(2)					
M1–P1A			221.44(8)	238.26(5)			231.6(3)
M2–P1A			222.65(8)	240.19(6)			
P1–P2–P3	102.53(6)	99.80(6)	103.41(4)	102.65(3)	98.84(7)	102.0(4)	103.2(2)
P2–P3–P4	108.55(6)	102.92(6)	86.69(4)	86.90(3)	104.13(7)	106.2(4)	86.0(2)
P3–P4–P5	103.25(6)	107.26(6)	85.31(4)	84.81(3)	108.74(7)	109.4(4)	84.4(2)
P3–P2–P5			85.19(4)	84.69(3)			85.2(2)
P1–P5–P4	100.78(6)	103.18(6)			101.69(7)	103.6(4)	
P4–P5–P2			86.67(4)	86.96(3)			85.9(2)
P5–P1–P2	104.64(6)	104.07(6)			106.33(7)	109.9(4)	
P5–P2–P1			101.12(4)	100.08(3)			102.2(2)
P1–M1–P6	111.72(4)	133.65(5)			172.91(4)	161.1(3)	
P1–M1–P7	135.46(4)						
P6–M1–P7	111.09(4)						
P1–M1–Cl1		112.39(4)					
P2–M2–Cl1		103.82(4)					
M1–Cl1–M2		103.35(4)					
P2–M2–P7		148.13(4)					
P1–M2–P1A			162.40(5)	160.31(3)			
M1–P1–M2			102.09(3)	102.32(2)			
M1–P1–M1A							102.2(2)
P1–M1–P1A			162.69(5)	162.83(3)			167.0(2)
P7–M2–P11						168.3(2)	
M1–P6–P7						117.0(3)	
M2–P7–P6						107.4(3)	
M1–P1–M3						94.6(3)	
P1–M3–P12						167.6(3)	
M2–P11–P12						104.9(3)	
M3–P12–P11						116.6(4)	
M1–P1–P2	100.22(5)	101.23(5)	113.21(4)	112.04(3)	98.09(6)	126.1(4)	112.4(2)
M1–P1–P5	121.03(6)	111.53(6)			107.99(6)	99.8(3)	
M2–P2–P1		113.81(5)					
M2–P2–P3		128.35(6)					
M2–P1–P2			112.50(4)	110.80(3)			
M1A–P1–P2							111.9(2)
P6–M1–Cl1		112.77(4)					
P7–M2–Cl1		107.57(4)					

an envelope conformation of the P_5 ring, in which the tip (P1 in **3** and P2 in **4**) deviates from the P_4 plane by ≈ -91.0 (**3**) and -98.8 pm (**4**).

The copper atoms in **3** and **4** display trigonal-planar geometries. Thus, Cu1 in **3** is nearly coplanar with the two phosphorus atoms of the PPh_3 ligands (P6 and P7) and the anionic P atom of the nonplanar (*cyclo*-$P_5t\mathrm{Bu}_4$)$^-$ ligand (P1). Cu1 and Cu2 in **4** are nearly coplanar with the two phosphorus atoms of the $PCyp_3$ ligands (P6 and P7) as well as with P1 (phosphorus atom of the P_5 ligand) and Cl1. The five-membered ring formed by Cu1, Cl1, Cu2, P1 and P2 has an envelope conformation in which the P2 atom deviates by only $\approx$20.9 pm from the best plane of the other atoms. The Cu–P_{ring} bond lengths of 228.6(2) (Cu1–P1 in **3**) and 225.6(1), 227.3(1) pm (Cu1–P1 and Cu2–P2 in **4**) are in the same range as those previously reported for other copper(I) phosphanido complexes.[12] The Cu–$P_{phosphane}$ bond lengths of 231.3(2) pm (Cu1–P6) and 227.1(2) pm (Cu1–P7) in **3** are

≈6 pm longer than in other copper(I) phosphane complexes.[11,12] This phenomenon is not observed in **4**, in which the $Cu-P_{phosphane}$ bond lengths are 221.0(1) (Cu1–P6) and 223.3(1) pm (Cu2–P7). The four P–P distances in the P_5 ring are in the range from 221.0(2) to 222.2(2) pm in **3** and from 220.0(2) to 221.8(2) pm in **4**, which are typical values for P–P single bonds.[20] However, the shorter P1–P2 bond length in **3** (214.6(2) pm) and P1–P5 bond length in **4** (214.6(2) pm) indicate multiple-bond character.

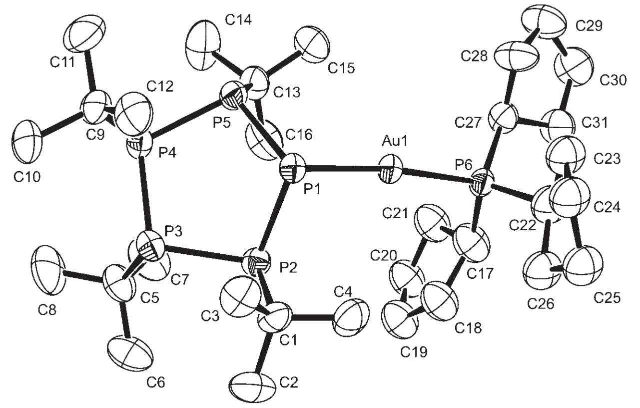


Figure 4. Molecular structure and atom-labelling scheme for **7** with thermal ellipsoids at 50 % probability (hydrogen atoms are omitted for clarity).

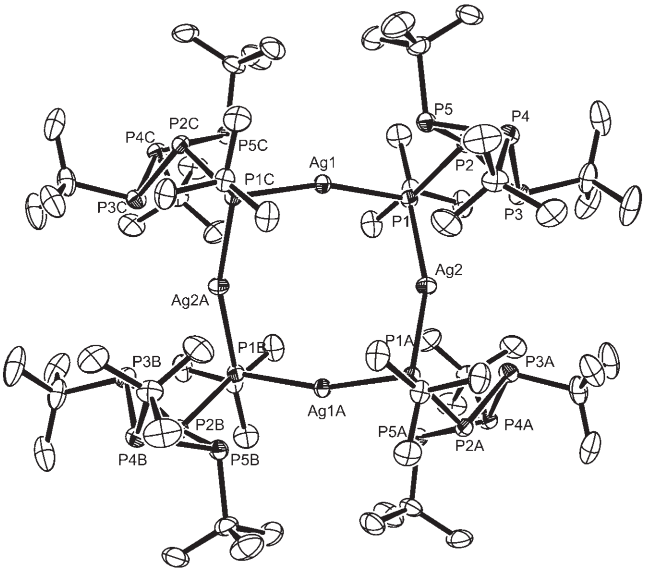


Figure 5. Molecular structure and atom-labelling scheme for silver complex **6** with thermal ellipsoids at 50 % probability level (hydrogen atoms are omitted for clarity). The copper complex **5** is isomorphous.

A similar arrangement to **3** is observed for the mononuclear complex [Au{*cyclo*-(P_5*t*Bu_4)}($PCyp_3$)] (**7**; Figure 4), which crystallises in the triclinic space group $P\bar{1}$ with two almost identical molecules in the asymmetric unit, only one of which is discussed below. The P_5 ring shows an all-*trans* arrangement of the *t*Bu groups and an envelope conformation in which P1 deviates by ≈89.3 pm from the best plane formed by P2-P3-P4-P5. Again, four of the five P–P bond lengths in the P_5 ring (P1–P2, P2–P3, P3–P4 and P4–P5) are close to 220 pm, in the range of P–P single bonds, but the P1–P5 distance of 217.3(2) pm is somewhat shorter. The gold atom shows an almost linear geometry (P1–Au1–P6 172.91(4)°) with bond lengths in the range of other Au^{I} phosphanido and phosphane complexes (Au1–P1 233.3(2), Au1–P6 230.1(2) pm).[13,21,22]

The tetranuclear complexes [Cu_4{*cyclo*-(P_4*t*Bu_3)P*t*Bu}$_4$] (**5**) and [Ag_4{*cyclo*-(P_4*t*Bu_3)P*t*Bu}$_4$] (**6**) crystallise in the orthorhombic centrosymmetric space group *Fddd* with eight molecules in the unit cell. The asymmetric unit contains one {M{*cyclo*-(P_4*t*Bu_3)P*t*Bu}M} fragment with two crystallographically independent copper and silver cations, respectively, and one *n*-hexane molecule. Rotation around three two-fold symmetry axes gives rise to an eight-membered M_4P_4 ring in which the metal atoms are bridged by the anionic P*t*Bu moieties (Figure 5). The four-membered *cyclo*-(P_4*t*Bu_3) groups in the ligands show an all-*trans* arrangement of the *t*Bu substituents and are in a butterfly conformation (Figure 5). The M–P bond lengths in **5** (221.44(8), 222.65(8) pm) and **6** (238.26(5), 240.19(6) pm) are similar to those reported for other Cu^{I}[11,12] and Ag^{I}[12] phosphanido complexes, respectively. The P–M–P angles deviate slightly from linearity (162.69(5) and 162.40(5)° for **5** and 160.31(3) and 162.82(3)° for **6**), which is not very common in silver(I) and copper(I) complexes. The P–P bond lengths (219.3(2)–222.5(2) pm in **5** and 218.69(8)–222.73(8) pm in **6**) are typical for P–P single bonds.[20] Packing diagrams of the molecular structures of **5** and **6** illustrate the presence of *n*-hexane solvent molecules in pockets formed by four molecules of **5** or **6** (Figure 6).

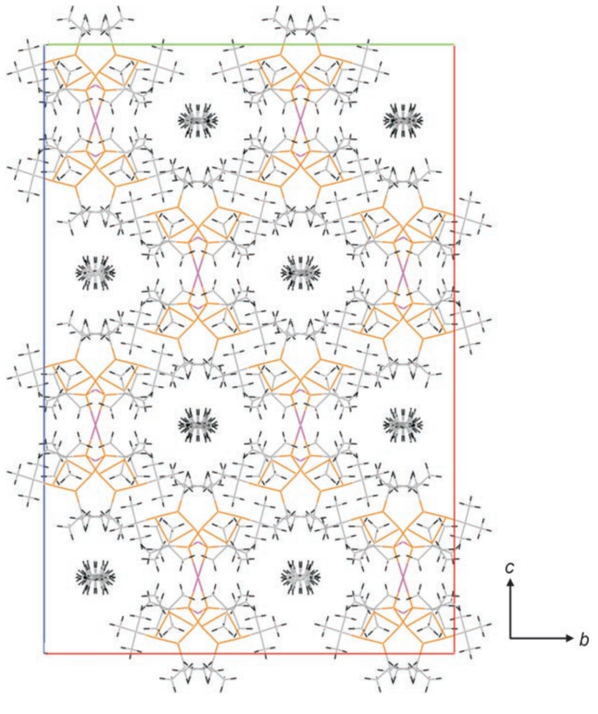


Figure 6. Packing diagram of **5**. View along the *a* axis.

The analogous gold complex $[Au_4\{cyclo\text{-}(P_4t\mathrm{Bu}_3)Pt\mathrm{Bu}\}_4]$ (**9**) crystallises in the tetragonal space group $I4_1/a$ with four molecules of **9** in the unit cell in addition to 16 THF solvent molecules. The asymmetric unit contains one $Au\{cyclo\text{-}(P_4t\mathrm{Bu}_3)Pt\mathrm{Bu}\}$ fragment and one THF molecule. The molecule is located on a crystallographic S_4 axis which coincides with the centre of the Au_4P_4 ring and generates the other three $Au\{cyclo\text{-}(P_4t\mathrm{Bu}_3)Pt\mathrm{Bu}\}$ fragments of the tetramer (Figure 7); therefore, the molecule belongs to the point group D_{2d}. As in the case of **5** and **6**, the central fragment of **9** is an eight-membered Au_4P_4 ring, which is in a butterfly conformation (Figure 7, maximum deviation of Au and P from the mean Au_4P_4 plane is 1.5 and 25.1 pm, respectively), similar to that observed in the related tetranuclear complex $[\{Au(PMes_2)\}_4]$.[13] Similar to **5** and **6**, the four-membered *cyclo*-($P_4t\mathrm{Bu}_3$) groups in the ligands show an all-*trans* arrangement of the *t*Bu substituents and are in a butterfly conformation (Figure 7). The Au–P bond lengths in **9** (231.6(3), 232.1(3) pm) are similar to those in other Au^I complexes.[13,21,22] The slightly bent coordination of the two-coordinate gold atoms (P1–Au1–P1A 167.0(2)°) is comparable to that of the related gold(I) phosphanido complex $[\{Au(PMes_2)\}_4]$.[13] The P–P bond lengths are typical for single bonds.[20] Gold(I) complexes often exhibit inter- or intramolecular Au–Au contacts (≈300 pm),[21,22] but the corresponding Au···Au distances in tetranuclear gold complex **9** are much longer (≈510.5 pm).

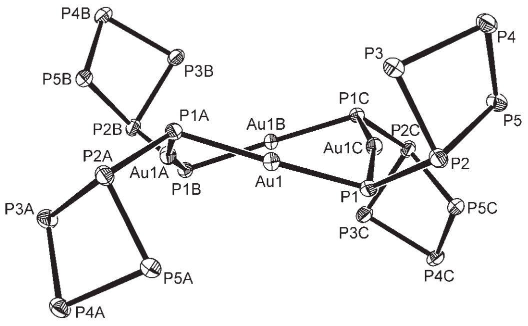


Figure 7. Section of the molecular structure of **9** with thermal ellipsoids at 50 % probability.

The trinuclear gold(I) complex $[Au_3\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}_3]$ (**8**) crystallises in the triclinic space group $P\bar{1}$ with four molecules in the unit cell. The two crystallographically independent molecules in the asymmetric unit are structurally almost identical, so only one of them is discussed here. The structure contains an unprecedented array of three $\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}^-$ ligands and three gold atoms which form a nearly planar eight-membered ring consisting of three gold atoms and five phosphorus atoms. Two of the $\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}^-$ ligands bridge the gold atoms through one anionic phosphorus atom each (P7, P11) as well as two adjacent phosphorus atoms (P6 and P12), whereas the third ring bridges two gold atoms through its anionic phosphorus atom alone (P1). The *t*Bu groups are in an all-*trans* arrangement and the P_5 rings are in an envelope conformation in which the tips P1, P7 and P11 deviate from the P_4 plane by ≈54.4, 80.8 and 78.8 pm, respectively (Figure 8). Most of the P–P bond lengths in each of the $\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}^-$ ligands are close to 220 pm and thus in the range of P–P single bonds. The gold atoms display slightly bent linear coordination in which the P–Au–P angles range from 161.1(3) to 168.3(2)°. The Au–P bond lengths (230.7(7)–233.2(7) pm) are in agreement with those reported for other Au^I complexes.[13,21,22] The Au···Au distances in **8** of between ≈341.6 and 401.2 pm indicate no interaction between the metal centres.[21,22]

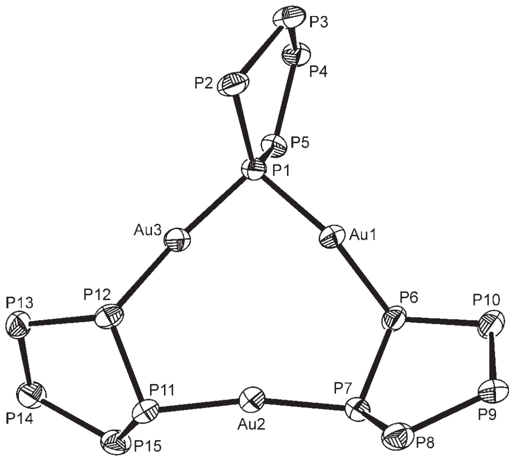


Figure 8. Section of the molecular structure of **8** with thermal ellipsoids at 50 % probability.

Conclusion

The $\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}^-$ ligand forms a variety of complexes with the coinage metals. Initially, monomeric species of the general type $[M\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}(PR_3)_n]$ (M = Cu, Ag, Au) are formed. Thus, the complexes $[Cu\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}(PCyp_3)_2]$ (**2**) and $[Cu\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}(PPh_3)_2]$ (**3**), $[Au\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}(PCyp_3)]$ (**7**) have been isolated and are the first examples of mononuclear copper(I) and gold(I) phosphanido complexes. The compound $[Cu_2(\mu\text{-}Cl)\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}(PCyp_3)_2]$ (**4**) is an unusual CuCl adduct of the monomer **2**. Although **4** appears to be relatively stable, the mononuclear complexes initially formed are labile and rearrange slowly to stable, oligomeric complexes, in particular the tetranuclear compounds $[M_4\{cyclo\text{-}(P_4t\mathrm{Bu}_3)Pt\mathrm{Bu}\}_4]$ (M = Cu, **5**; Ag, **6**; Au, **9**), in which the $\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}^-$ ligand has rearranged to the cyclotetraphosphane ligand $\{cyclo\text{-}(P_4t\mathrm{Bu}_3)Pt\mathrm{Bu}\}^-$. In this regard, the highly unusual trinuclear complex $[Au_3\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}_3]$ (**8**) is particularly interesting, as it shows an unprecedented bridging arrangement of the $\{cyclo\text{-}(P_5t\mathrm{Bu}_4)\}^-$ ligand and may thus resemble an intermediate in this rearrangement process.

Experimental Section

General methods: All experiments were performed under an atmosphere of dry argon by using standard Schlenk techniques. The NMR spectra were recorded at 25 °C on a Bruker AVANCE DRX 400 spectrometer. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.16 MHz): internal standard solvent, external standard TMS; ^{31}P NMR (161.9 MHz): external standard 85 % H_3PO_4. IR spectra: KBr pellets were prepared in a nitrogen-filled glove box and the spectra were recorded on a Perkin–Elmer System 2000 FTIR spectrometer in the range 350–4000 cm^{-1}. All solvents were purified by distillation, dried, saturated with argon, and stored over potassium mirror. Elemental analyses were performed by means of a VARIO EL (Heraeus). The melting points were determined in sealed capillaries under argon and are uncorrected.

Compound **1**,[6] $[CuCl(PCyp_3)_2]$,[11] $[CuCl(PPh_3)_3]$,[23] $[AgCl(PPh_3)_2]$,[24] and $[AuCl(PPh_3)]$[25] were prepared according to the literature procedures. $[AgCl(PCyp_3)]_4$ and $[AuCl(PCyp_3)]$ were prepared in situ by adding 1.1 equiv of $PCyp_3$ to solutions of $[AgCl(PPh_3)_2]$ and $[AuCl(PPh_3)]$, respectively. $[AgCl(PCyp_3)]_4$ was also prepared from AgCl and 1.1 equiv of $PCyp_3$ in toluene and structurally characterised (see the Supporting Information).

Data collection and structural refinement of 3–9: The data of **3**, **7**, **8** and **9** were collected on a Siemens SMART CCD diffractometer ($\lambda(Mo_{K\alpha})$ = 71.073 pm) by using φ scans mode, and those of **4**, **5** and **6** on a CCD Oxford Xcalibur S ($\lambda(Mo_{K\alpha})$ = 71.073 pm) by using ω and φ scan modes. Semi-empirical absorption corrections for **3**, **7**, **8** and **9** were carried out by using SADABS;[26] semi-empirical from equivalents absorption corrections for **4**, **5** and **6** were carried out by using SCALE3 ABSPACK.[27] All the structures were solved through direct methods.[28] Structure refinement was carried out by using SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically, and H atoms were located by difference maps and refined isotropically in all the structures except for **8**, in which carbon atoms were also refined only isotropically, owing to the poor quality of the crystals. Table 2 lists crystallographic details.

CCDC 672159 (**3**), 672160 (**4**), 672161 (**5**), 672162 (**6**) 672163 (**7**), 672164 (**8**) and 672165 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Cu{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)$_2$] (2): At −78 °C a solution of $[CuCl(PCyp_3)_2]$ (1.41 g, 2.46 mmol) in toluene (20 mL) was slowly added to a solution of **1** (1.00 g, 2.46 mmol) in toluene (20 mL). A colour change from yellow to dark orange occurred. After 1 h the solvent was evaporated and the residue dissolved in *n*-pentane (10 mL), filtered (to remove NaCl) and the solvent evaporated. The resulting orange residue is soluble in THF, toluene, diethyl ether, *n*-pentane and *n*-hexane. The ^{31}P NMR spectrum showed the presence of [Cu{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)$_2$] (**2**) and *cyclo*-(P$_5$*t*Bu$_4$H). Repeated crystallisation from *n*-hexane gave [Cu{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)$_2$] (**2**) as a yellow crystalline solid at −30 °C, which was isolated by filtration. Cooling the mother liquor to −30 °C afforded [Cu$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**5**). Yield of **2**: 0.65 g (29 %). Yield of **5**: 0.18 g (17 %).

Complex 2: M.p. 122–126 °C. ^{1}H NMR (C_7D_8): δ = 1.27–1.77 ppm (br, 36 H, *t*Bu and 54 H, Cyp); ^{13}C{^{1}H} NMR (C_7D_8): δ = 24.3–31.9 ppm (br, *t*Bu and Cyp); ^{31}P{^{1}H} NMR (C_7D_8): δ = 75 (br, 2P of P$_5$ ring), 67 (br, 2P of P$_5$ ring), 8 (PCyp$_3$), −94 ppm (br t, anionic P of P$_5$, J(P,P) ≈ 320 Hz); IR: $\tilde{\nu}$ = 2952(s), 2866 (s), 2850 (s), 2373 (vw), 2345 (vw), 1452 (m), 1382 (w), 1355 (m), 1300 (w), 1261 (s), 1169 (m), 1050 (s), 934 (w), 904 (m), 803 (s), 701 (w), 522 (m), 429 cm^{-1} (w); FAB MS (matrix: 3-NBA): *m*/*z*: (%): 922.1 (5.2) [M^+], 866.9 (1.9) [M^+−*t*Bu+H], 639.1 (22.5) [M^+−PCyp$_3$−3 Me−2H], 539.2 (50.3) [M^+−P$_5$*t*Bu$_4$], 301.0 (100.0) [M^+−P$_5$*t*Bu$_4$−PCyp$_3$], 249.0 (4.6) [M^+−PCyp$_3$−4 *t*Bu−3 Cyp=CuP$_6$]; elemental analysis calcd (%) for $C_{46}H_{90}CuP_7$ (923.57): C 59.82, H 9.82; found: C 59.44, H 9.91.

[Cu{*cyclo*-(P$_5$*t*Bu$_4$)}(PPh$_3$)$_2$] (3): Complex **3** was prepared in a similar manner to **2**. **1** (1.00 g, 2.46 mmol) and $[CuCl(PPh_3)_3]$ (2.18 g, 2.46 mmol). Yield of **3**: 0.81 g (34 %). Yield of **5**: 0.21 g (20 %). *Complex 3*: M.p. 133–134 °C; ^{1}H NMR (C_6D_6): δ = 1.23–1.77 (br, 36 H, *t*Bu), 7.00–7.04 (m, 18 H, *o*-H and *p*-H in Ph), 7.30–7.39 ppm (br, 12 H,

Table 2. Crystal data and structure refinement for **3–9**.

	3	**4**	**5**	**6**	**7**	**8**	**9**
formula	$C_{52}H_{66}CuP_7$	$C_{46}H_{90}ClCu_2P_7$	$C_{76}H_{172}Cu_4P_{20}$	$C_{76}H_{172}Ag_4P_{20}$	$C_{31}H_{63}AuP_6$	$C_{52}H_{118}Au_3OP_{15}$	$C_{80}H_{176}Au_4O_4P_{20}$
cryst. size [mm]	0.25 × 0.25 × 0.15	0.15 × 0.10 × 0.10	0.30 × 0.20 × 0.10	0.20 × 0.07 × 0.05	0.08 × 0.08 × 0.07	0.20 × 0.10 × 0.02	0.05 × 0.05 × 0.02
colour	pale orange	yellow	colourless	colourless	pale yellow	yellow	pale yellow
formula weight	971.38	1022.50	1959.70	2137.02	818.60	1814.91	2609.47
space group	triclinic $P\bar{1}$	triclinic $P\bar{1}$	orthorhombic $Fddd$	orthorhombic $Fddd$	triclinic $P\bar{1}$	triclinic $P\bar{1}$	tetragonal $I4_1/a$
a [pm]	1005.5(1)	1393.04(9)	1534.2(1)	1539.33(9)	1172.94(6)	15.366(6)	27.620(2)
b [pm]	1396.1(3)	1455.2(1)	3052.7(2)	3046.0(4)	1745.65(9)	20.674(7)	27.620(2)
c [pm]	2014.8(4)	1534.1(1)	4456.6(4)	4525.69(6)	2052.0(1)	26.414(9)	15.124(2)
α [°]	107.55(2)	84.650(1)	90	90	70.976(1)	89.986(6)	90
β [°]	94.97(1)	72.510(1)	90	90	77.310(1)	82.808(7)	90
γ [°]	103.76(1)	64.064(1)	90	90	86.863(1)	89.201(7)	90
V [nm^3]	2.5806(8)	2.6646(3)	20.87(1)	21.220(3)	3.8745(3)	8.324(5)	11.537(2)
Z	2	2	8	8	4	4	4
T [K]	130(2)	213(2)	150(2)	130(2)	233(2)	210(2)	203(2)
ρ_{calcd} [Mg m^{-3}]	1.250	1.274	1.247	1.338	1.403	1.448	1.502
reflns collected	48973	15387	27652	63005	19854	60039	35629
$2\theta_{max}$ [°]	52.74	49.42	52.74	58.26	52.84	46.70	52.78
unique reflns	10472	8284	5325	7148	13892	20420	5924
refl. obs. [$I > 2\sigma(I)$]	8313	6457	3916	5249	11881	11960	3202
no. of parameters/ restraints	553/0	481/0	219/9	236/25	553/0	749/17	226/10
μ [mm^{-1}]	0.673	1.088	1.146	1.064	4.063	5.591	5.386
R_1 [$I > 2\sigma(I)$]	0.0663	0.0491	0.0391	0.0325	0.0335	0.0969	0.0910
wR_2 (all data)	0.1749	0.1167	0.1162	0.0683	0.0852	0.2511	0.1708
GOF on F^2	0.998	1.130	1.086	1.070	1.024	1.006	1.051
residual density [e Å^{-3}]	3.895 and −1.617	1.184 and −1.504	1.390 and −0.410	0.555 and −0.546	1.472 and −1.768	3.734 and −2.685	1.361 and −1.204

m-H in Ph); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ=20.7–34.0 (br, *t*Bu), 124.7 (br, 4-C in Ph), 128.9 (s, 3,5-C in Ph), 133.7 (s, 2,6-C in Ph), 137.0 ppm (br, 1-C in Ph); ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ=71 (br, 4P of P$_5$), 67 (s, PPh$_3$), −97 ppm (br m, anionic P of P$_5$, *J*(P,P)= ≈172 Hz); IR: $\tilde{\nu}$=3053 (m), 2934 (s), 2884 (s), 2850 (s), 1958 (w), 1890 (w), 1816 (w), 1584 (m), 1478 (m), 1455 (m), 1434 (s), 1383 (m), 1355 (m), 1309 (w), 1261 (m), 1169 (s), 1092 (s), 1025 (m), 851 (w), 806 (s), 743 (s), 695 (s), 618 (w), 541 (m), 510 (s), 429 cm^{-1} (w); FAB MS (matrix: 3-NBA): *m*/*z*: (%): 971.1 (0.6) [M^+], 869.1 (3.3) [M^+−*t*Bu−3Me+H], 798.1 (6.0) [M^+−3*t*Bu−H], 709.2 (8.7) [M^+−PPh$_3$+H], 587.2 (88.2) [M^+−P$_5$*t*Bu$_4$], 325.0 (100.0) [M^+−P$_5$*t*Bu$_4$−PPh$_3$], 156.9 (3.5) [M^+−5*t*Bu−6Ph−4P=CuP$_3$]; elemental analysis calcd (%) for C$_{52}$H$_{66}$CuP$_7$ (971.38): C 64.29, H 6.85; found: C 64.31, H 7.03.

[Cu$_2$(μ-Cl){*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)$_2$] (4): Complex **4** was prepared in a similar manner to **2**. Compound **1** (0.50 g, 1.23 mmol) and [CuCl(PCyp$_3$)$_2$] (1.41 g, 2.46 mmol). Yield: 0.61 g (49%).

Complex 4: M.p. 183–188°C; ^{1}H NMR (C$_7$D$_8$): δ=1.26–1.79 ppm (br, 36H, *t*Bu and 54H; Cyp); ^{13}C{^{1}H} NMR (C$_7$D$_8$): δ=24.1–31.9 ppm (br, *t*Bu and Cyp); ^{31}P{^{1}H} NMR (C$_7$D$_8$): 64.0, (br, 4P of P$_5$ ring) 11.6 (br, PCyp$_3$), 5.2 (br, PCyp$_3$), −79.7 ppm (br t, anionic P of P$_5$, *J*(P,P) ≈382 Hz); IR: $\tilde{\nu}$=2953 (s), 2867 (s), 1453 (s), 1383 (m), 1355 (m), 1300 (w), 1261 (m), 1250 (w), 1120 (m), 1101 (m), 1050 (m), 997 (m), 935 (w), 905 (m), 807 (s), 702 (w), 515 (m), 408 cm^{-1} (m); FAB MS (matrix: 3-NBA): *m*/*z*: (%): 1022.2 (1.7) [M^+], 1020.2 (11.9) [M^+−2H], 733.1 (9.9) [M^+−Cl−Me−PCyp$_3$+H], 685.1 (2.4) [M^+−CuClPCyp$_3$−H], 639.0 (16.9) [M^+−P$_5$*t*Bu$_4$], 301.1 (100.0) [M^+−P$_5$*t*Bu$_4$−CuClPCyp$_3$], 249.0 (4.6) [M^+−CuClPCyp$_3$−4*t*Bu−3Cyp=CuP$_6$]; elemental analysis calcd (%) for C$_{46}$H$_{90}$Cu$_2$ClP$_7$ (1022.50): C 54.03, H 8.87; found: C 53.61, H 8.78.

[Cu$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (5): At −78°C a solution of [CuCl(PCyp$_3$)$_2$] (1.41 g, 2.46 mmol) or [CuCl(PPh$_3$)$_3$] (2.18 g, 2.46 mmol) in THF (20 mL) was slowly added to a solution of **1** (1.00 g, 2.46 mmol) in THF (20 mL). A colour change from yellow to dark orange occurred. Afterwards, the solution was refluxed overnight. The solvent was then evacuated and the orange residue dissolved in *n*-hexane (10 mL), filtered (to remove NaCl) and the solvent evaporated. The resulting yellow residue is soluble in THF, toluene, diethyl ether, *n*-pentane and *n*-hexane. Crystallisation from *n*-hexane gave yellow crystals of [Cu$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**5**). Yield: 0.19 g (18%).

Complex 5: M.p. 169–171°C; ^{31}P{^{1}H} NMR (C$_6$D$_6$) of the reaction mixture shows the same signals found for **2** or **3**, depending on the starting copper complex; IR: $\tilde{\nu}$=2951 (s), 2947 (s), 2988 (s), 2854 (s), 1468 (m), 1456 (s), 1386 (w), 1358 (s), 1261 (s), 1171 (s), 1126 (m), 1101 (m), 1050 (m), 997 (m), 806 (s), 743 (w), 696 (w), 572 (w), 489 cm^{-1} (w); ESI MS (CH$_3$CN:THF=1:1): *m*/*z*: 1671.2 [M^+−2*t*Bu+H], 1273.3 [M^+−Cu$_2$P$_4$*t*Bu$_3$P*t*Bu−2H]; elemental analysis calcd (%) for C$_{64}$H$_{144}$Cu$_4$P$_{20}$ (1787.49): C 43.00, H 8.12; found: C 43.47, H 8.38.

[Ag$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (6): Complex **6** was prepared in a similar manner to **5**. **1** (1.00 g, 2.46 mmol) and [AgCl(PCyp$_3$)]$_4$ (0.94 g, 0.62 mmol) or [AgCl(PPh$_3$)$_2$] (1.64 g, 2.46 mmol). Yield: 0.24 g (20%).

Complex 6: M.p. 182–185°C; ^{31}P{^{1}H} NMR (C$_6$D$_6$) of the reaction mixture with [AgCl(PCyp$_3$)]$_4$: δ=67 (br, 2P of P$_5$), 28 (br, 2P of P$_5$), 12 (s, PCyp$_3$), −94 ppm (br, anionic P of P$_5$); IR: $\tilde{\nu}$= 2957 (s), 2866 (s), 2701 (w), 2366 (w), 1454 (s), 1440 (m), 1384 (m), 1357 (s), 1300 (w), 1260 (s), 1171 (s), 1097 (m), 1055 (s), 934 (m), 904 (s), 863 (m), 804 (s), 700 (m), 571 (w), 518 (m), 402 cm^{-1} (m); ESI MS (CH$_3$CN:THF=1:1): *m*/*z*: 1740.0 [M^+−P$_2$*t*Bu$_2$−3Me−H]; elemental analysis calcd (%) for C$_{64}$H$_{144}$Ag$_4$P$_{20}$ (1964.78): C 39.12, H 7.39; found: C 38.55, H 7.00.

[Au{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)] (7): At room temperature, a solution of PCyp$_3$ (0.30 g, 1.26 mmol) in toluene (5 mL) was added dropwise to a suspension of [AuCl(PPh$_3$)] (0.60 g, 1.23 mmol) in toluene (10 mL) and the mixture stirred for 1 h. This mixture was then slowly added to a solution of **1** (0.50 g, 1.23 mmol) in toluene (10 mL) at −78°C. The solution turned orange and after 1 h the solvent was evaporated and the residue dissolved in *n*-hexane (20 mL), filtered (to remove NaCl) and the solvent evaporated. The resulting orange residue is soluble in THF, toluene, diethyl ether, *n*-pentane and *n*-hexane. Analysis of the ^{31}P NMR spectrum revealed the presence of [Au{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)] (**7**) and a very small amount of *cyclo*-(P$_5$*t*Bu$_4$H). Repeated crystallisation from *n*-hexane gave yellow crystals of [Au{*cyclo*-(P$_5$*t*Bu$_4$)}(PCyp$_3$)] (**7**) at −30°C, which were isolated by filtration. A mixture of [Au$_3${*cyclo*-(P$_5$*t*Bu$_4$)}$_3$] (**8**) and [Au$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**9**) was obtained on cooling the mother liquor to −30°C.

Complex **7**: Yield of **7**: 0.41 g (40%). M.p. 134–137°C; ^{1}H NMR (C$_7$D$_8$): δ=1.31 (br, 6H; Cyp), 1.33–1.67 (br, 36H; *t*Bu; 15H; Cyp), 1.75 ppm (br, 6H; Cyp); ^{13}C{^{1}H} NMR (C$_7$D$_8$): 20.4–35.7 ppm (several signals, *t*Bu and Cyp); ^{31}P{^{1}H} NMR (C$_7$D$_8$) (193 K): 65.4 (m, P$_A$; ^1J(A,X)=199.4, ^1J(A,D)=272.5, ^2J(A,B)=0.1, ^2J(A,E)=6.6, ^3J(A,C)=11.3 Hz), 63.7 (m, P$_B$; ^1J(B,D)=304.9, ^1J(B,E)=330.9, ^2J(B,X)=0.2, ^4J(B,C)=0.2 Hz), 64.6 (m, P$_C$; ^2J(C,X)=99.8, ^3J(C,E)=7.1 Hz), 42.3 (m, P$_D$; ^2J(D,E)=8.9, ^2J(D,X)=25.4 Hz), 29.6 (m, P$_E$; ^1J(E,X)=408.4 Hz), −55.8 ppm (m, P$_X$); IR: $\tilde{\nu}$=2960 (s), 2872 (s), 2860 (s), 2291 (vw), 1630 (m), 1597 (m), 1511 (m), 1457 (s), 1388 (w), 1359 (m), 1261 (s), 1170 (s), 1144 (m), 1099 (s), 947 (w), 867 (m), 806 (s), 747 (w), 698 (w), 585 (m), 548 (m), 475 (m), 437 (w), 411 cm^{-1} (m); FAB MS (matrix: 3-NBA): *m*/*z*: (%): 819.1 (1.7) [M^++H], 818.1 (0.4) [M^+], 801.1 (9.5) [M^+−Me], 719.0 (3.4) [M^+−Cyp-2Me], 673.2 (23.6) [M^+−2*t*Bu−2Me−H], 383.1 (37.8) [M^+−AuPCyp$_3$], 327.0 (100.0) [M^+−AuPCyp$_3$−*t*Bu+H]; elemental analysis calcd (%) for C$_{31}$H$_{63}$AuP$_6$ (818.60): C 45.48, H 7.76; found: C 44.78, H 8.22.

[Au$_3${*cyclo*-(P$_5$*t*Bu$_4$)}$_3$] (8) and [Au$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (9): A suspension of **1** (1.00 g, 2.46 mmol) in toluene (30 mL) was added dropwise to a solution of [AuCl(PPh$_3$)] (1.21 g, 2.46 mmol) in toluene (10 mL). The mixture was stirred for two days, the yellow suspension filtered and the colourless residue extracted twice with *n*-pentane (20 mL). The combined filtrates were evaporated. The resulting oil was dissolved in THF and the yellow solution was stored at −27°C. A yellow solid formed after two weeks, which was isolated and dried in vacuo for 20 min. The mother liquor was reduced to ≈3 mL and stored at −20°C. A crystalline solid formed which consisted of yellow and colourless crystals. A yellow crystal was subjected to X-ray crystallography and identified as [Au$_3${*cyclo*-(P$_5$*t*Bu$_4$)}$_3$] (**8**) according to its unit cell parameters; the colourless crystals were identified as [Au$_4${*cyclo*-(P$_4$*t*Bu$_3$)P*t*Bu}$_4$] (**9**). Crystals of **8** were also obtained when the crude product of the reaction was recrystallised from toluene. ^{31}P{^{1}H} NMR (C$_6$D$_6$) of the reaction mixture: δ= 124.7 (m), 118.2 (m), 93.7 (m), 83.2 (m), 67.2–39.6 (m), −1.8 to −15.6 (m), −39.6 to 59.0, −90.0 ppm (m, anionic P of P$_5$ in **8**); IR: $\tilde{\nu}$=2959 (s), 2871 (s), 2861 (s), 1630 (m), 1598 (m), 1511 (w), 1458 (m), 1388 (w), 1360 (m), 1262 (s), 1170 (s), 1140 (m), 1052 (s), 866 (m), 806 (s), 746 (w), 698 (w), 547 (m), 475 (w), 437 (w), 409 cm^{-1} (w); LDI MS: *m*/*z*: 1937 [Au$_4$(P$_5$*t*Bu$_4$)$_3$]$^+$, 1823 [Au$_4$(P$_5$*t*Bu$_4$)$_3$−2*t*Bu]$^+$, 1740 [Au$_3$(P$_5$*t*Bu$_4$)$_3$]$^+$, 1683 [Au$_3$(P$_5$*t*Bu$_4$)$_3$−*t*Bu]$^+$, 1357 [Au$_3$(P$_5$*t*Bu$_4$)$_2$]$^+$, 1301 [Au$_3$(P$_5$*t*Bu$_4$)$_2$−*t*Bu+H]$^+$, 1269 [Au$_3$(P$_5$*t*Bu$_4$)$_2$−P*t*Bu]$^+$, 1243 [Au$_3$(P$_5$*t*Bu$_4$)$_2$−2*t*Bu]$^+$, 721 [Au$_3$(P$_5$*t*Bu$_4$)−*t*Bu+H]$^+$.

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