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1,2,4-Triphospholyl gold(I) and copper(I) complexes: synthesis, crystal and molecular structures of $[\mathrm{Cu(PMe_3)_2(\mu\text{-}P_3C_2^{\mathit{t}}Bu_2)(\mu\text{-}I)Cu(PMe_3)_2}]$, $[\mathrm{Cu(PMe_3)_2(\mu\text{-}P_3C_2^{\mathit{t}}Bu_2)_2Cu(PMe_3)_2}]$ and $[\mathrm{Au(\eta^1\text{-}P_3C_2^{\mathit{t}}Bu_2)_2][Au(PEt_3)_2}]$

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Abstract

Treatment of $\mathrm{K(P_3C_2^{\mathit{t}}Bu_2)}$ with $\mathrm{Cu_2I_2}$ and $\mathrm{PMe_3}$ gave the binuclear complex $[\mathrm{Cu(PMe_3)_2(\mu\text{-}P_3C_2^{\mathit{t}}Bu_2)_2Cu(PMe_3)_2}]$ via the isolated intermediate compound $[\mathrm{Cu(PMe_3)_2(\mu\text{-}P_3C_2^{\mathit{t}}Bu_2)(\mu\text{-}I)Cu(PMe_3)_2}]$. The reaction of $\mathrm{K(P_3C_2^{\mathit{t}}Bu_2)}$ with $[\mathrm{AuCl(PEt_3)}]$ on the otherhand gave the cation:anion complex $[\mathrm{Au(PEt_3)_2][Au(\eta^1\text{-}P_3C_2^{\mathit{t}}Bu_2)_2}]$. All complexes were fully characterised by multinuclear spectroscopy and single crystal X-ray diffraction studies.

Keywords: Triphospholyl; Copper; Gold; Structures

1. Introduction

A very recent report by Zenneck and co-workers [1] of the gold(I) complex $[\mathrm{Au(PPh_3)(P_3C_2^{\mathit{t}}Bu_2)}]$ (**1**) containing the aromatic 1,2,4- triphospha-3,5-ditertiarybutylcyclopentadienyl anion, which is dimeric in the solid-state, prompts us to describe interestingly differing results of our own studies on the coordination chemistry of this $\mathrm{P_3C_2^{\mathit{t}}Bu_2}$ ring anion **2** towards both Au(I) and Cu(I) centres.

In contrast to the results described in reference [1] we find a completely different structure for the corresponding $\mathrm{PEt_3}$ compound $[\mathrm{Au(PEt_3)(P_3C_2^{\mathit{t}}Bu_2)}]$ (**5**) (which is also dimeric). Furthermore, whereas in a parallel unpublished study referred to in Ref. [1] on related Cu(I)-1,2,4-triphosphacyclopentadienyl derivatives, it is stated: 'most exhibit a remarkable structural flexibility which causes a big manifold of spectroscopic parameters, especially NMR spectroscopy and no unambiguous interpretation of data was possible', we on the other hand have isolated and fully structurally characterised two such Cu(I)-1,2,4-triphospha-cyclopentadienyl complexes namely $[\mathrm{Cu(PMe_3)_2(\mu\text{-}P_3C_2^{\mathit{t}}Bu_2)}$-$\mathrm{(\mu\text{-}I)Cu(PMe_3)_2}]$ (**3**) and $[\mathrm{Cu(PMe_3)_2(\mu\text{-}P_3C_2^{\mathit{t}}Bu_2)_2}$-$\mathrm{Cu(PMe_3)_2}]$ (**4**).

Previously in a series of papers we and others have shown that the 1,2,4- triphospha-3,5-tertiarybutylcyclopentadienyl anion, (**2**) could co-ordinate in an η^5-fashion to form sandwich complexes of the type $[\mathrm{M(\eta^5\text{-}P_3C_2^{\mathit{t}}Bu_2)_2}]$, M = Ti [2], Cr [3], Mn [4], Fe [5], Ru [6], and $[\mathrm{M(\eta^5\text{-}P_3C_2^{\mathit{t}}Bu_2)(\eta^5\text{-}C_5H_5)}]$ M = Fe [7,8] Ru [6]. The diverse nature of the bonding of the 1,2,4-triphospha-cyclopentadienyl ring system is exemplified by the structure of the recently reported hexaphosphastrontocene $[\mathrm{Sr(\eta^5\text{-}P_3C_2^{\mathit{t}}Bu_2)_2}]$ [9] whose structure in the solid-state consists of bent sandwich units linked in chains via further η^1-interaction involving one of the two adjacent ring phosphorus atoms. Similarly half-sandwich compounds of transition metals $[\mathrm{M(\eta^5\text{-}P_3C_2^{\mathit{t}}Bu_2)(CO)_3}]$ (M = Mn [4] or Re [10]) and main group elements $[\mathrm{M(\eta^5\text{-}P_3C_2^{\mathit{t}}Bu_2)}]$ (M = Ga, In or Tl) have also been described [11,12].

The triphospholyl ring anion can also bond in a simple η^1-fashion, for example in the Zn(II) and Cd(II)

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complexes $[M(\eta^1\text{-}P_3C_2^tBu_2)(pyridine)_n]$ ($M = Zn$ $n = 2$, $M = Cd$ $n = 3$) [13], in the square-planar complexes *trans* $[M(\eta^1\text{-}P_3C_2^tBu_2)_2(PEt_3)_2]$ M = Pd, or Pt [14,15] and in $[PPh_3Sn(\eta^1\text{-}P_3C_2^tBu_2)]$. [16] Some of these types of compounds are shown in Fig. 1.

2. Results and discussion

2.1. Cu(I) complexes

Treatment of $K(P_3C_2^tBu_2)$ with Cu_2I_2 in the presence of PMe_3 gave the binuclear complex **4**, $[Cu(PMe_3)_2(\mu\text{-}P_3C_2^tBu_2)_2Cu(PMe_3)_2]$, as pale yellow crystals, (m.p. (dec.) 105 °C) via the isolated intermediate **3**, $[Cu(PMe_3)_2(\mu\text{-}P_3C_2^tBu_2)(\mu\text{-}I)Cu(PMe_3)_2]$, (yellow crystals, m.p. (dec.) 140 °C) as shown in Scheme 1.

Both compounds **3** and **4** have been fully characterised by elemental analysis, and multinuclear NMR spectroscopy and their structures determined by single crystal X-ray diffraction studies. The $^{31}P\{^1H\}$-NMR spectra of **3** and **4** were almost identical, consisting of three slightly broad peaks centred at 253, 201 and −46 ppm. The ^1H spectra of each compound showed singlet resonances for both the ^tBu and Me protons in the expected 1:2 and 1:1 intensity ratios, respectively.

It was initially anticipated that a stoichiometric reaction between Cu_2I_2, PMe_3 and $K(P_3C_2^tBu_2)$ would lead to half-sandwich analogous to the well-known cyclopentadienyl derivatives $[Cu(C_5H_5)PPh_3]$ [17] and $[Cu(C_5Me_5)PR_3]$ (R = Et or Ph) [18], in which the cyclopentadienyl rings are η^5-ligated to the metal atom. However, the X-ray determined crystal structure of **3** (Fig. 2) reveals the interesting binuclear structure containing both iodide and the $P_3C_2^tBu_2$ ring bridging the two Cu(I) centres the latter via both the two adjacent ring P atoms. Each Cu centre has, therefore, a roughly tetrahedral geometry, with a mean Cu–P(Me) bond length of 2.2457 Å and Cu–P(ring) distance of 2.283 Å which are comparable to the reported Cu–P bond lengths in $[Et_3PCuI]_4$ [19,20] (2.254 Å) and in $[MePh_2PCuI]_4$ (2.250 Å) [21].

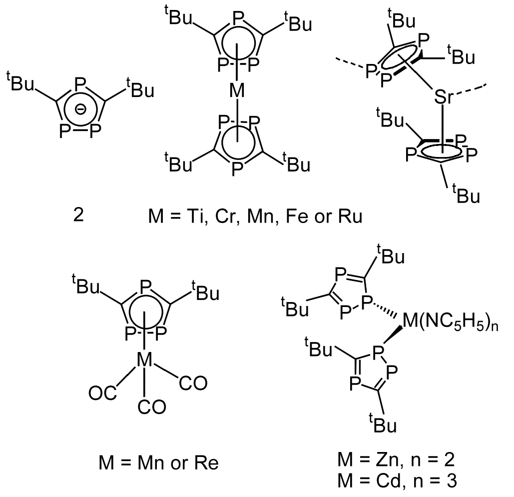


Fig. 1. Some typical examples of η^5- and η^1-bonded $P_3C_2^tBu_2$ complexes.

The sum of the angles around each bridging phosphorus centre in **3** are 358.8 and 357.1°, respectively, indicative of an almost planar system, and this presumably facilitates electron delocalisation leading to similar intra-ring C–P distances, (C(1)–P(1) 1.737, C(1)–P(3) 1.736, P(3)–C(2) 1.735, C(2)–P(2) 1.732 Å). Similar behaviour has been previously reported for *trans*-$[M(\eta^1\text{-}P_3C_2^tBu_2)_2(PEt_3)_2]$ (M = Pt or Pd) [14]. The Cu···Cu distance (4.306 Å) in **3** is too long for any significant interaction between the two metal centres to be likely, the sum of the van der Waals' radii of monovalent copper being 2.8 Å [22].

Complex **4** (Fig. 3) has a similar dimeric molecular structure to **3** except that the bridging iodide in **3** is replaced by a second bridging $P_3C_2^tBu_2$ ligand. The similarity of the P–C intra-ring distances of each $P_3C_2^tBu_2$ ring in complex **4** indicates significant delocalisation of π-electrons, although the bridging phosphorus centres are both pyramidal. As in **3** the Cu···Cu distance (4.512 Å) in **4** is too long for any significant bonding interaction between the two metal centres [22].

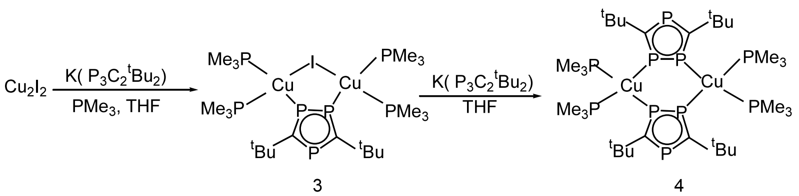
Interestingly, the structure of **4** is similar to that of the dimeric Ni(II) complex $[Ni_2(NO)_2(PPh_3)_2(\mu\text{-}P_3C_2^tBu_2)_2]$, recently reported by Zenneck and co-workers [23] which undergoes an interesting dissociation of Ph_3P in solution to give the monomeric compound $[Ni(NO)(\eta^5\text{-}P_3C_2^tBu_2)]$, having a piano-stool structure. Since this temperature dependent σ- to π- rearrangement of the $P_3C_2^tBu_2$ ring is reversible it suggests that there is little energetically to choose between the two bonding modes of the $P_3C_2^tBu_2$ ring system.

2.2. Au(I) complexes

Treatment of $K(P_3C_2^tBu_2)$ with $[Et_3PAuCl]$ in THF at room temperature (Scheme 2) afforded $[Au(P_3C_2^tBu_2)_2][Au(PEt_3)_2]$ (**5**) as yellow orange crystals.

Compound **5** was identified by multinuclear NMR spectroscopy and structurally characterised by a single crystal X-ray diffraction study. The solid-state structure of $[Au(P_3C_2^tBu_2)_2][Au(PEt_3)_2]$ (**5**), which is shown in Fig. 4, reveals the binuclear nature of the complex in which one Au atom is bound to two anionic $(P_3C_2^tBu_2)$ ligands, and the other is bonded to two neutral PEt_3 ligands. The complex may thus be regarded as an anion:cation pair with the $[Au(\eta^1\text{-}P_3C_2^tBu_2)_2]$ fragment designated as the anion and the $[Au(PEt_3)_2]$ the cation.

Binding of each $P_3C_2^tBu_2$ ring to one gold centre is via η^1-coordination from one of the two adjacent P atoms, resulting in equal Au–P bond distances (2.298 Å) and P(1)–Au(2)–P(4) bond angles (175.8°). The second Au



Scheme 1.

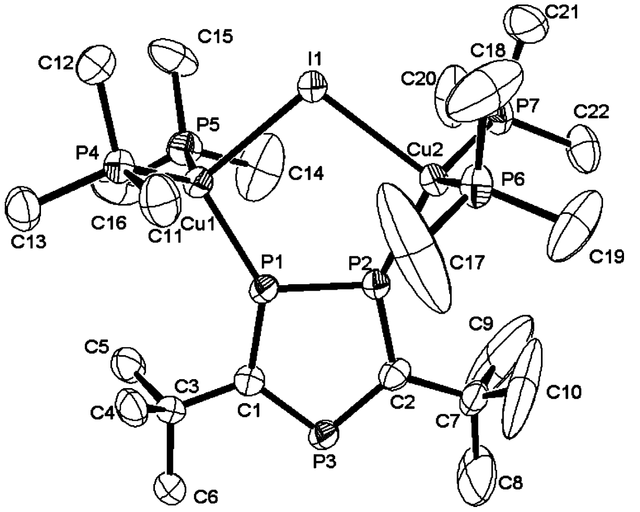


Fig. 2. Molecular structure of **3**. Selected bond distances (Å) and angles (°): Cu(1)–I(1) 2.765(1), Cu(2)–I(1) 2.765(1), Cu(1)–P(1) 2.288(2), Cu(1)–P(4) 2.244(2), Cu(1)–P(5) 2.251(2), Cu(2)–P(2) 2.276(2), Cu(2)–P(6) 2.256(2), P(1)–P(2) 2.069(3), P(1)–C(1) 1.737(7), C(1)–P(3) 1.736(7), P(3)–C(2) 1.735(8), C(2)–P(2) 1.732(7). Cu(1)–I(1)–Cu(2) 102.29(3), P(1)–Cu(1)–P(5) 109.29(8), P(1)–Cu(1)–I(1) 97.86(6), I(1)–Cu(1)–P(4) 99.94(6), P(4)–Cu(1)–P(5) 129.60(8), P(2)–Cu(2) I(1) 99.60(7), P(7)–Cu(2)–P(6) 118.02(8), P(6)–Cu(2)–I(1) 101.08(6), P(7)–Cu(2)–P(2) 122.37(9), P(2)–C(2)–P(3) 118.7(4), C(2)–P(3)–C(1) 102.1(3), P(3)–C(1)–P(1) 118.3(4), C(1)–P(1)–P(2) 100.6(2), C(2)–P(2)–P(1) 100.3(3).

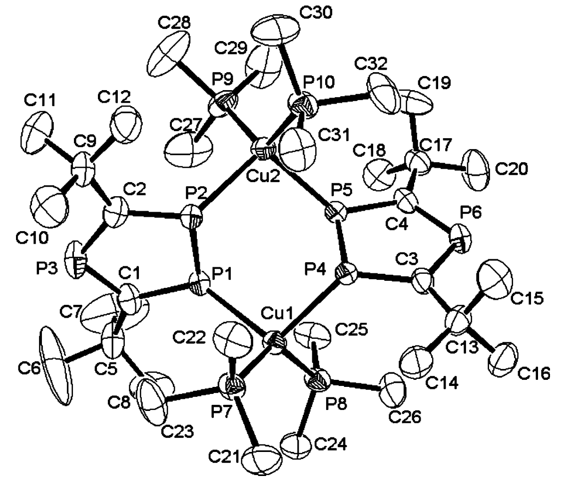


Fig. 3. Molecular structure of **4**. Selected bond distances (Å) and angles (°): Cu(1)–P(1) 2.408(2), Cu(1)–P(4) 2.431(2), Cu(1)–P(7) 2.257, Cu(1)–P(8) 2.262(2), Cu(2)–P(5) 2.369(2), Cu(2)–P(2) 2.365(2), Cu(2)–P(9) 2.260(2), Cu((2)–P(10) 2.270(2), P(1)–P(2) 2.093(2), P(1)–C(1) 1.734, C(1)–P(3) 1.748(6), P(3)–C(2) 1.742(6), C(2)–P(2) 1.737(5), P(5)–P(4) 2.088(2), P(4)–C(3) 1.744(5), C(3)–P(6) 1.746(6), P(6)–C(4) 1.744(6), C(4)–P(5) 1.751(5). P(1)–Cu(1)–P(4) 103.76(5), C(1)–P(1)–Cu(1) 128.7(2), P(7)–Cu(1)–P(8) 131.04(6), P(2)–Cu(2)–P(5) 99.25(6), P(9)–Cu(2)–P(10) 126.09(7), Cu(2)–P(2)–C(2) 132.7(2), P(1)–P(2)–Cu(2) 107.18(8), P(2)–P(1)–Cu(1) 102.66(7), Cu(1)–P(4)–P(5) 99.42(7), P(4)–P(5)–Cu(2) 105.35(7), C(1)–P(1)–P(2) 99.89, C(2)–P(2)–P(1) 100.7(2).

$$K(P_3C_2{}^tBu_2) + Et_3PAuCl \longrightarrow [Au(P_3C_2{}^tBu_2)_2][Au(PEt_3)_2]$$

5

Scheme 2.

centre is bound to the two PEt_3 ligands, with a mean Au–P bond distance 2.3165 Å, and P(7)–Au(1)–P(8) bond angle 171.6°. The distance between the two Au centres (3.0385°) lies well within the sum of the van der Waals' radii of gold (3.4 Å) [22], indicating a substantial bonding interaction between the two metal centres, which is presumably largely electrostatic. In complex **5** the sum of angles of each saturated P atom of the $Au(P_3C_2^tBu_2)_2$ unit are 346.7 and 341.5°, respectively, which indicates that unlike the other two ring phosphorus atoms, they are pyramidal, however the intramolecular C–P distances indicate some delocalisation of π-electrons within the ring.

Several Au(I) compounds have recently been reported in the literature which have Au···Au distances lying in the range of 2.9–3.4 Å implying a bond energy comparable with that of the hydrogen bond (6–11 $kcal.mol^{-1}$) [24,25] (see Fig. 5). This type of interaction may be explained by the concept of 'auriophilicity' (i.e. the tendency of a Au(I) centre to make extra bonding interaction with neighbouring Au(I) centres, in the presence of donors or acceptors. [26,27] Other L–Au–X systems which can aggregate by this type of interaction may lead to dimers typified by $Ph_3PAuSC_6H_4CO_2H$ with an Au···Au distance of 3.0756 Å [28] and $Ph_3PAuGeCl_3$ (2.960 Å) [29] (Fig. 5a), or alternatively to afford oligomers, depending on nature and bulk of the ligands, as in Me_3PAuCl [30] (Fig. 5b).

Redistribution of the ligands on gold is also possible to afford complexes containing both the $[AuL_2]$ cation and $[AuX_2]$ anion, as observed previously in $[Au(THT)_2][AuI_2]$ [31] and $\{[(C_5H_5N)_2Au][AuX_2]\}_n$ [32] (Fig. 5c) and also in the case of compound **5** described in this paper (Fig. 5d). A wide range of gold coordination compounds has been studied extensively by Schmidbaur

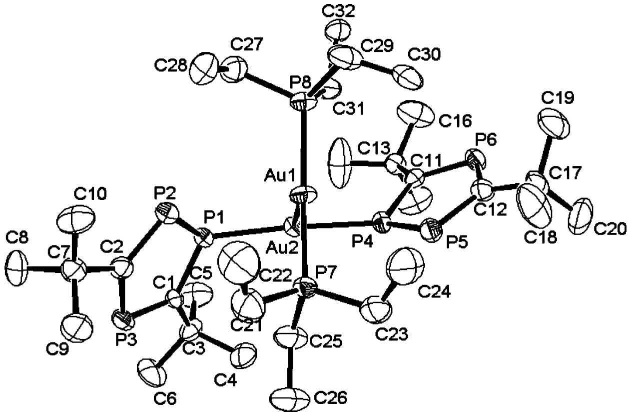
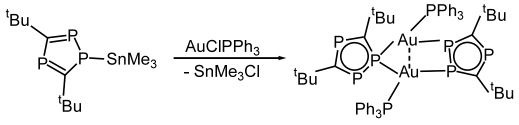


Fig. 4. Molecular structure of [Au($P_3C_2^tBu_2$)$_2$][Au(PEt_3)$_2$] (**5**). Selected bond distances (Å) and angles (°): Au(1)–Au(2) 3.0385(3), Au(1)–P(7) 2.319(2), Au(1)–P(8) 2.314(2), Au(2)–P(1) 2.298(2), Au(2)–P(4) 2.298(2), P(1)–P(2) 2.094(2), P(1)–C(1) 1.748(6), C(1)–P(3) 1.719(7), P(3)–C(2) 1.761(7), P(2)–C(2) 1.724(7), P(4)–C(11) 1.756(7), P(5)–P(4) 2.082(2), P(5)–C(12) 1.735(7), C(12)–P(6) 1.749(7), C(11)–P(6) 1.719(7). P(1)–Au(2)–P(4) 175.97(6), P(7)–Au(1)–P(8) 171.62(6), Au(2)–Au(1)–P(8) 92.36(4), Au(2)–Au(1)–P(7) 95.99(5), Au(1)–Au(2)–P(1) 87.79(4), Au(1)–Au(2)–P(4) 92.13(5), C(1)–P(1)–Au(2) 120.11(2), Au(2)–P(1)–P(2) 118.05(9), C(1)–P(1)–P(2) 103.3(2), P(5)–P(4)–C(11) 103.8(2), P(5)–P(4)–Au(2) 114.80(9), Au(2)–P(4)–C(11) 128.1(2).

and co-workers [33,34] who also have reviewed the field [27,35].

Interestingly, the solid-state structure of complex **5** contrasts with that reported [1] for the closely related 1,2,4-triphospholyl compound [Au($P_3C_2^tBu_2$)PPh_3]$_2$ (**1**), containing the PPh_3 co-ligand, which was made by treatment of [AuCl(PPh_3)] with $Ph_3SnP_3C_2^tBu_2$ (Scheme 3).

Although like **1** complex **5** also has a dimeric solid-state structure, it exhibits a completely different geometry and as noted by the authors of reference [1] the most striking structural feature is the range of different gold to $P_3C_2^tBu_2$ ligand interactions. Thus, one triphospholyl ring in **1** bridges the Au–Au unit solely via one of the two directly bonded P atoms, whereas the other ring is bonded to the Au–Au unit by both the P–P bonded ring atoms. The Au···Au distance in **1** of 3.14 Å is indicative of a rather weak interaction of the metal centres and is longer than that found in **5**.



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Scheme 3.

It has been suggested [1] that the unusual structure of **1** may reflect the pronounced s-character of both the P and Au atomic orbitals, leading to a shallow energy minimum in the potential energy. Although this factor may be important, it is nevertheless still surprising that the completely different structure we find for **5** results by merely a simple replacement of the attendant tertiary phosphine ligand from PPh_3 to PEt_3 and this aspect warrants further detailed study. Interestingly in preliminary studies we find the bulkier diphospholyl $P_2C_3^tBu_3$ anion shows no reaction with [AuClPEt$_3$] even at 80 °C [36].

The $^{31}P\{^1H\}$-NMR spectrum of **5** reveals that the compound is fluxional in solution, presumably as a result of rapid 1,2- shifts of the Au atom between the two adjacent P atoms in the [Au($P_3C_2^tBu_2$)$_2$] unit, and this dynamic behaviour is still rapid even at −70 °C. We have previously observed similar behaviour in other 1,2,4-triphospholyl metal systems such as *trans*-[M(η^1-$P_3C_2^tBu_2$)$_2$(PEt_3)$_2$] (M = Pt or Pd) [14], R_3Sn(η^1-$P_3C_2^tBu_2$) (R = Me, ᵗBu, or Ph) [16] and [M(η^1-$P_3C_2^tBu_2$)$_2$(NC_5H_5)$_n$] (M = Zn, *n* = 2, M = Cd, *n* = 3) [13].

3. Experimental

All procedures were conducted using conventional Schlenk and glove box techniques, under an atmosphere of high purity argon or nitrogen. The solvents were dried by refluxing over sodium-potassium alloy and were distilled and degassed before use. ^1H-, $^{31}P\{1H\}$- and ^{13}C-NMR spectra were recorded on either a Bruker AMX-500 or DPX-300 spectrometer in C_5D_5N and were referenced to the residual ^1H resonances of the solvent, the ^{13}C resonances of the deuterated solvent or to external 85% H_3PO_4 (δ 0.0, ^{31}P-NMR), respectively. Microanalyses were performed by Labor Pascher,

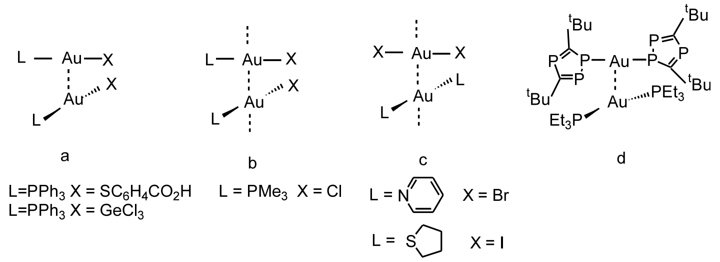

Fig. 5.

Remagen, Germany. PMe_3, Cu_2I_2 and Et_3PAuCl were commercial samples and were used as received. $KP_3C_2^tBu_2$ was synthesised by the literature procedure [11].

3.1. Preparation of $[(P_3C_2^tBu_2)Cu(PMe_3)_2Cu(PMe_3)_2I]$ (**3**)

A mixture of $[K(P_3C_2^tBu_2)]$ (0.125 g, 0.47 mmol) and Cu_2I_2 (0.18 g, 0.92 mmol) were stirred in THF (15 ml) in the presence of PMe_3 (1 ml) for 3 h. The solvent was removed and the product was extracted with hexane and recrystallisation from hexane at −30 °C, (Yield 30%, yellow crystals, melting point (m.p.) starts to decompose at 140 °C).

3.1.1. Spectroscopic data

(C_5D_5N, RT) $^{31}P\{^1H\}$: $\delta_P = 253$ ppm (b), $\delta_P = 201$ ppm (b), $\delta_P = -46$ ppm (b), ^1H: $\delta_H(^tBu) = 1.81(18H)$ ppm, $\delta_H(PMe_3) = 1.18$ (36H) ppm. $^{13}C\{^1H\}$: $\delta_C(\text{ring}) = 199.6$ ppm, $\delta_C(^tBu) = 40.5$ ppm, $\delta_C(CH_3) = 37.6$(b) ppm, $\delta_C(PMe_3) = 16.5$ ppm. (d) ($^1J_{PC} = 14.2$ Hz).

Microanalysis Found: C, 34.45; H, 6.91. Calc. C, 33,47; H, 6.89%.

3.1.2. Crystal data for **3**

$Cu_2IP_7C_{22}H_{54}$, $M = 789.42$, monoclinic $P2_1$(Number 4), $a = 9.6305(3)$, $b = 19.9560(5)$, $c = 19.678(5)$ Å, $\beta = 95.869(1)$, $V = 3762.0(2)$ Å^3, $T = 173(2)$, $Z = 4$, $\mu = 2.26$ mm^{-1}, $\lambda = 0.71073$ Å, 20 007 reflections collected, 12 033 independent, [$R_{int} = 0.050$], 10 873 with $I > 2\sigma(I)$, $R_1 = 0.0453$, $wR_2 = 0.106$ for $I > 2\sigma(I)$, $R_1 = 0.0650$, $wR_2 = 0.112$ for all data. Data collection KappaCCD. Refinement using SHELXL-97.There is two independent molecules in the unit cell.

3.2. Preparation of $[(P_3C_2^tBu_2)Cu(PMe_3)_2]_2$ (**4**)

$K(P_3C_2^tBu_2)$ (0.25 g, 0.92 mmol) and Cu_2I_2 (0.18 g, 0.92 mmol) were stirred in THF (15 ml) in the presence of PMe_3 (1 ml) overnight. The solvent was removed and the product was extracted with Et_2O and recrystallisation from Et_2O at −30 °C, (Yield 50% (yellow crystals, m.p., starts to decompose at 105 °C).

3.2.1. Spectroscopic data

(C_5D_5N, RT), $^{31}P\{^1H\}$: $\delta_P = 251$ ppm, $\delta_P = 206$ ppm (b), $\delta_P = -46$ ppm (b), ^1H: $\delta_H(^tBu) = 1.83$ (36H) ppm, $\delta_H(PMe_3) = 1.17$ (36 H) ppm. $^{13}C\{^1H\}$: $\delta_C(\text{ring}) = 201.4$ ppm, $\delta_C(^tBu) = 40.6$ ppm, $\delta_C(CH_3) = 37.7$(b) ppm, $\delta_C(PMe_3) = 16.7$ ppm. (d) ($^1J_{PC} = 13.7$ Hz).

Microanalysis Found: C, 43.20; H, 8.05. Calc. C, 43.00; H, 8.12%.

3.2.2. Crystal data for **4**

$Cu_2P_{10}C_{32}H_{72}$, $M = 893.68$, monoclinic $P2_1/n$ (Number 14), $a = 12.5047(3)$, $b = 21.0106(5)$, $c = 36.5333(10)$ Å, $\beta = 91.524(1)$, $V = 9595.0(4)$ Å^3, $T = 173(2)$, $Z = 4$, $\mu = 1.24$ mm^{-1}, $\lambda = 0.71073$ Å, 29 670 reflections collected, 12 757 independent, [$R_{int} = 0.055$], 8735 with $I > 2\sigma(I)$, $R_1 = 0.051$, $wR_2 = 0.104$ for $I > 2\sigma(I)$, $R_1 = 0.089$, $wR_2 = 0.119$ for all data. Data collection KappaCCD. Refinement using SHELXL-97.

3.3. Preparation of $[Au(\eta^1\text{-}P_3C_2^tBu_2)_2][Au(PEt_3)_2]$ (**5**)

$K(P_3C_2^tBu_2)$ (0.35 g, 1.29 mmol) and $[Au(PEt_3)Cl]$ (0.455 g, 1.29 mmol) were stirred in THF (15 ml) overnight. The solvent was removed and the product was extracted with hexane and recrystallisation from hexane at RT. (Yield 50% (yellow orange crystals, m.p. 144 °C spectroscopic data : (C_7D_8, RT) $^{31}P\{^1H\}$: $\delta_P = 263$ ppm, $\delta_P = 185$ ppm (b), $\delta_P = 37$ ppm. ^1H: $\delta_H(^tBu) = 1.92$ (36H) ppm, $\delta_H(CH_2,Et) = 1.31$ (8H) ppm, δ_H $(CH_3,Et) = 0.79$ (18H) ppm. $^{13}C\{^1H\}$: $\delta_C(\text{ring}) = 204.9$ ppm, $\delta_C(CMe_3) = 41.1$ ppm, ($^2J_{CP} = 21$ Hz), $\delta_C(CH_3,^tBu) = 37.4$ ppm ($^2J_{PC} = 11$ Hz), $\delta_C(CH_2,Et) = 18.1$(b) ppm, $\delta_C(CH_3,Et) = 8.8$ ppm.

Microanalysis Found: C, 35.67; H, 6.22. Calc. C, 35.18; H, 6.09%.

3.3.1. Crystal data for **5**

$Au_2P_8C_{32}H_{66}$, $M = 1092.54$, monoclinic $P2_1/c$ (Number 14), $a = 12.7922(4)$, $b = 11.0791(3)$, $c = 31.0699(5)$ Å, $\beta = 97.642(2)$, $V = 4364.3(2)$ Å^3, $T = 173(2)$, $Z = 4$, $\mu = 7.03$ mm^{-1}, $\lambda = 0.71073$ Å, 32 400 reflections collected, 10 398 independent, [$R_{int} = 0.069$], 7996 with $I > 2\sigma(I)$, $R_1 = 0.044$, $wR_2 = 0.100$ for $I > 2\sigma(I)$, $R_1 = 0.065$, $wR_2 = 0.110$ for all data. Data collection KappaCCD. Refinement using SHELXL-97.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 194295, 194296 and 194297 for compounds **3**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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