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Group 11 metal complexes of SPS-based pincer ligands: Syntheses, X-ray structures and reactivity†

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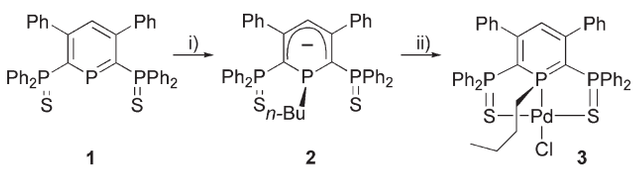
New group 11 d^{10} (Cu, Au) metal complexes with SPS pincer ligand were synthesized. Insoluble dimeric or oligomeric complexes $[(SP(R)S)Cu]_n$ (R = Bu: **4**, Me: **5**) were readily cleaved by several two-electron donor ligands (phosphines, isocyanides, pyridine) to yield a range of new complexes (**6**–**13**). X-Ray crystal studies were performed on complexes **7**, **8**, **9**, **11**, which revealed distorted tetrahedral geometries and proved once again the flexibility of the SPS ligand, which can accommodate square planar, tetrahedral, octahedral and trigonal bipyramidal geometries. A dimeric gold species with an Au–Au interaction **16** was also synthesized. This dimer could be cleaved with two electron donor ligand (PPh_3: **17**, RNC **18**). Reactivity of complex **11** with ethyl diazoacetate yielded new λ^5-phosphinine **14**.

Introduction

Since the pioneering work of Shaw and coworkers,[1] the synthesis and subsequent use of pincer ligands in coordination chemistry and catalysis has been a rapidly growing field of investigations over the past decade. These ligands share a common feature: an aromatic central moiety. To this unit are attached, in the *ortho* positions, two arms whose electronic and steric properties can be varied almost at will. These degrees of freedom in the tuning of the overall coordinating behaviour of these pincer ligands resulted in numerous applications in catalysis.[2] Early work mainly focused on PCP systems but CCC, CNC, CNS, NNN, NCN, PNP, OCO, SCS, SNS have been reported in recent years.[3] Sulfur-based ligands are particularly appealing since they can also be employed in the elaboration of synthetic models of enzymes.[4] Mainly four types of sulfur ligands are employed: classical thioethers,[5] thiolates,[6] sulfoxides,[7] in which coordination occurs through the remaining lone pair at sulfur, and phosphine sulfides.[8] The latter, which have not been employed in pincer type structures so far, have found an interesting application in the rhodium catalyzed carbonylation of methanol when they are incorporated in mixed P–P=S bidentate ligands.[9]

A different way of tuning the properties of the pincer ligand would be to replace the nitrogen or carbon atoms of the central unit by a phosphorus atom. Indeed, it is now well established that phosphorus in multiple bonds essentially behaves as relatively poor σ-donor ligands but display a powerful π-accepting capacity.[10] Therefore, their electronic properties markedly differ from those of classical phosphines and nitrogen analogs. Very different systems incorporating phosphaalkene (P analogs of alkenes) or heterocycles can be anticipated but, in practice, only aromatic phosphorus heterocycles (phosphinines) present sufficient stability.

We recently reported on the synthesis of mixed S–P–S ligands featuring a phosphinine as the central unit and two phosphine sulfides as ancillary ligands.[11] Such systems, like **1**, are easily available in large amounts (10 g scale) by sulfurization of the corresponding 2,6-bis(diphenylphosphino)-λ^3-phosphinines. In a first study, these systems were found to be particularly reactive towards nucleophilic attack because of the highly electropositive phosphorus atom of the phosphinine moiety, either as a free ligand or complexed to a palladium center. We thus devised a rational approach towards metal complexes through the use of 1-*R*-1-*P*-phosphahexadienyl anions (Scheme 1).



Scheme 1 Reagents and conditions: (i) BuLi; (ii) $[Pd(COD)Cl_2]$.

Thus, anion **2** which is straightforwardly obtained by reacting *n*BuLi with phosphinine **1** reacted with $[Pd(COD)Cl_2]$ to afford complex **3**. The latter was found to be particularly active (TON up to 10000) in the Miyaura catalyzed cross-coupling process that allows the synthesis of aryl boronic esters from halogeno aromatic and dialkoxyboranes.[11]

The coordination chemistry of these 1-*R*-1-*P*-phosphahexadienyl anions could be extended to group 9 metal centers (Rh), for which activation of small molecules (CO, O_2, CS_2) was observed.[12] Copper complexes are often used in catalysis in general and in the cyclopropanation of olefins in particular.[13] On the other hand, gold complexes have only seldom been used for catalytic transformations, but significant results have appeared lately.[14] This prompted us to start an investigation of the coordinating behaviour of our SPS ligands towards group 11 metal centers (Cu, Au), which we present here.

Results and discussion

Copper complexes

Synthesis. As previously described, reaction of **1** with equimolar amounts of MeLi in THF at −78 °C readily yielded anion **4**, which was not isolated but whose complete formation was checked by ^{31}P NMR (Scheme 2). It is characterized by a triplet at −65.7 ppm (PMe moiety, $^2J_{P-P}$ = 155.5 Hz) and a doublet at 45.9 ppm (PPh_2S, $^2J_{P-P}$ = 155.5 Hz). The tremendous variation of the chemical shift of the central phosphorus atom from **1** to **4** of over −320 ppm is by itself a proof of the change of sp^2 hybridization to sp^3 hybridization. On the other hand, the chemical shift of the PPh_2S moiety is not altered to a great extent: $\Delta\delta$ = 2.5 (**1**, δ = 43.4). Anion **4** was subsequently reacted with solid CuI (or $[CuBr{\cdot}SMe_2]$). The initially deep red solution turned orange with concomitant formation of an orange precipitate. After one night, a ^{31}P NMR spectrum of the crude mixture showed the absence of any signal indicating that all the ligand had been consumed. The product is insoluble in usual organic solvents, and is therefore isolated pure by washing and drying. Elemental analysis shows the composition to be a multiple of the [(SP(Me)S)Cu] moiety: **5**. In order to increase the solubility of this precipitate, the same reaction was carried out with BuLi in place

† Electronic supplementary information (ESI) available: Colour ORTEP views of complexes **8** and **9** (50% ellipsoids). See http://www.rsc.org/suppdata/dt/b4/b406792d/

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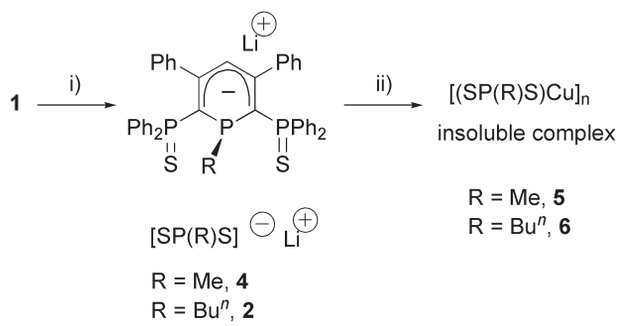
Table 1 ^{31}P NMR chemical shifts for **2**, **4**, **7**–**13**

Product no.	δ (P–R)[a]	^2J (P–P)[b]	δ (Ph_2PS)[a]	δ (P)[a]
2	−66.2	156.0	45.8	
4	−65.7	155.5	45.9	
7	−28.0	150.7	47.3	
8	−25.5	154.3	48.4	
9	−20.1	162.8	49.8	3.5 (PPh_3)
10	−19.6	159.1	49.1	113.7 ($P(OPh)_3$)
11	−36.0	151.9	46.6	
12	−15.5	152.5	47.5	
13	−17.9	143.4	46.8	

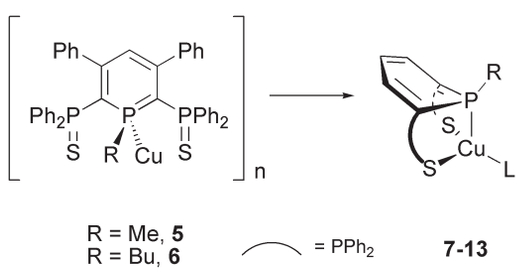
[a] In ppm. [b] In Hz.

of MeLi. Similarly, the formation of the anion **2** was observed which appeared as a triplet at −66.2 ppm (PBu moiety, $^2J_{P-P}$ = 156.0 Hz) and a doublet at 45.8 ppm (PPh_2S, $^2J_{P-P}$ = 156.0 Hz). Anion **2** was also reacted with CuI (or [$CuBr{\cdot}SMe_2$]), and here again an insoluble orange solid formed: **6**.



Scheme 2 Reagents and conditions: (i) RLi, THF, −78 °C to rt; (ii) CuI, THF, −78 °C to rt.

Despite their insolubility, these complexes reacted with several two-electron donor ligands, such as isocyanides, phosphines, phosphites or even pyridine to give soluble tetrahedral Cu(I) orange complexes in quasi-quantitative yields (Scheme 3).



Scheme 3 Reagents and conditions: *n* L, CH_2Cl_2, rt. **7**: R = Me, L = 2,6-dimethylphenylisocyanide; **8**: R = Me, L = t-butylisocyanide; **9**: R = Me, L = PPh_3; **10**: R = Me, L = $P(OPh)_3$; **11**: R = Me, L = Py; **12**: R = n-Bu, L = 2,6-dimethylphenylisocyanide; **13**: R = n-Bu, L = t-butylisocyanide.

These were fully characterized by NMR spectroscopy and elemental analysis and X-ray crystal studies were performed for **7**, **8**, **9** and **11**. In the complexes **7**–**11**, the ^{31}P NMR signals of the SPS moiety all appeared as expected sets of triplet and doublet at around −25 ppm (P–Me) and 49 ppm (PPh_2S), respectively (Table 1), with a large ^2J(P–P) coupling constant of about 150 Hz, and the complexes **12**–**13** as triplet and doublet at around −16 ppm (P–Bu) and 47 ppm (PPh_2S), respectively. One can note that the signal of the PPh_2S appeared as sharp lines whereas the other signals appeared broad. The variation of the chemical shifts for the P(R) moiety between **7** and **12** ($\Delta\delta$ = 12.5), and **8** and **13** ($\Delta\delta$ = 7.6) is consistent with the change of chemical shifts between PPh_2Me and PPh_2Bu ($\Delta\delta$ = 10).[15]

The signal of the P(Me) for the pyridine complex **11** resonated at higher frequency than in the other complexes, indicating a higher partial charge at the phosphorus (compared to −65.7 for anion **4**). In ^{1}H NMR, the chemical shift for H_4 (*para* to the P atom in the λ^5 phosphinine subunit) was not modified significantly by the electronic nature of the ligand L added (δ ranging from 5.50 for **11** to 5.66 for **8**, compared to 5.13 in [D8]-thf for **4**).[16] The X-ray crystal structures recorded all show similar tetrahedral like geometry around the Cu(I) center. Complexes **7** and **11** are presented here, and complexes **8** and **9** are reported in the ESI.† ORTEP views of one molecule of **7** and **11** are presented in Fig. 1 and Fig. 2, respectively, as well as the most relevant bond lengths and angles. Crystal data and structural refinement details are given in Table 2.

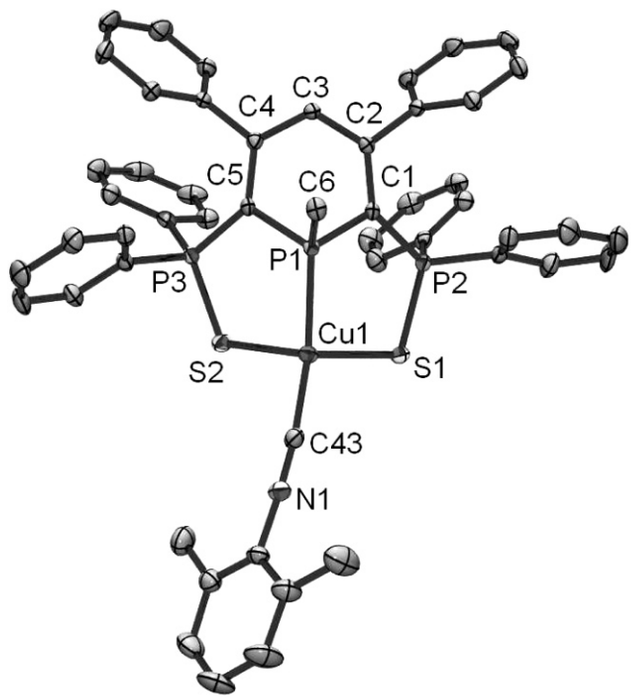


Fig. 1 ORTEP view of complex **7** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. Selected bond lengths (Å) and angles (°): P1–C1 1.794(2), C1–C2 1.410(2), C2–C3 1.406(2), C1–P2 1.781(2), P2–S1 2.0021(6), P1–C6 1.827(2), P1–Cu1 2.2377(5), S1–Cu1 2.3694(5), S2–Cu1 2.4321(6), Cu1–C43 1.887(2), C43–N1 1.154(2), P1–Cu1–C43 143.39(6), S2–Cu1–S1 112.64(2), N(1)–C(43)–Cu(1) 170.9(2), C(43)–N(1)–C(44) 176.4(2).

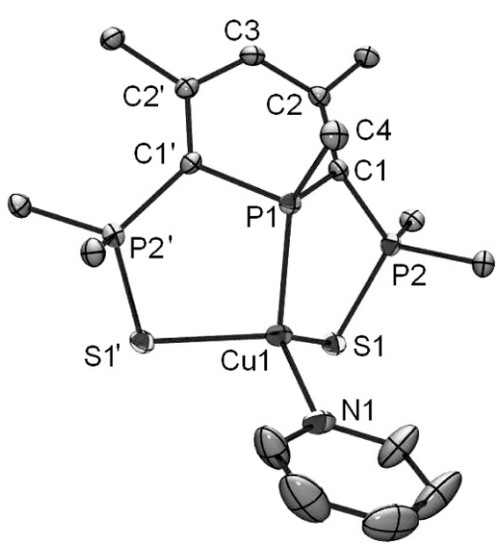


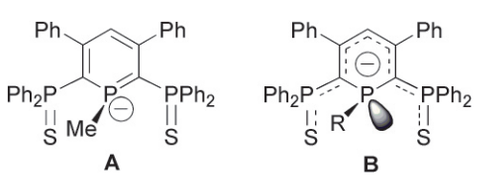
Fig. 2 ORTEP view of complex **11** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. Phenyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C1 1.797(2), C1–C2 1.403(3), C2–C3 1.413(3), C1–P2 1.776(2), P2–S1 2.0072(8), P1–C4 1.835(3), C1′–P1–C1 101.5(1), P1–Cu1 2.2088(8), S1–Cu1 2.3621(6), Cu1–N1 2.026(3), P1–Cu1–N1 124.5(1), S1–Cu1–S1′ 101.35(3).

As noted above, the two structures show tetrahedral like geometry. The angles at the copper center deviate from the ideal 109° to a different extent in these two complexes. In complex **7**, the angle

Table 2 Crystal data and refinement parameters for **7**–**9**, **11**, **16** and **17**

	7	**8**	**9**	**11**	**16**	**17**
Formula	$C_{51}H_{43}CuNP_3S_2$	$C_{47}H_{43}CuNP_3S_2$	$C_{62}H_{53.50}ClCuP_4S_2$	$C_{62}H_{54}CuN_4P_3S_2$	$C_{85}H_{70}Au_2Cl_2P_6S_4$	$C_{60}H_{49}AuP_4S_2$
Molecular weight	890.43	842.39	1085-54	1075.66	1870.30	1154.96
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	Cm	$C2/c$	$P\bar{1}$
a/Å	10.8652(2)	8.773(5)	15.7730(10)	15.4940(10)	13.631(1)	12.595(5)
b/Å	13.2635(2)	12.595(5)	17.3780(10)	17.1260(10)	19.509(1)	13.589(5)
c/Å	15.6616(3)	39.454(5)	20.3450(10)	11.6850(10)	28.894(1)	17.267(5)
α/°	86.741(7)		75.4440(10)			70.440(5)
β/°	73.493(6)		78.7570(10)	121.4650(10)	91.8768(1)	68.800(5)
γ/°	87.071(8)		89.2700(10)			70.900(5)
Z	2	4	4	2	4	2
μ/cm^{-1}	0.751	0.740	0.704	0.628	4.165	3.164
Reflections measured	18811	10282	39341	6931	19109	16814
Reflections used	9720	9129	21349	6675	8163	8806
wR_2	0.1096	0.0964	0.1197	0.0986	0.1038	0.0811
R_1	0.0403	0.0384	0.0412	0.0386	0.0346	0.0401

S2–Cu1–S1 measures 112.64(2)° and P1–Cu1–C43 143.39(6)° whereas in complex **11** S1–Cu1–S1′ measures 101.35(3)° and P1–Cu1–N1 124.5(1)° which shows that **6** is more distorted. The most interesting piece of data is given by the external P–C bond lengths (C1–P2 1.781(2) Å C5–P3 1.769(2) Å in **7** and C1–P2 1.776(2) Å in **11**) which are clearly shorter than in the free ligand (P–C 1.826(2) Å),[16] and therefore have gained significant double bond character. Moreover, they are shorter than the internal P–C bond lengths (P1–C1 1.794(2), Å C5–P1 1.797(2) Å in **7** and P1–C1 1.797(2) Å in **11**). These internal P–C bonds are now much longer than in the free ligand (1.742(2) Å) but compare to those in reported square planar Pd(II) complexes (1.776(3) Å).[11] Nevertheless, these values are still much shorter than the P–Me bond length (P1–C6 1.827(2) Å in **7** and C4–P1 1.835(3) Å in **11**). The P=S bond lengths (P2–S1 2.0021(6) Å, P3–S2 2.0014(6) Å for **7** and P2–S1 2.0072(8) Å for **11**) are in turn slightly elongated when compared to free ligand (1.956(1) Å).[16] From this data and the data collected with the Pd and Ni complexes reported earlier it is relatively difficult to establish whether the ligand behaves as an anionic λ^4-phosphinine (form A) or as classical tertiary phosphine (form B) (Scheme 4).[16] On the one hand, short internal P–C bond lengths suggest that the ylidic structure of the phosphinine has been restored upon complexation (form A) but, on the other hand, relatively long P–S bonds and short external P–C connections point out that delocalization takes place within the unsaturated part of the ligand (form B). Reasonably, one may propose that the two forms can contribute to the bonding, the respective contributions being determined by the nature of the metal centre and its formal oxidation state.



Scheme 4

Interestingly also in complex **7**, the isocyanide ligand is not perfectly linear: C43–N1–C44 measures 176.4° and N1–C43–Cu1 measures 170.9° which points towards a small change in hybridization at C43. In this case a Cu1–C43 showing a partial double bond character would be expected. In fact, the bond length Cu1–C43 at 1.887(2) Å is normal and comparable with the Cu1–C43 measured in complex **7** (1.890(2) Å, see ESI†), for which the N1–C43–Cu1 is almost linear at 177.4(3)°. These two results seem to contradict each other and a close inspection of the IR CN stretches was warranted. The results are given in Table 3. Both complexes **7** and **12** showed only a marginal increase in the value when compared to the free isocyanide. On the other hand, somewhat unexpectedly, the increase in the stretch is significant for complex **13** (18 cm^{-1}) and large for complex **8** (36 cm^{-1}). This type of increase has been observed previously in the case of $[Cu(CO)_n]^+$ (n = 1,2) complexes, and was investigated

Table 3 IR spectra for copper isocyanide complexes

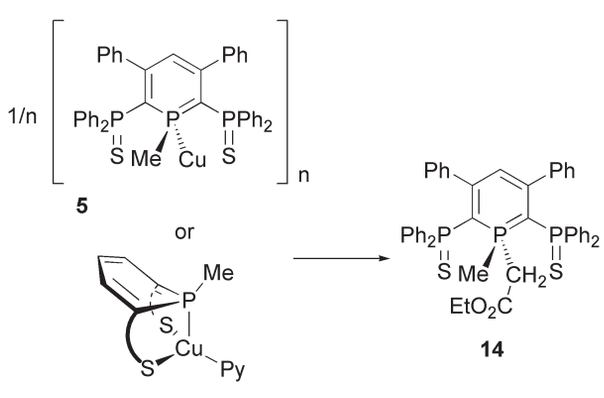
Complex	ν(CN)[a]	Complex	ν(CN)[a]	Free L ν(CN)[a,b]
7	2131	**12**	2130	2122
8	2174	**13**	2158	2140 (CH_2Cl_2)
				2138

[a] In cm^{-1}. [b] See ref. 18.

by DFT calculations.[17] It was thus shown that in these complexes, there was negligible π-back donation from Cu(I) into the ligand. This implied that the coordination is only based on σ donation.

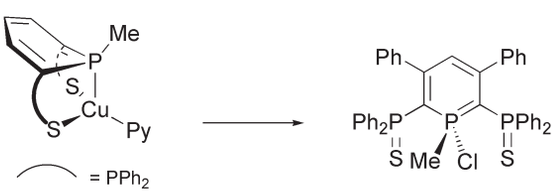
Reactivity. In a first step, based on literature precedence, we focused our studies on the catalytic cyclopropanation of alkenes. We had selected the cyclopropanation of styrene with ethyldiazoacetate. In complexes **7**–**10** and **12**–**13**, the coordination sphere at the copper center is saturated and accordingly they proved rather robust. We thus envisioned the use of either the insoluble complex **5** or the pyridine complex **11** for further reactions. Indeed, as shown above, complex **5** reacted with 2 electron donors to yield mononuclear complexes and we had hoped that, even though alkenes are weaker ligands than pyridine for copper complexes, excess of alkenes would lead to a soluble mononuclear complex. We also hoped that the pyridine ligand in **11** would be easily displaced and therefore that this complex would serve as a masked unsaturated complex, which is a prerequisite for catalytic reactions.

However, addition of large amounts of styrene to suspensions of complex **4** in various solvents did not lead to any dissolution (even partial) as indicated by ^{31}P NMR spectroscopy, nor did styrene alone displaced pyridine in complex **10**. This prompted us to study the reaction of these complexes with the diazoacetate alone (Scheme 5).



Scheme 5 Reagents and conditions: 2 eq. ethyldiazoacetate, CH_2Cl_2.

The first surprising point was the need of two equivalents of diazo per copper center to obtain a clean reaction. Indeed, after addition of the diazo, the solution turned dark orange and a unique product formed characterized by a set of triplet at 18.2 ppm (PMe moiety, $^2J_{P-P}$ = 42.0 Hz) and doublet at 35.7 ppm (PPh_2S, $^2J_{P-P}$ = 42.0 Hz) in ^{31}P NMR. At this point, we had hoped to obtain a new stable copper–carbene complex, which are quite rare species,[19] but the very small value of the coupling constant compared to the other complexes perturbed us. This species proved to be quite stable and soluble in all common organic solvents. It was purified by chromatography on silica gel and fully characterized by NMR spectroscopy. The formation of the previously unknown λ^5-phosphinine **14** was proved by the following data: presence of a new CH_2 signal in ^{13}C NMR coupled with phosphorus (δ 34.5, $^1J_{P-C}$ = 42.2 Hz). This moiety appears in ^1H NMR also as a doublet at 3.3 ppm ($^2J_{H-P}$ = 16.7 Hz). The CH_3–CH_2 unit is also visible as an expected set of triplet-quartet at 1.2 and 4.1 ppm, respectively. The H_4 (proton *para* to the P atom) appeared as the usual weakly coupled triplet at 5.50 ppm ($^4J_{H-P}$ = 4.8 Hz). In short, the addition of the diazo resulted in a clean oxidation of the Cu(I) species which resulted in the loss of the ligand. It is the first time that we observed such a phenomenon with all of the SPS complexes we had obtained so far. Indeed, for example, oxidation of Rh(I) centers resulted in the isolation of Rh(III) species and heating Pd(II) complexes in oxygenated and oxidizing solvents did not lead to decomposition. The reactivity towards different oxidizing agents was therefore studied. Dissolving complex **11** in $CDCl_3$ and following the reaction by both ^{31}P NMR and ^1H NMR provided the following information. After one night at room temperature, about ½ of the starting complex had evolved into two new products in 5/1 ratio characterized by a doublet at 31.9 ppm (PPh_2S, $^2J_{P-P}$ = 26.7 Hz) and a triplet at 42.8 ppm (PMe moiety, $^2J_{P-P}$ = 26.7 Hz) for the major species and a doublet at 35.9 ppm (PPh_2S, $^2J_{P-P}$ = 43.7 Hz) and a triplet at 66.2 ppm (PMe moiety, $^2J_{P-P}$ = 43.7 Hz) for the minor species (**15**). After two days, all of the starting complex had evolved to a mixture of four phosphorus containing products, which could not be separated. One of the by products of this reaction, **15**, is the known 1-Me-1-Cl-λ^5-phosphinine which was prepared alone by oxidation of **11** with equimolar amounts of C_2Cl_6 (Scheme 6).

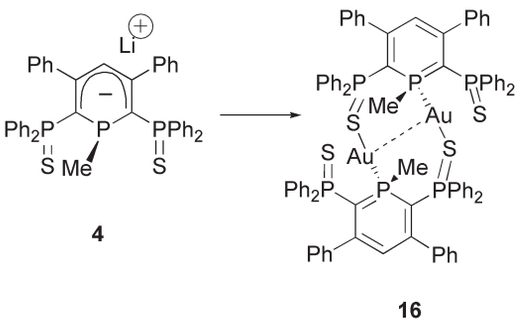


Scheme 6 Reagents and conditions: C_2Cl_6, CH_2Cl_2, rt.

We then turned our attention to gold(I) complexes whose coordination chemistry towards λ^4-phosphinine anions was not known.

Gold complexes

The anion **4** was prepared as above and reacted with equimolar amounts of the [AuCl·SMe_2] precursor at low temperature followed by warming to room temperature (Scheme 7). The initial red solution turned orange and ^{31}P NMR showed complete formation of a single new product after one hour. Three sets of signals appeared at 45 (doublet), 39 (doublet) and −12 ppm (doublet of doublet). These coupling figures could only be accounted for by postulating a structure in which one sulfur ligand would bind to a gold center. In turn, knowing that the geometry of AuL_2 complexes is linear, a dimeric structure had to be envisioned. In fact, after isolation of the pure complex, accumulation on a smaller spectral window in ^{31}P revealed that the signal at −12 ppm is in fact not a doublet of doublets but a much more complicated feature consistent with the dimeric structure proposed for which an AA′MM′XX′ spin system is expected. On the other hand, the two signals at 45 and 39 ppm remain deceptively simple (doublets). The ^1H NMR spectrum is also more simple than expected and only a doublet at 1.20 ppm is observed for the methyl substituent and a triplet at 5.72 ppm is observed for the H_4 proton of the phosphinine ring. X-Ray quality crystals were obtained after diffusion of hexanes into a $CDCl_3$ solution of the complex. These were subjected to X-ray structure analysis which definitely proved the complex to be a dimer. An ORTEP view of one molecule of **16** is presented in Fig. 3 as well as the most relevant bond lengths and bond angles. Crystal data and structural refinement details are given in Table 2.



Scheme 7 Reagents and conditions: [AuCl·SMe_2], THF, −78 °C to rt.

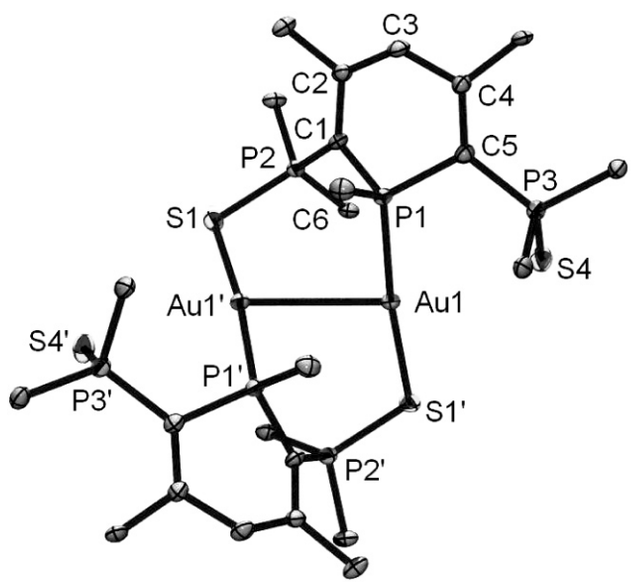
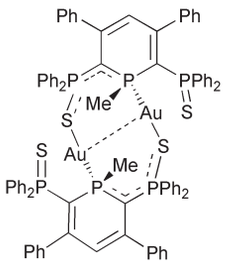


Fig. 3 ORTEP view of complex **16** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. Phenyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.759(3), C(1)–C(2) 1.431(4), C(2)–C(3) 1.369(4), C(3)–C(4) 1.441(4), C(4)–C(5) 1.377(4), P(1)–C(5) 1.829(3), P(1)–C(6) 1.837(3), P(2)–C(1) 1.746(3), S(1)–P(2) 2.037(1), C(1)–P(1)–C(5) 102.6(2), Au(1)–Au(1′) 3.0481(2), P(1′)–Au(1)–S(1) 173.87(3).

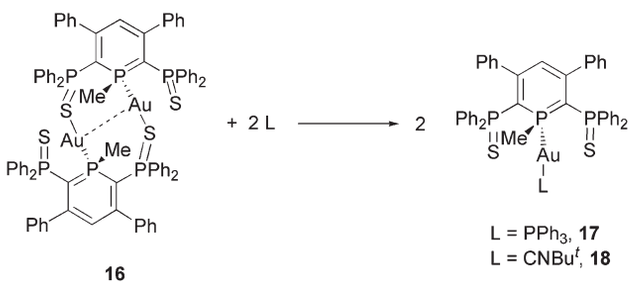
As envisioned, the geometry around the Au(I) centers is (almost) linear dicoordinate, the sulfur of one ligand located *trans* to the phosphorus atom of the other ligand. Apparent in the structure is the aurophilic interaction between the two gold centers (Au(1)–Au(1′) 3.0481(2) Å). This interaction is strong enough to force the geometry to deviate slightly from linearity (P(1′)–Au(1)–S(1) 173.87(3) Å). Interesting results were provided by the external P–C bond lengths. In fact, they are very different within the ligand itself: P(2)–C(1) measures 1.746(3) Å whereas P(3)–C(5) measures 1.799(3) Å. The first one has now gained a strong double bond character (comparable to delocalized internal P=C bond in the free phosphinine **1**: 1.742(2) Å) whereas the second one is only slightly shorter than in the free ligand (P–C 1.826(2) Å). This desymmetrization is also found in the P–S bonds: S(4)–P(3) 1.967(1) Å *vs.* S(1)–P(2) 2.037(1) Å. Concerning the internal P–C bonds, here also P(1)–C(1) 1.759(3) Å is much shorter than P(1)–C(5) 1.829(3) Å, which is in turn similar to the P(1)–C(6) 1.837(3) Å bond and therefore can be considered as a real single bond. Bond alternance is also found for the C–C bonds: C(1)–C(2) 1.431(4) Å, C(2)–C(3) 1.369(4) Å,

C(3)–C(4) 1.441(4) Å, C(4)–C(5) 1.377(4) Å, which gives an overall electronic picture for the dimer as follows (Scheme 8).

This dimer can be cleaved by two electron donors as in the case of copper complexes (Scheme 9).



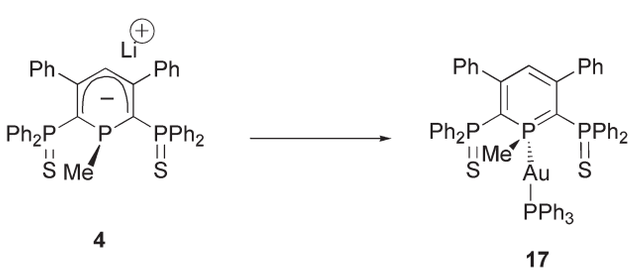
Scheme 8



Scheme 9

When PPh_3 was added to a CH_2Cl_2 solution, a new complex, **17**, formed within minutes at room temperature. This complex is characterized by three sets of peaks in ^{31}P NMR: a doublet of triplets at 3.0 ppm (PPh_3, $^2J_{P-P}$ = 286 Hz, $^3J_{P-P}$ = 91 Hz), a doublet at 41.5 ppm (PMe, $^2J_{P-P}$ = 286 Hz) and a doublet at 42.5 ppm (PPh_2S, $^3J_{P-P}$ = 91 Hz). The very large coupling constant of 286 Hz is indicative of the two ligands located *trans* to each other. This complex was also characterized by ^1H and ^{13}C NMR spectroscopy, elemental analysis and its 3-D structure obtained by X-ray crystallographic methods. As for the copper complexes, in ^1H NMR, the H_4 (*para* to the P atom of the phosphinine moiety) is observed as a triplet at 5.53 ppm ($^4J_{P-H}$ = 10.9 Hz) and therefore is not coupled to the PMe.

This complex was also obtained *via* a second method starting from the [$AuPPh_3Cl$] precursor, as shown below (Scheme 10).



Scheme 10 Reagents and conditions: [$AuClPPh_3$], rt.

X-Ray quality crystals were obtained after diffusion of hexanes into a CH_2Cl_2 solution of the complex. An ORTEP view of one molecule of **17** is presented in Fig. 4 as well as the most relevant bond lengths and bond angles. Crystal data and structural refinement details are given in Table 2.

The first interesting point of this structure is the presence of a S–Au bond which gives an overall T-shape geometry. This bond is rather long at 2.7903(6) Å, which already points towards its weakness. Obviously in solution this geometry is not preserved as it would lead to electronically different PPh_2S moieties and therefore different signals which we did not observe. The two Au–P bond distances of 2.2862(7) and 2.3080(6) Å are normal. Unlike what was observed in the dimer **16**, the λ^4-phosphinine subunit is almost symmetrical with nearly identical external and internal P–C bonds (P(2)–C(1) 1.787(2) Å and P(3)–C(5) 1.771(3) Å, and P(1)–C(5)

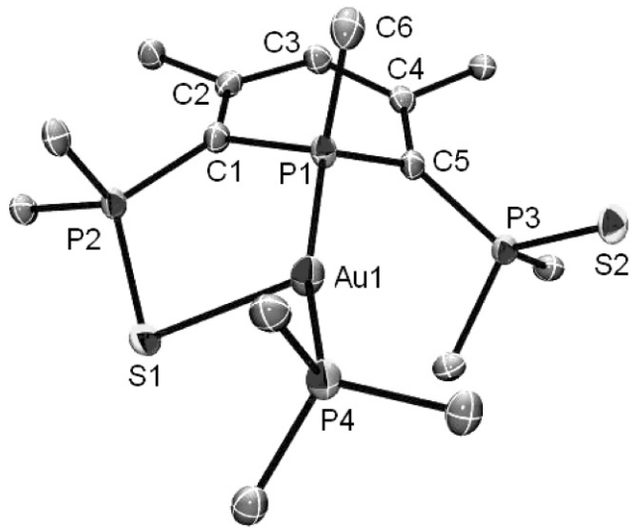


Fig. 4 Caption ORTEP view of complex **17** (50% ellipsoids). The numbering is arbitrary and different from that used in NMR data. Phenyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.799(2), C(1)–C(2) 1.400(3), C(2)–C(3) 1.417(3), C(3)–C(4) 1.402(3), C(4)–C(5) 1.404(3), P(1)–C(5) 1.776(2), P(2)–C(1) 1.787(2), P(3)–C(5) 1.771(3), S(1)–P(2) 1.983(1), S(2)–P(3) 1.9709(8), Au(1)–P(1) 2.3080(6), Au(1)–S(1) 2.7903(6), Au(1)–P(4) 2.2862(7), C(5)–P(1)–C(1) 102.3(1), P(4)–Au(1)–P(1) 162.93(2), P(4)–Au(1)–S(1) 108.90(2).

1.776(2) Å, P(1)–C(1) 1.799(2) Å, respectively), and C–C bonds. As already indicated by ^{31}P NMR, the two phosphorus atoms are located *trans* to each other (angle P(4)–Au(1)–P(1) 162.93(2)°). The deviation from linear geometry is caused by the Au–S interaction. Apart from that the structure does not deserve further comments.

The reaction of the dimer with a threefold excess of the isocyanide, on the other hand, was sluggish and took several hours at room temperature to yield an orange complex, **18**. Once isolated, the complex partially reverted (≈20%) to the starting complex when redissolved, pointing towards a weak interaction between the isocyanide ligand and the gold center. This reflects the poorer σ donor ability of isocyanides and confirms the negligible π back donating ability of gold(I) centers. In the same vein, it is worth noting that the dimer was not cleaved by excesses of pyridine, alkynes or alkenes.

Conclusion

We have presented here the first examples of SPS pincer complexes with group 11, d^{10} (Cu(I) and Au(I)) metal centers. All of the Cu(I) complexes proved very stable except for complex **11**. Because of a weakly bound ligand (pyridine), this complex proved reactive towards a variety of oxydizing agents (oxygen, chlorinated solvents, C_2Cl_6). A quite unexpected increase in the ν(CN) stretches in IR for isocyanide complexes (**7**, **8**, **12**, **13**) was measured which implied a negligible π back donation from filled d orbitals at the Cu(I) center into the empty π* orbitals of the isocyanide ligand, and therefore a σ donation only coordination. A dimeric complex of Au(I) was synthesized, **16**, for which a gold–gold interaction was observed by X-ray crystallographic studies. This dimer was readily cleaved as expected by two electron donors. The isocyanide complex **18** was shown to revert back to the dimer which suggests a weak σ donation only type interaction between Au and CNR.

Experimental

General

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone and dry ether from $CaCl_2$ and then NaH and dry CH_2Cl_2 from P_2O_5. $CDCl_3$ was dried from P_2O_5 and stored on 4 Å Linde molecular sieves. CD_2Cl_2, [D_5]-pyridine were used as purchased and stored in the glovebox. Nuclear magnetic resonance spectra were recorded on

a Bruker AC-200 SY spectrometer operating at 300.0 MHz for ^{1}H, 75.5 MHz for ^{13}C and 121.5 MHz for ^{31}P. Solvent peaks are used as internal reference relative to Me_4Si for ^{1}H and ^{13}C chemical shifts (ppm); ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. Coupling constants are given in hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; p, pentuplet; m, multiplet; v, virtual; b, broad. Mass spectra were obtained at 70 eV with a HP 5989B spectrometer coupled to a HP 5980 chromatograph by the direct inlet method. Elemental analyses were performed by the 'Service d'analyse du CNRS', at Gif sur Yvette, France. Phosphinine **1**,[11] anions **2**[11] and **4**[16] and $[AuClPPh_3]$,[20] $[AuCl{\cdot}SMe_2]$,[21] were prepared according to reported procedures.

Copper complex 4

A solution of MeLi in Et_2O (1.25 mL, C = 0.16 M, 2.0 mmol) was syringed into a solution of **1** (1.36 g, 2.0 mmol) in THF (30 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. ^{31}P NMR indicated then the complete formation of anion **4**, to which solid CuI (380 mg, 2.0 mmol) was added. The initially red solution turned rapidly orange with concomitant formation of an orange precipitate. The mixture was stirred for an additional 15 h. The solid was then filtered, washed with THF and dried under vacuum. Yield: 92%, 1.40 g. $[C_{42}H_{34}P_3S_2Cu]_n$ $(759.33)_n$: calcd. C 66.43, H 4.51; found C 66.63, H 4.75%.

Copper complex 6

A solution of BuLi in hexanes (1.25 mL, C = 0.16 M, 2.0 mmol) was syringed into a solution of **1** (1.36 g, 2.0 mmol) in THF (30 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. ^{31}P NMR indicated then the complete formation of anion **2**, to which solid CuI (380 mg, 2.0 mmol) was added. The initially red solution turned rapidly orange with concomitant formation of an orange precipitate. The mixture was stirred for an additional 15 h. The solid was then filtered, washed with thf and dried under vacuum. Yield: 89%, 1.40 g. $[C_{42}H_{34}P_3S_2Cu]_n$ $(801.40)_n$: calcd. C 67.44, H 5.03; found C 67.69, H 5.31%.

Copper complex 7

To a suspension of complex **5** (100 mg, 0.13 mmol) in CH2Cl2 (5 mL) was syringed xylyl-isocyanide (17 mg, 0.13 mmol) resulting in an instantaneous dissolution of the solid. The ^{31}P NMR spectrum of the crude mixture showed the formation of a unique product. The solution was then taken to dryness. Yield: 95%, 110 mg. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.44 (d, ^{2}J (H–P) = 2.5, 3H, CH_3), 2.19 (s, 6H, CH_3), 5.65 (t, ^{2}J (H–P) = 4.1, 1H, H_4), 6.70–7.9 (m, 33H, CH of Ph). ^{31}P NMR (121.5 MHz, CDCl3, 298 K): δ = −25.5 (AX_2, t, ^{2}J (P_A–P_X) = 154.3, P_A), 48.4 (AX_2, d, ^{2}J (P_A–P_X) = 154.3, P_XPh_2). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K): δ = 11.2 (dt, ^{1}J (C–P) = 12.1, ^{3}J (C–P) = 9.1, CH_3 of P–Me), 18.8 (s, CH_3 of xylyl), 65.6 (dd, J (C–P) = 85.31, J (C–P) = 23.4, $C_{2,6}$), 119.6 (m, C_4H), 127.0–132.6 (m, CH of Ph), 135.3 (s, C of Ph), 135.7 (d, J (C–P) = 86.7, C of Ph), 136.7 (d, J (C–P) = 78.8, C of Ph), 143.5 (d, J (C–P) = 3.8, C of Ph), 152.9 (d, J (C–P) = 8.3, $C_{3,5}$). C of isocyanide was not seen. IR (KBr): ν 2131 cm^{-1}. $C_{51}H_{43}P_3S_2NCu$ (890.51): calcd. C 68.79, H 4.87; found C 69.01, H 5.10%.

Copper complex 8

To a suspension of complex **5** (100 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was syringed tert-butylisocyanide (14 µL, 0.13 mmol) resulting in an instantaneous dissolution of the solid. The ^{31}P NMR spectrum of the crude mixture showed the formation of a unique product. The solution was then taken to dryness. The product was washed with hexanes and dried to yield an orange solid. Yield: 96%, 110 mg. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.37 (s, 9H, CH_3), 1.41 (d, ^{2}J (H–P) = 2.2, 3H, CH_3), 5.66 (t, ^{2}J (H–P) = 4.0, 1H, H_4), 6.70–7.9 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ = −28.0 (AX_2, t, ^{2}J (P_A–P_X) = 150.7, P_A), 47.3 (AX_2, d, ^{2}J (P_A–P_X) = 150.7, P_XPh_2). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 12.2 (dt, ^{1}J (C–P) = 12.2, ^{3}J (C–P) = 8.2, CH_3 of P–Me), 30.5 (s, CH_3 of *t*-Bu), 56.0 (s, C of *t*-Bu), 66.41 (ddd, J (C–P) = 84.8, J (C–P) = 26.5, J (C–P) = 2.9, $C_{2,6}$), 119.7 (td, ^{3}J (C–P) = 10.9, ^{3}J (C–P) = 5.5, C_4H), 127.1–132.8 (m, CH of Ph), 136.3 (d, J (C–P) = 80.5, C of Ph), 137.4 (d, J (C–P) = 85.2, C of Ph), 143.6 (m, C of Ph), 153.0 (m, $C_{3,5}$). C of isocyanide was not seen. IR (KBr): ν 2175 cm^{-1}. $C_{47}H_{43}P_3S_2NCu$ (842.46): calcd. C 67.01, H 5.14; found C 67.25, H 5.35%.

Copper complex 9

To a suspension of complex **5** (100 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was added solid PPh_3 (34.1 mg, 0.13 mmol) which resulted in the dissolution of the starting complex. The ^{31}P NMR spectrum of the crude mixture showed the formation of a unique product. The solution was then taken to dryness. The product was washed with hexanes and dried to yield an orange solid. Yield: 93%, 123 mg. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.30 (d, ^{2}J (H–P) = 2.0, 3H, CH_3), 5.60 (t, ^{2}J (H–P) = 4.0, 1H, H_4), 6.70–7.9 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ = −20.1 (b, P_A), 3.5 (b, PPh_3), 49.8 (AX_2, d, ^{2}J (P_A–P_X) = 162.8, P_XPh_2). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 11.8 (dt, ^{1}J (C–P) = 11.8, ^{3}J (C–P) = 9.9, CH_3 of P–Me), 66.4 (m, $C_{2,6}$), 119.7 (m, C_4H), 127.1–134.4 (m, CH of Ph), 135.1 (dd, J (C–P) = 29.0, J (C–P) = 2.9, C of Ph), 136.4 (d, J (C–P) = 86.9, C of Ph), 137.6 (d, J (C–P) = 86.2, C of Ph), 144.1 (m, C of Ph), 152.8 (m, $C_{3,5}$). $C_{60}H_{48}P_4S_2Cu$ (1021.62): calcd. C 70.54, H 4.73; found C 70.90, H 5.03%.

Copper complex 10

To a suspension of complex **5** (100 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was syringed $P(OPh)_3$ (34.6 µL, 0.13 mmol) which resulted in the dissolution of the starting complex within 5 min. The ^{31}P NMR spectrum of the crude mixture showed the formation of a unique product. The solution was then taken to dryness. The product was washed with hexanes and dried to yield an orange solid. Yield: 93%, 129 mg. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.91 (d, ^{2}J (H–P) = 2.2, 3H, CH_3), 5.53 (t, ^{2}J (H–P) = 4.2, 1H, H_4), 6.70–7.9 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ = −19.6 (b, P_A), 49.8 (AM_2X, dd, ^{2}J (P_A–P_M) = 159.1, ^{2}J (P_M–P_X) = 19.5, P_MPh_2), 113.7 (b, $P(OPh)_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 10.8 (m, CH_3), 66.34 (ddd, J (C–P) = 86.5, J (C–P) = 25.5, J (C–P) = 2.2, $C_{2,6}$), 115.9 (s, CH of Ph), 119.5 (m, C_4H), 121.5–133.1 (m, CH of Ph), 135.9 (d, J (C–P) = 77.5, C of Ph), 136.8 (d, J (C–P) = 84.7, C of Ph), 143.6 (d, J (C–P) = 2.8, C of Ph), 151.4.6 (bs, C of Ph), 152.8 (m, $C_{3,5}$). $C_{60}H_{48}P_4S_2O_3Cu$ (1069.62): calcd. C 67.37, H 4.52; found C 67.43, H 4.72%.

Copper complex 11

Complex **5** (50 mg, 0.065 mmol) was dissolved in pyridine to give a dark orange solution. The ^{31}P NMR spectrum of the crude mixture shows the formation of a unique product. The solution was then taken to dryness. The product was washed with hexanes and dried to yield an orange solid. Yield: 100%, 129 mg. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.31(s, 3H, CH_3), 5.50 (t, ^{2}J (H–P) = 4.3, 1H, H_4), 6.70–7.9 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ = −36.0 (b, P_A), 46.6 (AX_2, d, ^{2}J (P_A–P_X) = 151.9, P_XPh_2). ^{13}C NMR (75.5 MHz, C_5D_5N, 298 K): δ = 11.4 (dt, ^{1}J (C–P) = 9.2, ^{3}J (C–P) = 7.9, CH_3), 68.1 (ddd, J (C–P) = 86.6, J (C–P) = 26.0, J (C–P) = 3.3, $C_{2,6}$), 119.0 (td, ^{3}J (C–P) = 10.6, ^{3}J (C–P) = 5.0, C_4H), 123.7 (s, CH of Py), 126.9–132.7 (m, CH of Ph), 135.7 (s, CH of Py), 136.6 (d, J (C–P) = 81.4, C of Ph), 137.8 (d, J (C–P) = 85.8, C of Ph), 144.0 (vq, J (C–P) = 3.4, C of Ph), 149.9 (s, CH of Py), 153.1 (m, $\sum J$ = 12.4, $C_{3,5}$). $C_{47}H_{39}P_3S_2NCu$ (838.43): calcd. C 67.33, H 4.68; found C 67.63, H 4.72%.

Copper complex 12

To a suspension of complex **6** (104 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was syringed xylyl-isocyanide (17 mg, 0.13 mmol) resulting

in an instantaneous dissolution of the solid. The ^{31}P NMR spectrum of the crude mixture showed the formation of a unique product. The solution was then taken to dryness. Yield: 96%, 116 mg. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.91 (t, ^{3}J (H–H) = 7.1, 3H, CH_3 of Bu), 1.52 (m, $\sum J$ = 33.9, 4H, CH_2), 1.84 (m, $\sum J$ = 19.7, 2H, CH_2), 2.22 (s, 6H, CH_3), 5.59 (t, ^{2}J (H–P) = 4.0, 1H, H_4), 6.70–7.75 (m, 33H, CH of Ph). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): δ = −15.5 (AX_2, t, ^{2}J (P_A–P_X) = 152.5, P_A), 47.5 (AX_2, d, ^{2}J (P_A–P_X) = 152.5, P_XPh_2). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K): δ = 13.1 (s, CH_3 of Bu), 17.6 (s, CH_3 of xylyl), 22.4 (dd, J (C–P) = 15.9, J (C–P) = 8.3, CH_2), 23.2 (d, J (C–P) = 14.3, CH_2), 25.6 (d, J (C–P) = 10.6, CH_2), 63.6 (m, $C_{2,6}$), 119.5 (m, C_4H), 126.0–131.5 (m, CH of Ph), 127.8 (s, C of Ph), 134.3 (s, C of Ph), 135.2 (d, J (C–P) = 81.5, C of Ph), 135.9 (d, J (C–P) = 85.7, C of Ph), 142.2 (s, C of Ph), 152.4 (s, $C_{3,5}$). C of isocyanide was not seen. IR (KBr): ν 2129.9 cm^{-1}. $C_{54}H_{49}P_3S_2NCu$ (932.57): calcd. C 69.55, H 5.30; found C 69.34, H 5.07%.

Copper complex 13

To a suspension of complex **6** (104 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was syringed tert-butylisocyanide (14 µL, 0.13 mmol) resulting in an instantaneous dissolution of the solid. The ^{31}P NMR spectrum of the crude mixture showed the formation of a unique product. The solution was then taken to dryness. The product was washed with hexanes and dried to yield an orange solid. Yield: 94%, 110 mg. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 0.91 (t, ^{3}J (H–H) = 7.0, 3H, CH_3 of Bu), 1.24 (bs, 2H, CH_2), 1.42 (m, $\sum J$ = 41.2, 20H, CH_2 of Bu and CH_3 of *t*-Bu), 1.79 (m, $\sum J$ = 16.0, 2H, CH_2), 5.56 (t, ^{2}J (H–P) = 4.2, 1H, H_4), 6.70–7.72 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, CD_2Cl_2, 298 K): δ = −17.9 (AX_2, t, ^{2}J (P_A–P_X) = 143.4, P_A), 46.8 (AX_2, d, ^{2}J (P_A–P_X) = 143.4, P_XPh_2). ^{13}C NMR (75.5 MHz, CD_2Cl_2, 298 K): δ = 13.3 (s, CH_3 of Bu), 22.4 (dd, J (C–P) = 14.5, J (C–P) = 7.9, CH_2), 23.2 (d, J (C–P) = 14.0, CH_2), 25.6 (d, J (C–P) = 10.3, CH_2), 29.4 (s, CH_3 of *t*-Bu), 52.5 (s, C of *t*-Bu), 64.1 (m, $C_{2,6}$), 119.6 (m, C_4H), 126.0–131.8 (m, CH of Ph), 135.2 (d, J (C–P) = 81.6, C of Ph), 135.9 (d, J (C–P) = 85.5, C of Ph), 142.2 (s, C of Ph), 152.4 (s, $C_{3,5}$). C of isocyanide was not seen. IR (KBr): ν 2158.6 cm^{-1}. $C_{50}H_{49}P_3S_2NCu$ (884.32): calcd. C 67.89, H 5.58; found C 67.51, H 5.23%.

Gold complex 16

A solution of MeLi in Et_2O (625 µL, C = 0.16 M, 1.0 mmol) was syringed into a solution of **1** (680 mg, 1.0 mmol) in THF (15 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. ^{31}P NMR indicates then the complete formation of anion **4**, to which solid [AuCl·SMe_2] (294 mg, 1.0 mmol) was added at −78 °C. The initially red solution turned rapidly orange. The mixture was stirred for an additional hour. The ^{31}P NMR spectrum of the crude mixture shows the formation of a unique product. The volatiles were then removed under vacuum. The product was washed with hexanes and dried to yield an orange solid. Yield: 95%, 848 mg.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.20 (d, ^{2}J(H–P) = 8.6, 3H, CH_3), 5.72 (t, ^{2}J (H–P) = 4.4, 1H, H_4), 6.70–7.9 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ = −12.6 (m, AA′MM′XX′, $P_{A,A'}$), 39.2 (d, AA′MM′XX′, $\sum J$ (P_A–P_M) = 72.9, P_MPh_2), 45.2 (d, AA′MM′XX′, $\sum J$ (P_A–P_X) = 86.3, P_XPh_2). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 13.7 (s, CH_3), 72.0 (m, $C_{2\text{ or }6}$), 90.5 (m, $C_{6\text{ or }2}$), 120.6 (m, C_4H), 127.0–134.3 (m, CH of Ph), 135.1 (m, C of Ph), 135.6 (m, C of Ph), 142.9 (bs, C of Ph), 145.0 (bs, C of Ph), 155.7 (bs, $C_{3\text{ or }5}$), 157.6 (s, $C_{5\text{ or }3}$). $(C_{42}H_{34}P_3S_2Au)_2$ (892.75)$_2$: calcd. C 56.51, H 3.84; found C 56.80, H 4.02%.

Gold complex 17

Method A: Dimeric complex **16** (200 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (5 mL) and PPh_3 (57 mg, 0.22 mmol) was added solid. ^{31}P NMR indicates then the complete formation of monomeric complex **17** within minutes. The volatiles were then removed under vacuum. The product was washed with hexanes and dried to yield an orange solid. Yield: 97%, 129 mg.

Method B: A solution of MeLi in Et_2O (125 µL, C = 0.16 M, 0.2 mmol) was syringed into a solution of **1** (136 mg, 0.2 mmol) in THF (3 mL) at −78 °C. The solution was warmed to room temperature and stirred for 20 min. ^{31}P NMR indicates then the complete formation of anion **4**, to which [AuClPPh_3] (99 mg, 0.2 mmol) dissolved in THF (2 mL) was added at −78 °C. The solution was warmed back to room temperature to yield an orange solution which was then stirred for 1 h. The volatiles were removed *in vacuo* and the compound extracted in CH_2Cl_2. After filtration and drying, the title complex was recovered as an orange powder. Yield 92%, 212 mg.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.55 (d, ^{2}J(H–P) = 7.7, 3H, CH_3), 5.53 (t, ^{2}J (H–P) = 10.9, 1H, H_4), 6.70–7.9 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ = 2.17 (dt, AMX_2, ^{2}J (P_A–P_M) = 286.0, ^{2}J (P_A–P_X) = 90.9, P_A), 41.46 (d, AMX_2, ^{2}J (P_A–P_M) = 286.0, P_M), 42.55 (d, AMX_2, ^{2}J (P_A–P_X) = 90.9, P_X). ^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): δ = 15.5 (s, CH_3), 69.5 (m, $C_{2,6}$), 118.8.6 (td, ^{3}J (C–P) = 9.6, ^{3}J (C–P) = 5.8, C_4H), 128.8–135.0 (m, CH of Ph), 137.7 (d, J (C–P) = 85.8, C of Ph), 137.8 (d, J (C–P) = 85.8, C of Ph), 144.1 (t, J (C–P) = 6.4, C of Ph), 155.7 (bs, $C_{3,5}$). $C_{60}H_{49}P_4S_2Au$ (1155.04): calcd. C 62.39, H 4.28; found C 62.60, H 4.62%.

Gold complex 18

Dimeric complex **16** (200 mg, 0.11 mmol) was dissolved in CH_2Cl_2 (5 mL) and tert-butylisocyanide (73 µL, 0.66 mmol) was syringed in. The solution was then stirred at room temperature for several hours. ^{31}P NMR indicated the complete formation of the desired complex **15**. The volatiles were then removed under vacuum. The solid was dissolved in $CHCl_3$ and hexanes was layered on top of the solution. The orange crystals which deposited were dissolved in $CDCl_3$ showing the partial reformation of the starting material (20%). The ^{1}H NMR spectrum was thus recorded with the mixture.

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 1.35 (s, 9H, CH_3), 1.45 (d, ^{2}J (H–P) = 9.5, 3H, CH_3), 5.52 (t, ^{2}J (H–P) = 10.9, 1H, H_4), 6.70–7.9 (m, 30H, CH of Ph). ^{31}P NMR (121.5 MHz, $CDCl_3$, 298 K): δ = −7.18 (t, AX_2, ^{2}J (P_A–P_X) = 83.7, P_A), 41.30 (d, AX_2, ^{2}J (P_A–P_X) = 83.7, P_M).

Crystallography

Data were collected at 150.0(1) K on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. Experimental details are described in Table 2. The crystal structures were solved using SIR 97[22] and Shelxl-97.[23] ORTEP drawings were made using ORTEP III for Windows.[24]

CCDC reference numbers 238093 to 238098.

See http://www.rsc.org/suppdata/dt/b4/b406792d/ for crystallographic data in CIF or other electronic format.

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