Synthesis, X-ray Crystal Structures and Reactivity Towards Alkynes of Gold(I)–Phosphinine Complexes

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The coordination behaviour of 2,6-disilyl-substituted phosphinines towards gold(I) has been examined. The reaction of the bis(trimethylsilyl)phosphinine **1** with [AuCl(SMe_2)] gives the corresponding AuCl derivative **2**. X-ray crystal structure analysis reveals that the aromaticity of the phosphinine ring is slightly reduced as a result of the poor π-back bonding ability of the AuCl fragment. The same phenomenon is observed in the cationic complex [Au(**1**)$_2$][$GaCl_4$] (**3**) which was readily prepared by reaction of two equivalents of **1** with [AuCl(SMe_2)] followed by treatment with $GaCl_3$ at low temperature. Reaction of 2,6-bis(phenylethynyldimethylsilyl)phosphinine (**4**) with the same precursor leads similarly to the complex [AuCl(**4**)] (**5**). Interestingly, this complex dimerizes upon crystallization to give the bis(phosphabarrelene) complex **6**, also structurally characterized. The formation of **6** results from a [4 + 2] cycloaddition between one alkynyl group of each phosphinine with the other phosphinine subunit. The formation of the cationic complex [Au(**4**)][$GaCl_4$] (**8**) occurs under classical conditions but it disproportionates to give the cationic complex [Au(**4**)$_2$][$GaCl_4$] (**9**) and colloidal gold deposition. The formation of **9** has been ascertained by treating **8** with one equivalent of ligand **4**. Additionally, **9** can also be obtained in a straightforward fashion by treating two equivalents of **4** with [AuCl(SMe_2)] followed by treatment with $GaCl_3$ at low temperature. The structure of **9** has been elucidated. Despite a particular arrangement of the alkyne groups which encapsulate the gold coordination sphere, no gold–alkyne interactions are visible.

Introduction

It is now well established that phosphinines are strong π-acceptor ligands whose electronic properties markedly differ both from their nitrogen counterparts, pyridines, and classical tertiary phosphanes (R_3P).[1] This singularity, which mainly results from the presence of an electropositive sp^2-phosphorus atom, has recently been exploited to stabilize electron-rich transition-metal species which are usually unstable with other ligands, except CO. The studies of Elschenbroich et al. on the synthesis of homoleptic complexes of the parent compound C_5H_5P[2] and our work with 2,2′-biphosphinine complexes are illustrative of such uncommon reactivity.[1][3] Although significant progress has recently been achieved in this direction, our knowledge of the coordination chemistry of phosphinines still remains to be improved. Indeed, the understanding of phosphinine−metal interactions is a prerequisite to the use of these ligands in more applied projects such as homogeneous catalysis, an area which has just been explored,[4] and for the elaboration of sophisticated supramolecular edifices using, for example, phosphinine-based macrocycles.[5] Furthermore, it is clear that this useful information could be transposed to other species containing sp^2-hybridized P atoms (heterocycles or acyclic derivatives) whose properties are quite similar to those of phosphinines.

The study presented here, which deals with the synthesis of a series of gold(I) complexes of phosphinines, was also motivated by the fact that phosphinine complexes of group 11 are rather rare. Indeed, whereas some derivatives of copper(I) have been described,[6] very little is known of silver and gold derivatives. As far as we are aware, only one gold complex of the 2,4,6-triphenylphosphinine has been mentioned by Schmidbaur et al. but its spectroscopic and structural data remain unknown.[7] Another important motivation concerns the highly specific properties exhibited by phosphane−gold complexes[8] in different areas such as homogeneous catalysis,[9] photochemistry (luminescence)[10] and medicine (cytotoxic and antitumour activity).[11] Furthermore, the coordination of strong π-acceptor ligands such as phosphinines raises the problem of π-back-donation from gold. Experimental results and calculations made on carbonyl complexes tend to show that this back-donation is rather weak in gold(I) and gold(0) complexes.[12] As the stability of complexed phosphinines was shown to be dramatically dependent on the electron density available at the metal centre for π-back-donation,[13] it was also interesting to probe whether the coordination to gold(I) would enhance the reactivity of phosphinines or not. Herein, we present the results of these investigations.

Results and Discussion

All our experiments were conducted with 2,6-disilylphosphinines. This choice was dictated by their availability and by the fact that we had recently developed a very efficient synthetic approach to polydentate ligands such as bis(trisphosphinines)[14] and phosphinine-based macrocycles[5] in which phosphinine units are linked by dimethylsilyl groups. Consequently, before extending our investigations to these sophisticated species, it seemed logical to focus our work on these simple models.

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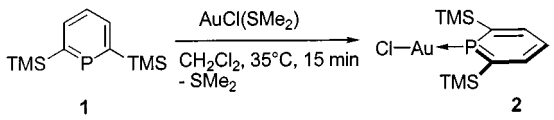
As a preliminary experiment, to assess the effects of gold coordination to the phosphinine, we investigated the reaction of the 2,6-bis(trimethylsilyl)phosphinine (**1**) with AuCl(SMe$_2$). The reaction proceeded cleanly in dichloromethane affording complex **2** which was obtained as a pale yellow solid after precipitation with hexanes (Scheme 1).



Scheme 1. Synthesis of complex **2**

The NMR data of **2** deserves comment. In the ^{31}P-NMR spectrum, **2** displays a singlet [δ (CD_2Cl_2) = 199.50] as expected since no $^1J(^{197}Au-^{31}P)$ coupling constants can be observed because of the large value of the quadrupole moment of gold ($Q = 0.59 \times 10^{-28}$ m^2)[15] which leads to a short value of the relaxation time. The strong shielding of the ^{31}P signal [δ ($CDCl_3$) = 254.50 for **1**, $\Delta\delta$ = 55.00 ppm) is difficult to rationalize and a similar effect has already been observed for (2,2′-biphosphinine)copper(I) complexes.[6] Apart from group-6 metal complexes of phosphinines, where a trend in the shielding has been noted, variations of ^{31}P-NMR chemical shifts of phosphinine complexes have not, so far, been correlated with electronic effects on the ligands. As observed for copper(I) complexes, ^{1}H signals of the β and γ protons (3,3′-H and 4,4′-H) in **2** are shifted towards lower field compared to those of the free ligand **1**. This phenomenon is accompanied by a significant increase in the corresponding coupling constant ^3J(P−H) from 9.39 Hz in **1** to 31.20 Hz in **2**. Similar effects are generally observed for other phosphinine complexes. In the ^{13}C-NMR spectrum, the coordination induces an upfield shift which correlates with the distance to the phosphorus atom. Thus, the chemical shift of C-4 is not modified (δ = 127.50 in **1** vs. δ = 127.00 in **2**), but C-3 and C-2 are more shielded by 4.50 and 11.00 ppm, respectively. This steady increase in shielding of the nuclei closest to the metal atom, which has already been observed for group-6 metal complexes, reflects that the shielding constant σ of these nuclei is mainly governed by the shielding contribution of the metal atom. Also noteworthy is the magnitude of the ^1J(P−C) coupling constant which varies from 84.40 Hz in **1** to 4.0 Hz in **2**. This very large variation, also observed to a lesser extent in other phosphinine complexes, is caused by two competing factors which are generally encountered in the case of classical complexes of tertiary phosphanes:[16] the higher degree of coordination of the P atom (decrease of the magnitude of the coupling) and the loss of the lone-pair effect (algebraic increase of the coupling). Finally, we also note the very large magnitude of the ^3J(P−C4) coupling constant indicating that the electronic delocalisation within the ring has been strongly perturbed. In order to gain structural information, an X-ray crystal analysis of **2** was carried out. An ORTEP drawing of **2** is presented in Figure 1.

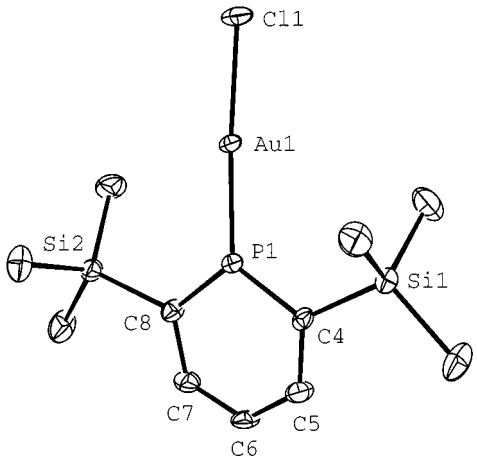
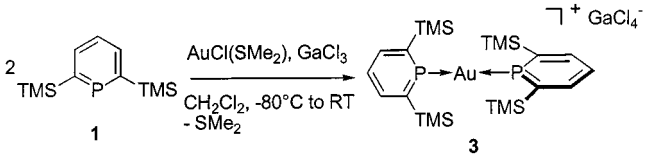


Figure 1. ORTEP drawing of **2** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 50% of the electron density; hydrogen atoms are omitted for clarity; the crystallographic labelling is arbitrary and different from the numbering used for assignments of the ^{13}C-NMR spectra; selected bond lengths [Å] and angles [°]: Au1−Cl1 2.281(2), Au1−P1 2.211(2), P1−C4 1.710(6), P1−C8 1.702(7), C4−C5 1.406(9), C5−C6 1.38(1), C6−C7 1.38(1), C7−C8 1.41(1); Cl1−Au1−P1 175.36(7), Au1−P1−C4 122.6(2), C4−P1−C8 110.4(3), P1−C4−C5 117.5(5), C4−C5−C6 125.3(6), C5−C6−C7 123.7(6), C6−C7−C8 125.7(6), P1−C8−C7 117.2(5), P1−C4−Si1 120.6(4)

As expected for an [LAuX] complex, the geometry around the metal atom is perfectly linear. Whereas the Au−Cl bond length [2.281(2) Å] falls in the normal range, the Au−P(1) bond length [2.211(2) Å] appears to be slightly shorter than that observed for [AuCl(phosphane)] complexes [2.227(2) Å in the AuCl(DMPP) complex].[17] Nevertheless, this shortening cannot be considered as reflecting a better π-back-donation from the metal centre to the ligand since the hybridization of the phosphorus atom in **2** is sp^2 versus sp^3 in tertiary phosphanes.[16] More interesting information can be retrieved from an examination of bond lengths and angles within the ring. The value of the internal angle [Θ(CPC) = 110.4°] is quite large when compared to values usually recorded for free phosphinines (between 101° and 103°).[18] However, part of the effect is due to the disubstitution by silyl groups. Indeed, although the X-ray structure of ligand **1** is unknown (**1** is a liquid), we can compare this value to the angle recorded for the silacalix[4]phosphinine macrocycle which includes four dimethylsilylphosphinine units [Θ = 106.3(2)°].[5] In general, a similar increase in Θ(CPC) values is observed for phosphinines upon complexation.[19] The P=C bond lengths also allow the estimation of the extent of aromaticity within the ring. In **2**, it clearly appears that these bonds are shortened [1.710(6) and 1.702(7) Å] when compared to the parent phosphinine [1.73 Å] and to the dimethylsilyl derivative quoted above [1.734(5) and 1.746(5) Å]. This phenomenon, which has also been observed in other complexes such as Mo(C_5H_5P)$(CO)_5$[20] and homoleptic [M($C_5H_5P)_6$] (M = Cr, Mo, W) derivatives,[2d] indicates that the P−C bonds are more localized and acquire a higher double-bond character. As expected, this effect reflects a poor π-back-donation from the gold atom to the phosphinine ligand.

Indeed, a strong electronic transfer from the metal centre would tend to increase the P−C bond length since the lowest unoccupied π* molecular orbital (LUMO) of phosphinines is P−C-antibonding.[21] Another piece of data corroborates this fact. The C−C bond lengths present a significant disymmetry, $C_\alpha-C_\beta$ [1.406(9) and 1.41(1) Å] bonds being slightly longer than $C_\beta-C_\gamma$ [1.38(1) Å] bonds.

These effects are not specific to the chloride complex and similar results are also observed in the cationic $[Au(\mathbf{1})_2][GaCl_4]$ complex **3**. This complex was readily obtained by treating two equivalents of ligand **1** with $[AuCl(SMe_2)]$, followed by $GaCl_3$, which was used as a chloride abstractor at low temperature (see Scheme 2).



Scheme 2. Synthesis of complex **3**

Complex **3**, which was characterized as a pale yellow solid, exhibits NMR data which are overall similar to those recorded for **2**. Although a slight downfield shift is observed in the ^{31}P-NMR spectrum, the signal of **3** [$\delta(CD_2Cl_2) = 206.00$] remains shielded compared to that of the free ligand **1**. Apparently, the replacement of the chloride ion by a second phosphinine unit does not modify the electronic effects within the rings, also consistent with very poor π-back-donation from the gold atom.

To ascertain this point, the structure of **3** was elucidated by an X-ray diffraction study. An ORTEP view of **3** is presented in Figure 2. As in **2**, the geometry around the gold centre is linear[22] with the two ligands lying in two nearly perpendicular planes ($\Theta = 70.57°$). Very likely, this particular conformation allows through-space interactions between bulky trimethylsilyl groups to be minimized. The structure of **3** is comparable to that of **2** and the same trends are observed: an increase of the internal angle (mean Θ = 112.2°), short P−C bond lengths and a disymmetry between C−C bond lengths.

We then attempted to synthesize trigonal-planar Au^I species. Unfortunately, reaction of a large excess of ligand **1** with $[AuCl(SMe_2)]$, followed by treatment with $GaCl_3$ at low temperature, only led to the recovery of complex **3** and no traces of the desired $[Au(\mathbf{1})_3][GaCl_4]$ complex could be observed whatever experimental conditions were used. Very likely, this failure results from the strong steric hindrance generated by the bulky trimethylsilyl groups.

In view of these quite disappointing results, we focused our work on the preparation of hemilabile complexes of phosphinines. A recent report has demonstrated the affinity of Au^I centres for strained alkynes which are coordinated in an η^2-fashion.[23] Postulating that cationic trigonal-planar complexes incorporating two η^2-bonded alkynes and an η^1-bonded phosphinine could be prepared, we first investigated the reaction of the bis(phenylethynyldimethylsilyl)-

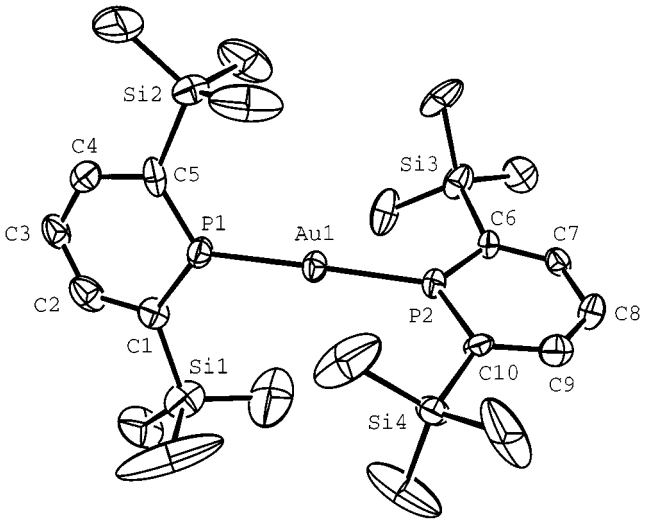
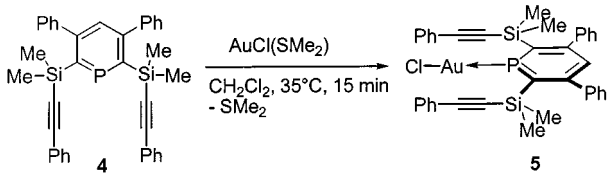


Figure 2. ORTEP drawing of **3** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 50% of the electron density; hydrogen atoms are omitted for clarity; the crystallographic labelling is arbitrary and different from the numbering used for assignments of the ^{13}C-NMR spectra; selected bond lengths [Å] and angles [°]: Au1−P1 2.274(4), Au1−P2 2.290(4), P1−C1 1.73(1), P1−C5 1.69(2), P2−C(6), 1.71(1), P2−C10 1.71(1), C1−C2 1.41(2), C2−C3 1.39(2), C3−C4 1.37(2), C4−C5 1.44(2), C6−C7 1.38(2), C7−C8 1.40(2), C8−C9 1.35(2), C9−C10 1.43(2); P1−Au1−P2 175.3(2), Au1−P1−C1 123.5(5), Au1−P1−C5 123.9(5), C1−P1−C5 112.3(7), Au1−P2−C6 122.6(5), Au1−P2−C10 125.0(5), C6−P2−C10 112.1(6), P1−C1−C2 115.1(1), C1−C2−C3 127.0(1), C2−C3−C4 125.0(1), C3−C4−C5 125.0(1), P1−C5−C4 117.1(1), P2−C6−C7 116.0(1), C6−C7−C8 126.0(1), C7−C8−C9 123.0(1), C8−C9−C10 128.0(1)

phosphinine **4** towards $[AuCl(SMe)_2]$. As previously described for the synthesis of **3**, the reaction proceeds smoothly in dichloromethane at room temperature. Complex **5** was isolated in a 95% yield as a yellow solid after a simple precipitation with hexanes (Scheme 3).



Scheme 3. Synthesis of complex **5**

Whereas ^{13}C-NMR data of the ring carbon atoms compare in every respect to those recorded for **2** and **3**, the ^{31}P-NMR signal of **5** appears at low field [δ (CD_2Cl_2) = 222.00]. This deshielding does not reflect a particular electronic situation since the signal of the free ligand is also strongly downfield shifted [δ (CD_2Cl_2) = 273.00] from that of **2**. It must be noted that chemical shifts of the alkyne moiety are not significantly perturbed when compared to those recorded for the bis(phenylethynyl)dimethylsilane. This observation indicates that no η^2-alkyne coordination to the AuCl fragment occurs in **5**.

Before studying the formation of the corresponding cationic derivative $[Au(\mathbf{4})]^+$, we performed an X-ray crystal structure analysis of **5** to probe whether the structure observed in solution is maintained in the solid or not. This

experiment led to a quite unexpected result. Every attempt to crystallize **5** failed and each experiment systematically led to insoluble microcrystals whose structure was established by an X-ray diffraction study. The structure of complex **6** is a symmetrical dimer consisting of two (1-phosphabarrelene)AuCl complex units which are connected by two $SiMe_2$ bridges. An ORTEP drawing of **6** is presented in Figure 3.

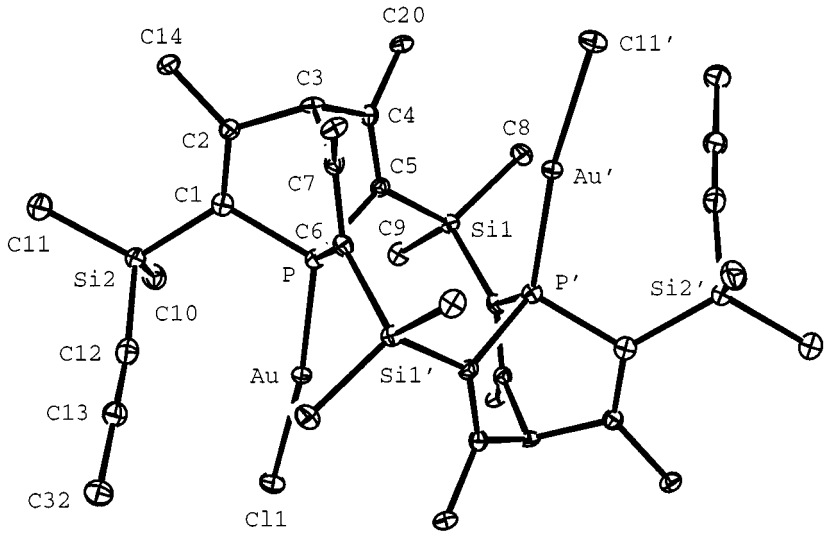
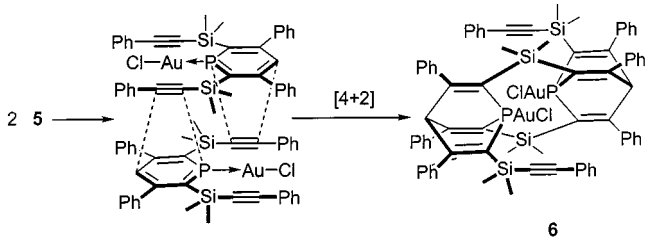


Figure 3. ORTEP drawing of **6** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 40% of the electron density; hydrogen atoms are omitted for clarity; the crystallographic labelling is arbitrary and different from the numbering used for assignments of the ^{13}C-NMR spectra; selected bond lengths [Å] and angles [°]: Au−Cl1 2.286(1), Au−P2.218(1), P−C1 1.834(5), P−C5 1.835(5), P−C(6) 1.825(6), C1−C2 1.333(7), C2−C3 1.546(6), C3−C4 1.538(9), C3−C7 1.533(7), C4−C5 1.347(7), C6−C7 1.352(7); Cl1−Au−P 171.87(4), Au−P−C1 110.9(1), Au−P−C5 120.9(2), Au−P−C6 121.2(1), C1−P−C5 100.6(2), C1−P−C6 100.5(3), C5−P−C6 99.2(2), P−C1−C2 11.5(3), C1−C2−C3 116.3(4), C2−C3−C4 106.5(4), C2−C3−C7 108.1(4), C4−C3−C7 11.8(4), C3−C4−C5 118.1(4), P−C5−C4 109.4(4), P−C6−C7 109.4(4), C3−C7−C6 118.2(5)

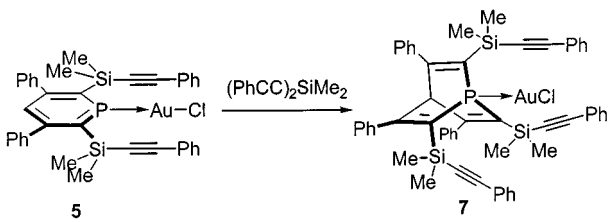
Unfortunately, due to its insolubility in common organic solvents, no NMR data of **6** could be recorded. The formation of **6** results from two [4 + 2] Diels−Alder reactions between two molecules of complex **5**, each phosphinine unit playing the role of a 1-phosphadiene (see Scheme 4).



Scheme 4. Intermolecular [4+2] cycloaddition leading to complex **6**

Apparently, this transformation only occurs during the formation of crystals and parallel experiments aimed at reproducing the synthesis of **6** under dilution conditions failed and led to colloidal Au^0 deposition. The formation of 1-phosphabarrelenes is not totally unprecedented. Usually, phosphinines do not react with alkynes, except when the latter are substituted by strongly electron-withdrawing groups (e.g. CF_3, CN) or when the triple bond is included into a strained structure.[24] Activated phosphinines in which CH unit(s) have been replaced by phosphorus or nitrogen such as 1,4-diphospha-[25a,25b] or monoaza- and diazaphosphinines[14,25c−25f] display a particular ability to react with various alkynes to give the corresponding aza- and diazabarrelenes. Moreover, it was also reported that $P-W(CO)_5$ complexes give [4 + 2] cycloadditions with activated alkynes such as dimethyl acetylenedicarboxylate or *N*-phenylmaleimide to afford 1-phosphabarrelenes and 2,3-dihydrobarrelenes complexes, respectively.[26] However, this was the first time that this kind of reaction has been observed in such mild conditions. Interestingly, as noted above, similarities are observed between the structure of these complexes and that of gold(I) studied here.

To validate the hypothesis of the double [4 + 2] Diels−Alder reaction, we decided to investigate the reaction of phosphinine **4** towards an alkyne with the hope of obtaining a soluble [4 + 2] cycloadduct. For obvious reasons, we chose the bis(phenylethynyl)dimethylsilane whose reaction with **4** should provide a symmetrical barrelene. In order to reproduce the conditions of crystallization of **6**, the reaction was carried out in concentrated medium, at room temperature. It led to total conversion into the desired symmetrical barrelene **7** within 48 h [δ (CD_2Cl_2) = −7.00] (see Scheme 5). The remarkable ease of this reaction explains why complex **5** could not be crystallized.



Scheme 5. Trapping of complex **5** with $(PhCC)_2SiHe_2$

To the best of our knowledge, **7** is the first example of a gold(I) barrelene complex. All NMR data (see Experimental Section) are in good agreement with the symmetrical structure proposed, thus confirming the regioselectivity of the Diels−Alder reaction. The fact that the alkyne carbon atom bearing the silicon group is attached to the P atom confirms that this latter bears a substantial positive charge.[14] Indeed, the observed regioselectivity compares with that observed in the case of 1,2 and 1,3,2-diazaphosphinines which are known to behave as strongly polarized [1,4] dipoles. To ascertain its formulation, an X-ray crystal structure analysis was carried out. An ORTEP drawing of **7** is presented in Figure 4. The structure of **7** reveals no particular features and no interactions between gold and alkynyl groups (C8−C9, C24−C25 and C40−C41) can be noted. Indeed, gold−carbon bond lengths appear to be quite long between 3.444 and 3.890 Å] and C≡C triple bond lengths fall in the expected range [from 1.203(8) to 1.212(8) Å].

Unfortunately, the isolation of the cationic derivative $[Au(\mathbf{4})]^+$ turned out to be more complicated than expected. The reaction of **5** with one equivalent of $GaCl_3$ at low temperature proceeds cleanly in dichloromethane to give complex **8** which was identified by ^{31}P-NMR spectroscopy only [δ (CH_2Cl_2) = 227.00] (see Scheme 6). Cationic complex **8** displays a poor stability in solution and after several minutes standing in dichloromethane, a purple color typical of the formation of colloidal gold can be observed concomitant with the appearance of a new signal in ^{31}P NMR at δ = 231.70.

Postulating that the latter could be the cationic complex $[Au(\mathbf{4})_2]^+$ **9**, resulting from the disproportionation of two molecules of **8**, we studied the reaction of **8** with one equivalent of ligand **4**. Indeed, complex **9**, which exhibits the expected ^{31}P-NMR resonance, was produced as pale yellow solid with a 90% yield. It must be noted that **9** can also be readily obtained by reacting two equivalents of **4** with

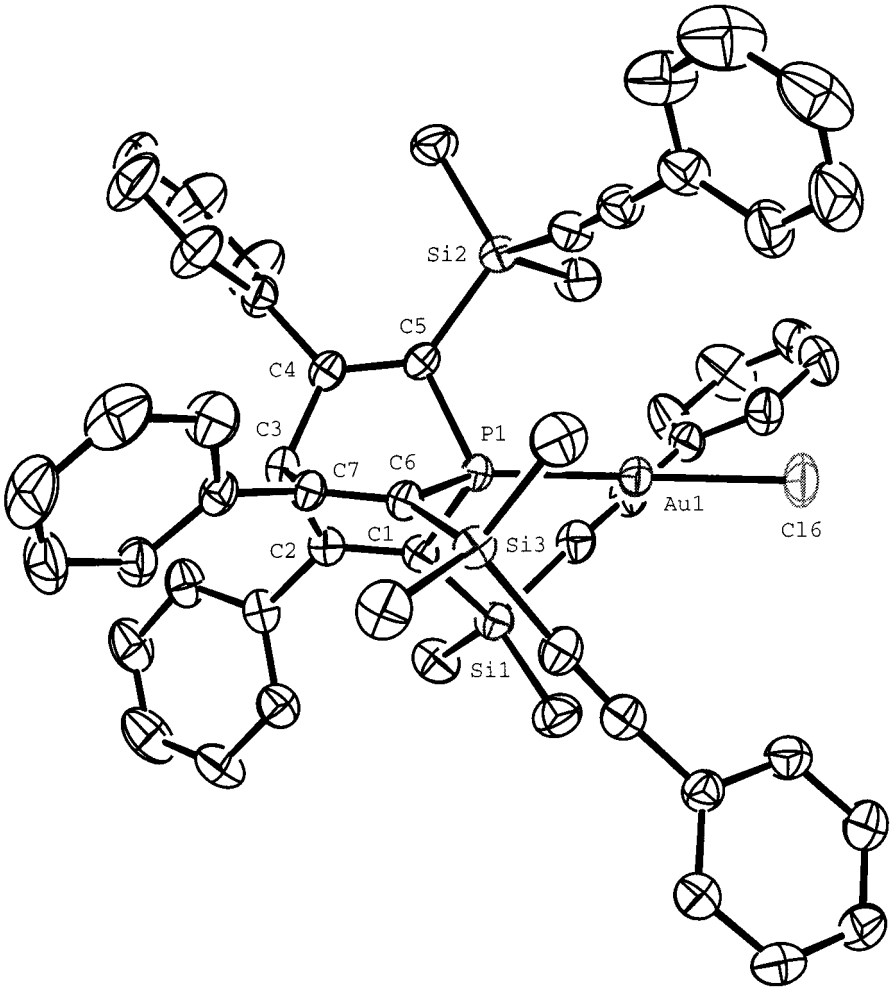
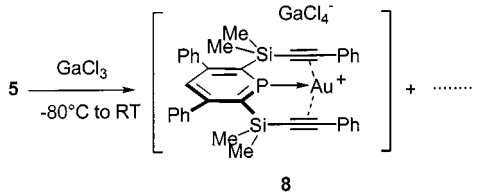
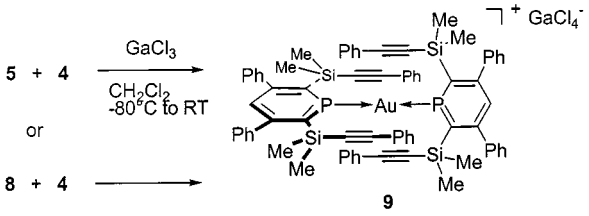


Figure 4. ORTEP drawing of **7** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 50% of the electron density; hydrogen atoms are omitted for clarity; the crystallographic labelling is arbitrary and different from the numbering used for assignments of the ^{13}C-NMR spectra; selected bond lengths [Å] and angles [°]: Au1−Cl 2.273(2), Au1−P1 2.211(1), P1−C1 1.829(5), C1−C2 1.354(7), C2−C3 1.534(7), C4−C5 1.344(7), C6−C7 1.331(7), C8−C9 1.212(8), C24−C25 1.203(8), C40−C41 1.205(8); Cl−Au1−P1 176.92(7), Au1−P1−Cl6 176.92(7), Au−P1−C1 119.6(2), Au1−P1−C5 118.7(2), Au1−P1−C6 115.2(2), P1−C1−C2 109.8(4), C1−C2−C3 118.1(4), C2−C3−C4 111.1(4), Si(1)−C(8)−C(9) 174.9(5), Si2−C24−C25 174.3(5), Si(3)−C40−C41 169.8(5)



Scheme 6. Possible structure of complex **8**

$[AuCl(SMe_2)]$ in the presence of $GaCl_3$ as previously described for the synthesis of complex **3** (see Scheme 7).



Scheme 7. Synthesis of complex **9**

All the NMR data, which is comparable with those of **3**, confirm the proposed structure. An X-ray crystal structure analysis was undertaken. An ORTEP view of **9** is shown in Figure 5. As observed in the structure of **3**, P=C bond lengths appear to be rather short at 1.72(1) and 1.71(1) Å (compared to those of free silylphosphinines) and the presence of the two bulky silyl groups at the α positions of the phosphorus atom implies that the two phosphinines are twisted against each other [interplane angle Θ = 66.7(3)°]. The most interesting feature of **9** is provided by the arrangement of the four alkynyl substituents which encapsulate the gold coordination sphere. Despite this particular geometry, no interactions between the gold centre and these alkynyl groups are noted. Indeed, although shorter than in complex **7**, all Au−C bonds appear to be too long (between 3.043 and 3.308 Å) to favour an overlap between the filled 5d orbitals of the gold atom and the π* system of the triple bond. Besides, this assumption is confirmed by the C≡C triple-bond lengths which fall in the expected range [from 1.19(1) to 1.21(2) Å]. Additionally, it must be noted that no π overlap occurs between the phenyl groups and the phosphinine units.

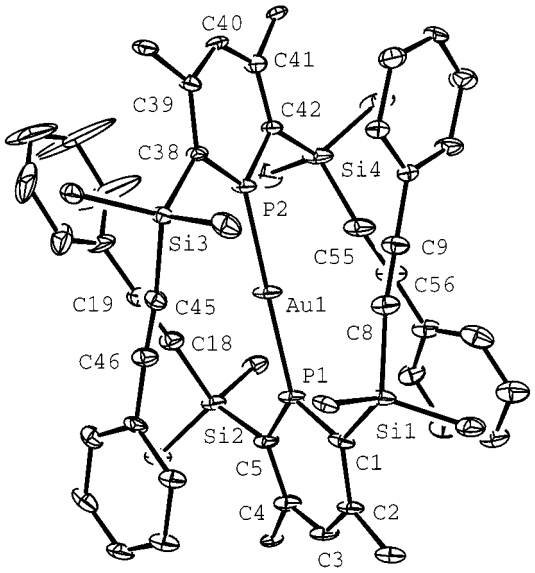


Figure 5. ORTEP drawing of **9** as determined by a single-crystal X-ray diffraction analysis; ellipsoids are drawn to enclose 50% of the electron density; hydrogen atoms are omitted for clarity; selected bond lengths [Å] and angles [°]: Au1−P1 2.263(2), Au1−P2 2.262(2), P1−C1 1.72(1), C1−C2 1.41(1), C2−C3 1.40(1), C3−C4 1.38(1), C4−C5 1.42(1), P1−C5 1.71(1), Si1−C8 1.861(9), C8−C9 1.19(1), C18−C19 1.21(1), C45−C46 1.20(1), C55−56 1.21(2); P1−Au1−P2 177.1(1), P1−C1−C2 117.0(7), C1−C2−C3 123 (1), C2−C3−C4 128.0(8), C3−C4−C5 123 (1), C4−C5−P1 116.4(8), C5−P1−C1 112.4(4), Si1−C8−C9 165(1), Si2−C18−C19 168(1), Si3−C45−C46 167.7(8), Si4−C55−C56 168(1)

In conclusion, we have shown that the poor π-back-donating ability of gold(I) significantly increases the dipole [1,4] character of monophosphinine ligands which are able to react under very mild conditions with alkynes to give phosphabarrelenes [4 + 2] cycloadducts. On the other hand, the existence and the appreciable stability of cationic derivatives such as **3** and **9** opens the way for a systematic investigation of the coordination chemistry of multidentate ligands including phosphinine units. Accordingly, studies aimed at including Au^+ into phosphinine-based macrocycles are currently under investigation.

Experimental Section

General: All reactions were routinely performed under nitrogen using Schlenk techniques and dry, oxygen-free solvents. Dry toluene, hexane, and *n*-pentane were obtained by distillation from sodium/benzophenone and dry CH_2Cl_2 was obtained by distillation from P_2O_5. Dry Celite was used for filtration. − NMR: Bruker AC-200 SY operating at 200.12 MHz for ^1H, 50.32 MHz for ^{13}C, and 81.91 MHz for ^{31}P; chemical shifts (ppm) are relative to TMS (^1H and ^{13}C) or 85% H_3PO_4 (^{31}P). List of abbreviations used: s, singlet; d, doublet; t, triplet; q, quadruplet; p, pseudo. − Elemental analyses: "Service d'analyse du CNRS", Gif-sur Yvette, France. Phosphinines **1**[14b] and **4**,[14b] $AuCl(SMe_2)$[27] were prepared according to published methods.

Synthesis of Complex 2: Phosphinine **1** (0.046 g, 1.9×10^{-4} mol) and $AuCl(SMe_2)$ (0.056 g, 1.9×10^{-4} mol) were weighed in air and placed under N_2. Freshly distilled CH_2Cl_2 (3 mL) was then added by syringe into the Schlenk flask, and the mixture allowed to stir at 35°C. ^{31}P-NMR spectroscopy indicated that the reaction was finished within 15 min. Reduction of the volume, followed by hexane precipitation and filtration yielded a pale yellow solid (0.085 g, 95%). Crystallization was achieved by layering hexanes onto a CH_2Cl_2 solution of complex, m.p. 120°C. − ^{31}P NMR (CD_2Cl_2): δ = 199.50 (s). − ^{13}C NMR (CD_2Cl_2): δ = 0.50 (d, $^3J_{C,P}$ = 4.31 Hz, 2 × $SiMe_3$), 127.00 (d, $^3J_{C,P}$ = 50.0 Hz, C-4), 143.50 (d, $^2J_{C,P}$ = 18.00 Hz, C-3,5), 160.00 (d, $^1J_{C,P}$ = 4.00 Hz, C-2,6). − ^1H NMR (CD_2Cl_2): δ = 0.50 (s, 18 H, 2 × $SiMe_3$), 7.51−7.62 (td, 1 H, $^4J_{H,P}$ = 6.70 Hz, $^3J_{H,H}$ = 8.20 Hz, 4-H), 8.20−8.40 (dd, 2 H, $^3J_{H,P}$ = 31.20 Hz, $^3J_{H,H}$ = 8.20 Hz, 3,5-H). − $C_{11}H_{21}AuClPSi_2$ (472.85): calcd. C 27.94, H 4.48; found C 28.15, H 4.66.

Synthesis of Complex 3: Phosphinine **1** (0.060 g, 2.5×10^{-4} mol) and $AuCl(SMe_2)$ (0.037 g, 1.25×10^{-4} mol) were weighed in air and placed under N_2. Freshly distilled CH_2Cl_2 (3 mL) was then added by syringe into the Schlenk flask, and the mixture allowed to stir at room temperature for 10 min. In a glove box, $GaCl_3$ (0.022 g, 1.25×10^{-4} mol) was weighed and put in a second

Schlenk flask. Outside the box, CH_2Cl_2 was added by syringe into the flask and the solution added to the first flask at −78°C using a cannula. The mixture was warmed to room temperature and stirred. ^{31}P-NMR spectroscopy indicated that the reaction was finished within 15 min. Reduction of the volume, followed by hexanes precipitation and filtration yielded a pale yellow solid (0.10 g, 90%). Crystallization was achieved by layering hexanes onto a CH_2Cl_2 solution of the complex, m.p. 140°C. − ^{31}P NMR (CD_2Cl_2): δ = 206.10 (s). − ^{1}H NMR (CD_2Cl_2): δ = 0.57 (s, 36 H, 4 × $SiMe_3$), 7.80−7.89 (m, 2 H, 2 × 4-H), 8.50−8.71 (ptd, 4 H, $\Sigma J_{H,P}$ = 42.35 Hz, 2 × 3,5-H). − ^{13}C NMR (CD_2Cl_2): δ = 0.85 (s, 4 × $SiMe_3$), 129.90 (pt AXX′, $\Sigma J_{C,P}$ = 50.60 Hz, 2 × C-4), 144.40 (pd AXX′, $\Sigma J_{C,P}$ = 14.75 Hz, 2 × C-3,5), 164.55 (s, 2 × C-2,6). − $C_{22}H_{42}AuCl_4GaP_2Si_4$ (889.37): calcd. C 29.71, H 4.76; found C 30.05, H 4.96.

Synthesis of Complex 5: Phosphinine **4** (0.200 g, 3.55 × 10^{-4} mol) and AuCl(SMe_2) (0.104 g, 3.55 × 10^{-4} mol) were weighed in air and placed under N_2. Freshly distilled CH_2Cl_2 (5 mL) was then added by syringe into the Schlenk flask, and the mixture allowed to stir at 35°C. ^{31}P-NMR spectroscopy indicated that the reaction was finished within 15 min. Reduction of the volume, followed by hexanes precipitation and filtration yielded a pale yellow solid (0.269 g, 95%), m.p. 160°C. − ^{31}P NMR (CD_2Cl_2): δ = 222.00 (s). − ^{13}C NMR (CD_2Cl_2): δ = 2.20 (d, $^3J_{C,P}$ = 4.20 Hz, 2 × $SiMe_2$), 94.60 (d, $^3J_{C,P}$ = 8.90 Hz, 2 × CCPh), 110.70 (s, CCPh), 123.0−129.70 (m, CH of Ph), 127.05 (d, $^3J_{C,P}$ = 50.0 Hz, C-4), 144.20 (d, $^2J_{C,P}$ = 12.000 Hz, C-3,5), 151.20 (d, $^2J_{C,P}$ = 12.00 Hz, Cq of C_6H_5), 158.40 (d, $^1J_{C,P}$ = 15.85 Hz, C-2,6). − ^{1}H NMR (CD_2Cl_2): δ = 0.30 (s, 12 H, 2 × $SiMe_2$), 7.10−7.60 (m, 21 H,4 × Ph, 4-H). − $C_{37}H_{33}AuClPSi_2$ (797.24): calcd. C 55.74; H 4.17; found C 55.95, H 4.46.

Synthesis of Complex 6: A CH_2Cl_2/hexane solution of gold complex **5** was placed in a tube and left under a static N_2 pressure. Pale yellow crystals slowly grew out of the solution together with a slight purple precipitate of colloidal gold. These crystals were very insoluble which prevented spectrocopic analysis. The crystal gave a combustion analysis consistent with the starting complex, m.p. 200°C. − $C_{37}H_{33}AuClPSi_2$ (797.24): calcd. C 55.74 H 4.17; found C 55.95, H 4.46.

Synthesis of Complex 7: Complex **5** (0.239 g, 3.00 × 10^{-4} mol) and bis(phenylethynyl)dimethylsilane (0.078 g, 3.00 × 10^{-4} mol) were weighed in air and placed under N_2. Freshly distilled toluene (5 mL) was then added by syringe into the Schlenk flask, and the mixture stirred at room temperature for 48 h. Purple gold(0) colloids were removed by filtration through a pad of Celite. Reduction of the volume and hexanes precipitation yielded a pale yellow solid (0.269 g, 85%). Suitable crystals for X-ray analysis were grown by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution of the complex, m.p. 175°C. − ^{31}P NMR (CD_2Cl_2): δ = −7.00 (s). − ^{13}C NMR (CD_2Cl_2): δ = 1.10 (d, $^3J_{C,P}$ = 2.20 Hz, 3 × $SiMe_2$), 78.90 (d, $^3J_{C,P}$ = 44.11 Hz, C-4), 92.50 (s, 3 × CCPh), 109.30 (s, 3 × CCPh), 127.60−132.90 (m, CH of Ph), 141.50 (d, $^2J_{C,P}$ = 12.14 Hz, C-3), 173.80 (d, $^1J_{C,P}$ = 9.85 Hz, C-2). − $C_{55}H_{49}AuClPSi_3$ (1057.65): calcd. C 62.46, H 4.67; found C 62.58, H 4.93.

Synthesis of Complex 9: Phosphinine **4** (0.141 g, 2.5 × 10^{-4} mol) and AuCl(SMe_2) (0.037 g, 1.25 × 10^{-4} mol) were weighed in air and placed under N_2. Freshly distilled CH_2Cl_2 (3 mL) was then

Table 1. Crystal data of **2** and **3**

	2	**3**
Crystal size [mm]	0.10 × 0.10 × 0.20	0.20 × 0.20 × 0.25
Empirical formula	$C_{11}H_{21}AuClPSi_2$	$C_{22}H_{42}AuCl_4GaP_2Si_4$
Molecular mass	472.86	889.37
Crystal system	triclinic	monoclinic
Space group	$P-1$	$P2_1/c$
a [Å]	7.126(1)	14.924(1)
b [Å]	10.599(1)	16.604(2)
c [Å]	11.439(2)	30.162(3)
α [°]	89.21(1)	90
β [°]	74.03(1)	90.66(2)
γ [°]	84.48(1)	90
V [Å^3]	826.8(3)	7473(2)
Z	2	8
D [g cm^{-3}]	1.90	1.58
F (000)	452	3504
μ [cm^{-1}]	9.260	5.145
Diffractometer	Enraf−Nonius CAD4	Enraf−Nonius CAD4
θ_{max} [°]	29.97	28.05
Reflections measured	5034	19411
Independent reflections	4796	18095
hkl ranges	−9 to 10 0 to 14 −16 to 16	−19 to 0 −21 to 0 −39 to 39
Reflections used	4198	6469
Criterion	> 2.0σ(I)	> 2.0σ(I)
Refinement type	F; full matrix	F; full matrix
Hydrogen atoms	no refinement	no refinement
Parameters refined	145	613
Reflections/parameter	33	10
$R1$ factor or $wR2$	0.044	0.057
Rw or $R1$	0.063	0.069
Weighting scheme	$4F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$	$4F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$
GOF	1.3	1.2
Min/max peaks in final Fourier [eÅ^{-3}]	5.47(62)/−0.67(62)	1.761(23)/−0.28(23)

Table 2. Crystal data of **6**, **7** and **9**

	6	**7**	**9**
Crystal size [mm]	0.10 × 0.10 × 0.10	0.08 × 0.10 × 0.14	0.20 × 0.20 × 0.20
Empirical formula	$C_{38}H_{35}Si_2PCl_3Au$	$C_{55}H_{49}AuClPSi_3$	$C_{78}H_{46}AuCl_{12}GaP_2Si_4$
Molecular mass	882.17	1058.61	1849.53
Crystal system	triclinic	monoclinic	triclinic
Space group	P1bar	$P2_1/c$	P1bar
a [Å]	12.005(1)	9.90000(10)	21.687(2)
b [Å]	13.128(2)	22.9960(3)	22.357(2)
c [Å]	13.763(2)	23.4260(3)	22.352(2)
α [°]	68.38(1)	90	96.42(1)
β [°]	77.75(1)	96.1270(6)	116.90(1)
γ [°]	66.85(1)	90	117.57(1)
V [Å^3]	1848.3(4)	5302.7(1)	7828.1(5.3)
Z	2	4	4
D [g cm^{-3}]	1.59	1.326	1.569
F (000)	872	2132	3656
μ [cm^{-1}]	4.323	2.956	2.771
Diffractometer	Enraf−Nonius CAD4	KappaCCD	Enraf−Nonius CAD4
θ_{max} [°]	29.97	26.32	28.04
Reflections measured	11156	11060	18332
Independent reflections	10739	10765	20437
hkl ranges	−16 to 16 −17 to 18 0 to 19	0 to 12 0 to 28 −29 to 29	0 to 28 −29 to 24 −29 to 25
Reflections used	6547	8418	17879
Criterion	> 3.0σ(*I*)	> 2.0σ(*I*)	> 2.0σ(*I*)
Refinement type	F; full matrix	Fsqd; full matrix	Fsqd; full matrix
Hydrogen atoms	no refinement	riding	riding
Parameters refined	406	550	1619
Reflections/parameter	16	15	11
*R*1 factor or *wR*2	0.039	0.1364	0.0584
Rw	0.038	0.0400	0.0567
Weighting scheme[a]	$4F_o^2/[\sigma^2(F_o^2) + 0.0064\ F_o^4]$	$a = 0.0869$ $b = 0.0000$	$a = 0.0816$ $b = 88.567$
GOF	1.0	1.08	1.90
Min/max peaks in final Fourier [eÅ^{-3}]	1.30(15)/−0.33(15)	2.22(0.15)/−0.80(0.15)	−1.56(43)/0.12(43)

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$; *R*1 is the conventional *R* factor as defined in SHELXL-97.[28]

added by syringe into the Schlenk flask, and the mixture allowed to stir at room temperature for 10 min. In a glove box, $GaCl_3$ (0.022 g, 1.25×10^{-4} mol) was weighed and placed into a second Schlenk flask. Outside the box, CH_2Cl_2 was added by syringe into the flask and the solution added to the first flask at −78°C using a cannula. The mixture was warmed to room temperature and stirred. ^{31}P-NMR spectroscopy indicated that the reaction was finished within 15 min. Reduction of the volume, followed by hexane precipitation and filtration yielded a pale yellow solid (0.10 g, 90%). Crystallization was achieved by layering hexanes onto a CH_2Cl_2 solution of the complex, m.p. 165°C. − ^{31}P NMR (CD_2Cl_2): δ = 231.70 (s). − ^{1}H NMR (CD_2Cl_2): δ = 0.25 (s, 24 H, 4 × $SiMe_2$), 7.10−7.60 (m, 42 H,8 × Ph, 2 × H-4). − ^{13}C NMR (CD_2Cl_2): δ = 2.60 (s,4 × $SiMe_2$), 95.35 (pt, AXX′, $\Sigma J_{C,P}$ = 4.60 Hz, 4 × CCPh), 113.90 (s, CCPh), 128.20−132.50 (m, CH of Ph), 133.90 (pt, AXX′, $\Sigma J_{C,P}$ = 18.25 Hz, 2 × C-4), 143.40 (pt, $\Sigma J_{C,P}$ = 6.10 Hz, 2 × C-3,5), 151.40 (pt, AXX′, $\Sigma J_{C,P}$ = 4.60 Hz, 2 × Cq of C_6H_5), 158.75 (pt, AXX′, $\Sigma J_{C,P}$ = 6.10 Hz, 2 × C-2,6). − $C_{74}H_{66}AuCl_4GaP_2Si_4$ (1538.13): calcd. C 57.79, H 4.33; found C 55.85, H 4.46.

X-ray Structural Analysis: For compounds **2**, **3, 6** and **9**, data were collected at 123 ± 0.5 K with an Enraf Nonius CAD4 diffractometer; data collection for **7** was conducted at room temperature using a KappaCCD diffractometer. Mo-K_α (λ = 0.71073 Å) radiation and a graphite monochromator were used in all cases. The crystal structures were solved and refined using the Enraf Nonius MOLEN package (maXus for the kappaCCD). In the case of **7**, final refinement was made with SHELX-97.[28] The structure of **9** calls for an additional comment. The asymmetric unit contains two dichloromethane molecules of crystallization. While one molecule can be directly modelled, the second one is very highly disordered. To address this problem, we used the Platon[29] SQWEEZE function and completed refinement using SHELX-97, thus leading to an acceptable *R* value. Other experimental details are given in Table 1 (compounds **2** and **3**) and 2 (compounds **6**, **7** and **9**) . Crystallographic data (excluding structure factors) for the structures reported have been deposited with the Cambridge Data Centre as supplementary publications CCDC-115213 to -115217. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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