Synthesis and Reactivity Towards Cationic Group 11 Metal Centers of an Extended Silacalix-[3]-phosphinine Macrocycle

Audrey Moores,[a] Nicolas Mézailles,[a] Nicole Maigrot,[a] Louis Ricard,[a] François Mathey,*[a] and Pascal le Floch*[a]

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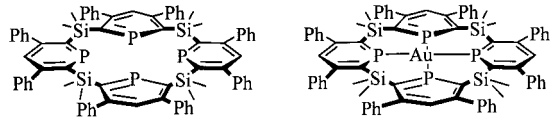
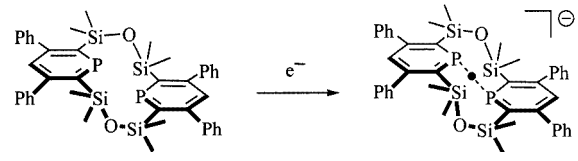
A synthetic route to a new type of phosphinine-based macrocycle has been developed. This approach involves the reaction of a phosphinine bearing two pendant $SiMe_2OSiMe_2CCR$ (R = Ph) (**5**) groups with two equivalents of a diazaphosphinine (**1**). The 2,6-bis(azaphosphininedimethylsilyl)-phosphinine (**6**) formed was then reacted under dilute conditions with a second equivalent of phosphinine **5** to produce the new macrocycle **4**. The X-ray crystal structure of **4** reveals no particular strain, and the macrocycle was fluxional in solution even at low temperature (–60 °C). Reactions of macrocycle **4** with $[Cu(MeCN)_4][BF_4]$, $[Ag][BF_4]$ and $[AuCl(SMe_2)]$ in the presence of $GaCl_3$ as chloride abstractor yielded the corresponding cationic complexes **8**, **9**, and **10**. The X-ray crystal structure of the copper complex **8** was recorded. As expected, the overall geometry around copper is trigonal planar. The macrocycle adopts a distorted arrangement to accommodate this geometry, and the phosphinines do not bind copper in a linear fashion. The examination of metric parameters suggests that the aromaticity of the rings has not been perturbed due to a weak bonding between phosphorus atoms and copper.

Introduction

Silacalix-[*n*]-phosphinines are a new class of phosphorus macrocycles that possess unusual electronic properties relative to classical sp^3-hybridized phosphorus species.[1] Recently we showed that the combination of a rigid structure (when $n = 4$) and the presence of strong π-acceptor phosphorus atoms within these macrocycles make them suitable ligands for the stabilization of reduced transition metal centers.[2] Thus, when cationic gold(I) was encapsulated in the cavity, these macrocycles behaved as phosphorus equivalents of CO matrices and the corresponding reduced gold(0) complex proved to be particularly stable.[3]



Another exciting feature of their reactivity was recently shown by studying their reduction. In the case of small macrocycles, the close vicinity of the two phosphorus atoms can be exploited to create new types of bonding. Thus, when two phosphinine units are linked by $-(Me_2Si-O-SiMe_2)-$ linkers in a cyclophane type structure, the mono-electronic reduction affords a mono-radical anion featuring a one-electron phosphorus–phosphorus single bond.[4]



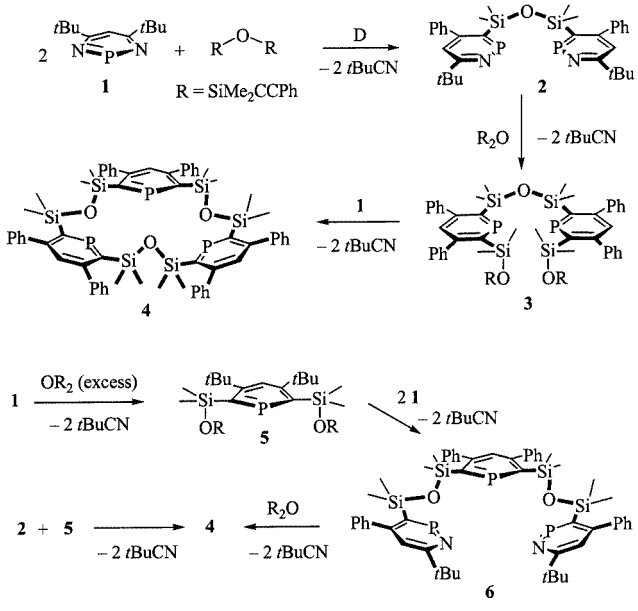
Regarding their coordinative properties, it appears that most species synthesized to date are quite rigid and allow the coordination of metal fragments that adopt a very specific geometry. Thus, silacalix-[*n*]-phosphinines incorporating $SiMe_2$ linkers are well adapted for the stabilization of metals that adopt a square planar or linear geometry ($n = 4$), or that might be coordinated through the face of an octahedron ($n = 3$).[1a] On the other hand, phosphorus analogs of cyclophane cannot incorporate metallic fragments and essentially behave as classical chelates.[5] With the aim of expanding the range of available macrocycles we recently investigated the synthesis of large and flexible species. Herein, we report on the synthesis of an extended silacalix-[3]-phosphinines and on a preliminary investigation of their coordinative properties towards cationic group 11 metals.

Results and Discussion

Among the different synthetic pathways, we deliberately chose one that relies on the reactivity of 1,3,2-diazaphosphinines towards functional alkynes. Indeed, as showed in previous studies, this method proved to be the most convenient way of assembling polyfunctional ligands and soph-

[a] Laboratoire "Hétéroéléments et Coordination" UMR CNRS 7653, Ecole Polytechnique,91128 Palaiseau Cedex, France

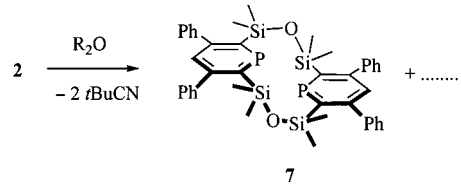
isticated edifices in one or two steps.[1b] In order to synthesize the extended and flexible structure **4** we focused our study on the preparation of a macrocycle incorporating $-(Me_2Si-O-SiMe_2)-$ spacer groups. Three different synthetic strategies were envisaged. The first one involved the condensation of the bidentate ligand **3** (formed from **2**), bearing two pendant $SiMe_2OSiMe_2CCPh$ groups, with one equivalent of a diazaphosphinine **1**. This approach was clearly advantageous since it could be carried out using a "one-pot sequence". The second and the third approach were different, but also utilized the same 2,6-disusbstituted phosphinine **5** as precursor. In the second approach, the macrocycle was built step by step from **5** by reacting two equivalents of **1** before closing the cavity with a third equivalent of diyne.[6] Finally, the third approach hinged on the direct condensation of **5** with the bis(monoazaphoshinine) **2**. All these pathways are summarized in the following scheme (Scheme 1).



Scheme 1

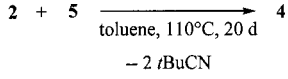
In the first approach, the preparation of the intermediate **2** was easily achieved by heating the diyne with two equivalents of **1** at 80 °C for 18 hours in toluene. Bis(azaphosphinine) **2**, which is highly sensitive towards moisture, was characterized by ^{31}P NMR exclusively (δ = 305.6 ppm). Unfortunately, whatever the amount of diyne used (from 2 to 10 equiv.), the second step did not cleanly afford the expected bis(phosphinine) **3**, but mainly the diphosphacyclophane **7**[1c] and a mixture of unidentified side-compounds (Scheme 2).

As previously noted, the close vicinity of the two reacting sites clearly favors the cyclisation. The two other pathways proved to be much more adapted to the synthesis of **4**. These require as a prerequisite the synthesis of phosphinine **5**. This was readily achieved by reacting diyne in excess with one equivalent of diazaphosphinine **1** in toluene at 110 °C



Scheme 2

for 5 hours. In the second method, reaction of **5** in toluene at 50 °C for 18 hours with two equivalents of **1** yielded compound **6** nearly quantitatively as attested by ^{31}P NMR spectroscopy (δ = 305.3 ppm). As with **2**, the high reactivity of the P=N moiety precluded the isolation and further characterization of **6**. The closing of the cavity was realized by reacting **6** with one equivalent of diyne. The use of dilute conditions turned out to be necessary to avoid the formation of linear oligomers and a series of competitive experiments showed the ideal concentration to be 5×10^{-3} mol/L. Additionally, as previously noted, we found that maintaining a steady concentration of reagents was absolutely necessary to achieve a complete conversion.[1b,1c] Unfortunately, these conditions dramatically increased the duration of experiments and the formation of **4** necessitated 2 weeks of heating. Following this experimental procedure, macrocycle **4** was isolated with an overall yield of 20% after chromatography. Finally, the third approach yielded **4** with a comparable yield. In both experiments, macrocycle **4** was easily purified by chromatography over silica gel and isolated as a very stable white powder.



Scheme 3

As expected, ^{31}P NMR spectroscopic data suggest that the macrocycle is fluxional and its signal appeared as a singlet even at −60 °C. The formulation of **4** was also confirmed by ^{1}H and ^{13}C spectroscopy. Additional evidence was given by an X-ray crystal structure analysis. An ORTEP view of one molecule of **4** is presented in Figure 1 and the most relevant bond lengths and bond angles are listed in the corresponding legend. As can be seen, the size of the cavity is large and the distance between the two closest P atoms (P1 and P3) is 4.620 Å (P2−P3, 5.256 Å; P1−P2, 6.177 Å). No particular strain can be observed in the macrocycle and metric parameters within each ring are quite similar and roughly similar to those recorded for other silylphosphinines. Apart from these data, the structure of **4** does not deserve particular comments.

To test the coordinative ability of **4**, we logically turned our attention to cationic group 11 metal centers, which are known to accommodate a trigonal planar geometry when they are encapsulated in a suitable environment.[7] Ligand **4** was reacted with $[Cu(MeCN)_4][BF_4]$,[8] $[Ag][BF_4]$, and $[Au(Me_2S)Cl]$[9] in the presence of $GaCl_3$ as chloride ab-

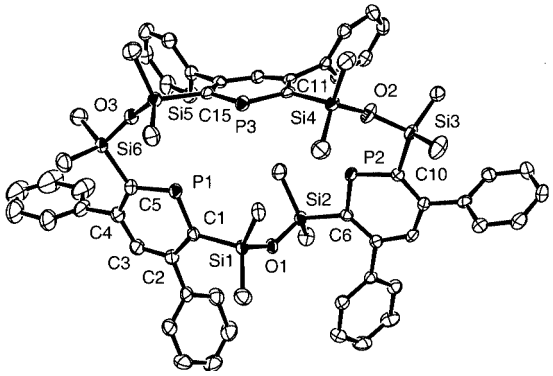
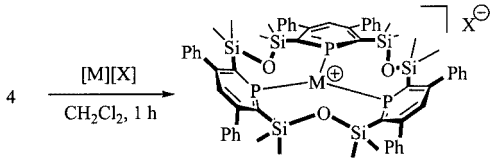


Figure 1. X-ray structure [50% TME (Thermal Motion Ellipsoids)] of one molecule of macrocycle **4**. All the hydrogen atoms and the solvents of crystallization (1 toluene, $^1/_2$ hexane and 1 H_2O) have been omitted. The numbering is arbitrary and different from that used for in the assignment of NMR spectroscopic data; selected bond lengths [Å] and angles [°]: P1−C1, 1.740(3); C1−C2, 1.411(4); C2−C3, 1.383(4); C3−C4, 1.395(4); C4−C5, 1.404(4); C5−P1, 1.742(3); C1−Si1, 1.890(3); Si1−O1, 1.638(2); O1−Si2, 1.638(2). P1−C1−C2, 121.5(2); C1−C2−C3, 122.8(3); C2−C3−C4, 126.0(3); C3−C4−C5, 123.1(3); C4−C5−P1, 121.2(2); C5−P1−C2, 105.3(1); P1−C1−Si1, 114.4(1); P1−C5−Si6, 113.9(2); C1−Si1−O1, 109.6(1); Si1−O1−Si2, 141.9(1)

stractor. All reactions cleanly proceeded at room temperature, in CH_2Cl_2 as solvent, to yield complexes **8**, **9**, and **10**, respectively, within 1 hour (Scheme 4). All three complexes were isolated as very stable powders and characterized by NMR spectroscopy and elemental analysis. The magnetic equivalency of the three phosphinine rings in each complex, which is in good agreement with a planar geometry around the metal, is evidenced by a singlet in ^{31}P NMR. Apparently, the coordination of the metal does not significantly affect the aromaticity within the phosphinine rings and, in ^{13}C NMR spectroscopic data, only minor differences can be noted between chemical shifts of the free ligand and those in complexes **8**, **9**, and **10**. A comparison between **4** and its gold derivative **10** is highly illustrative. Thus, for the carbon ring atoms, the $\Delta\delta$ ($\delta_{complex} - \delta_{ligand}$) are small: −8.74 ppm for C2, 3.3 ppm for C3 and 0.5 ppm for C4. This observation tends to show that the coordination of the macrocycle to the metal is relatively weak.



8: M = Cu, X = BF_4
9: M = Ag, X = BF_4
10: M = Au, X = $GaCl_4$

Scheme 4

In order to gain structural information, the X-ray structure of the copper complex **8** was recorded. A view of one molecule of **8** is presented in Figure 2 and the most relevant bond lengths and angles are listed in legend below. The structure consists of discrete monomeric units of the cationic copper complex and a tetrafluoroborate anion. As can be seen, the ligands adopt a highly distorted arrangement to accommodate the trigonal planar geometry around the central Cu atom. Interestingly, the copper atom is not located in the ideal axis of the phosphorus atom lone pair and in each phosphinine subunit, an important deviation is noted. Thus, the P1−Cu bond protrudes from the plane defined by the ring by 42° (34° for P2 and 22° for P3). This phenomenon is not unprecedented and reflects the important 3s character of the phosphorus atom lone pair. Similar deviations have already been observed in a helical edifice incorporating cationic biphosphinine Cu^I subunits and in chelate diphosphaferrocene based structures.[10] In P-sp^2 based ligands this geometric distortion is generally associated with a weak phosphorus−metal bonding. On the other hand, phosphorus−copper bond lengths compare with those recorded in other phosphinine[11] and tertiary phosphane Cu^I complexes.[12]

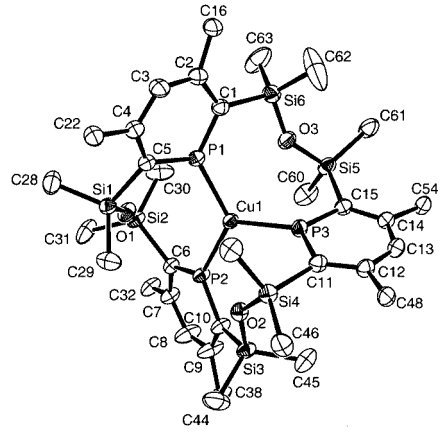


Figure 2. X-ray structure [50% TME (Thermal Motion Ellipsoids)] of one molecule of complex **8**. All the hydrogen atoms and the counter anion have been omitted for clarity. The numbering is arbitrary and different from that used in the assignment of NMR spectroscopic data.Selected bond lengths [Å] and angles [°]: P1−C1, 1.724(3); C1−C2, 1.409(4); C2−C3, 1.395(4); C3−C4, 1.399(4); C4−C5, 1.405(3); C5−P1, 1.727(3); C1−Si6, 1.890(3); Si1−O1, 1.624(2); O1−Si2, 1.628(2); C1−Si6, 1.890(3); P1−Cu1, 2.2419(7); P2−Cu1, 2.2386(7); P3−Cu1, 2.2318(7); P1−C1−C2, 118.4(2); C1−C2−C3, 123.2(2); C2−C3−C4, 126.8(2); C3−C4−C5, 121.9(3); C4−C5−P1, 119.5(2); C1−P1−C5, 108.8(1); P1−C5−Si1, 115.2(1); P1−C1−Si6, 117.1(2); C5−Si1−O1, 103.0(1); Si1−O1−Si2, 169.6(1); P1−Cu1−P2, 124.91(3); P2−Cu1−P3, 118.41(3); P3−Cu1−P1, 116.66(3)

Another interesting feature is provided by the analysis of metric parameters within the phosphinine subunits. Apart from the opening of the internal P−C−P angle, which ranges from 105.3(1) in **4** to 108.8(1) in **8** as a result of the re-hybridization at phosphorus, bond lengths and angles are not dramatically modified. In general, coordination of a phosphinine onto a metal fragment results in a lengthening of the P=C bond as a result of π-back donation in the π* LUMO, which is antibonding between P and C.[13] In **8**, P=C bond lengths compare with those of the free macrocycle **4**.

In conclusion, we have developed a straightforward route to a new type of an extended silacalix-[3]-phosphinine that

is well-tailored for the encapsulation of metal fragments adopting a trigonal planar geometry. Further studies aimed at studying the coordination of metallic centers having a catalytic activity are currently in progress in our laboratories.

Experimental Section

General: All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques with dry deoxygenated solvents. Dry THF and hexanes were obtained by distillation from Na/benzophenone and dry CH_2Cl_2 and $CDCl_3$ from P_2O_5. Dry CD_2Cl_2 was distilled and stored, like $CDCl_3$, on 4-Å Linde molecular sieves. Nuclear magnetic resonance spectra were recorded on a Bruker Avance 300 spectrometer. Solvent peaks are used as internal reference relative to Me_4Si for ^1H and ^{13}C chemical shifts (ppm). ^{31}P chemical shifts are relative to a 85% H_3PO_4 external reference. The following abbreviations are used: b; broad, singlet; d, doublet; t, triplet; m, multiplet; p, pentuplet; sext, sextuplet; sept, septuplet; v, virtual, q, quaternary. 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.

Synthesis of Phosphinine 5: A solution of diazaphosphinine **1** in toluene (21.7 mL, 0.0858 mmol/mL, 1.85 mmol) and 1,1,3,3-tetramethyl-1,3-bis-phenylethynyl-disiloxane (4.63 g, 13 mmol) was heated at 110 °C for 5 hours. After cooling to room temperature, celite (2 g) was added and toluene was evaporated yielding a brown powder. This solid was then added onto the top of a silica gel packed column for flash chromatography. A first fraction eluted with hexanes to yield excess diyne. A second fraction eluted with a mixture of hexane/toluene (90:10) and yielded mixed products. A third fraction gave the correct product. After evaporation of the solvents, phosphinine **5** was recovered as an orange oil. Yield: 1.13 g (85.8%). ^1H NMR (300 MHz, $CDCl_3$, 278 K): δ = 0.11 [s, 12 H, $Si(CH_3)_2OSi(CH_3)_2C{\equiv}C$], 0.24 [s, 12 H, $C{\equiv}CSi(CH_3)_2$], 7.2−7.5 (m, 21 H, phenyls and phosphinines *H*) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 278 K): δ = 2.8 [s, $C{\equiv}CSi(CH_3)_2$], 3.4 [d, *J* = 8.0 Hz, $Si(CH_3)_2OSi(CH_3)_2C{\equiv}C$], 94.2 (s, $C{\equiv}C{-}Si$), 104.35 (s, C_6H_5-$C{\equiv}C$), 123.3 (s, C^4 of $C{\equiv}C$-C_6H_5), 127.8 (s, C^4 of C_6H_5 on phosphinine), 128.1 (s, C^3 of C_6H_5 on phosphinine), 128.5 (s, C^3 of $C{\equiv}C$-C_6H_5), 128.9 (s, C^2 of $C{\equiv}C$-C_6H_5), 129.5 (s, C^2 of C_6H_5 on phosphinine), 132.2 (s, C^1 of $C{\equiv}C$-C_6H_5), 133.0 (d, *J* = 20.7 Hz, C^4 of phosphinine), 145.7 (d, *J* = 2.9 Hz, C^1 of C_6H_5 on phosphinine), 154.1 (d, *J* = 10.3 Hz, C^3 of phosphinine), 164.3 (d, *J* = 87.9 Hz, C^2 of phosphinine) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 278 K): δ = 275.6 (s) ppm. $C_{41}H_{45}O_2PSi_4$ (713.11): calcd. C 69.06, H 6.36; found C 69.36, H 6.18.

Synthesis of Macrocycle 4: Phosphinine **5** (2.07 g, 2.9 mmol) was added to a solution of diazaphosphinine **1** in toluene (79 mL, 73.5 mmol/L, 5.8 mmol) at room temperature. The volume of the solution was reduced to half and the resulting mixture was then heated at 50 °C for 18 hours. After checking the complete formation of the bis(monoazaphosphinine)phosphinine **6** by ^{31}P NMR spectroscopy, dry toluene (300 mL) was added prior to one equivalent of 1,1,3,3-tetramethyl-1,3-bis-phenylethynyl-disiloxane (0.97 g, 2.9 mmol). The resulting solution was heated at 130 °C for 20 days. After cooling to room temperature, celite (5 g) was added and the solvent was evaporated to yield a brown powder. This coated celite was the added onto the top of a silica gel packed column for flash chromatography. After eluting traces of remaining diyne with hexane, macrocycle **4** was eluted with a mixture of hexane/toluene (80:20). After evaporation of the solvents, **4** was recovered as a colorless powder. Yield: 635 mg (20%). ^1H NMR (300 MHz, $CDCl_3$, 278 K): δ = 0.00 [s, 36 H, $Si(CH_3)_3$], 7.2−7.5 (m, 33 H, C_6H_5 and H_4 of phosphinines) ppm. ^{13}C NMR (75.5 MHz, $CDCL_3$, 278 K): δ = 3.7 [s, $Si(CH_3)_3$], 127.4 (s, C_{ipso} of C_6H_5), 127.8 (s, C^3 of C_6H_5), 129.6 (s, C^2 of C_6H_5), 132.5 (d, *J* = 20.9 Hz, C^4 of phosphinines), 145.8 (s, C^1 of C_6H_5), 153.3 (d, *J* = 9.5 Hz, C^4 of phosphinines), 164.5 (d, *J* = 90.1 Hz, C^2 of phosphinines) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 278 K): δ = 276.9 ppm. MS (*m*/*z*, relative intensity): 1135 (M − 1, 50). $C_{63}H_{69}O_3P_3Si_6$ (1135.65): calcd. C 66.63, H 6.12; found C 66.05, H 5.94.

Synthesis of Complex 8: Macrocycle **4** (57 mg, 0.050 mmol) and $[Cu(MeCN)_4][BF_4]$ (15.8 mg, 0.050 mmol) were allowed to react in CH_2Cl_2 (3 mL) at room temperature. After one hour of stirring, the solvent was evaporated and complex **8** was washed twice with hexanes (2 × 2 mL). After filtration and drying under vacuum, **8** was recovered as a yellow powder. Yield: 62 mg (96%). ^1H NMR (300 MHz, $CDCl_3$, 278 K): δ = 0.00 [s, 36 H, $Si(CH_3)_3$], 7.2−7.5 (m, 33 H, C_6H_5 and H^4 of phosphinines) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 278 K): δ = 3.73 [s, $Si(CH_3)_3$], 3.79 [s, $Si(CH_3)_3$], 128.7 (s, C_{ipso} of C_6H_5), 128.8 (s, C^3 of C_6H_5), 129.1 (s, C^2 of C_6H_5), 132.9 (AXX′X′′, ΣJ = 35.6 Hz, C^4 of phosphinines), 143.5 (s, C^1 of C_6H_5), 156.4 (AXX′X′′, ΣJ = 14.9 Hz, C^3 of phosphinines), 159.2 (AXX′X′′, ΣJ = 40.2 Hz, C^2 of phosphinines) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 278 K): δ = 217.7 ppm. $C_{63}H_{69}BCuF_4O_3P_3Si_6$ (1286.01): calcd. C 58.84, H 5.41; found C 58.72, H 5.54.

Synthesis of Complex 9: Macrocycle 4 (50 mg, 0.044 mmol) and $AgBF_4$ (8.6 mg, 0.044 mmol) were dissolved in CH_2Cl_2 (2 mL) at room temperature. The solution was stirred for one hour. It became light brown. After evaporation of the solvent, the solid obtained was washed twice with hexanes (2 × 2 mL). Complex **9** was collected by filtration. After drying under vacuum, **9** was recovered as a beige powder. Yield: 54 mg (92%).^1H NMR (300 MHz, $CDCl_3$, 278 K): δ = 0.00 [s, 36 H, $Si(CH_3)_3$], 7.2−7.5 (m, 33 H, C_6H_5 and H^4 of phosphinines) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 278 K): δ = 4.11 [s, $Si(CH_3)_3$], 4.18 [s, $Si(CH_3)_3$], 128.6 (s, C_{ipso} of C_6H_5), 128.7 (s, C^3 of C_6H_5), 128.9 (s, C^2 of C_6H_5), 133.9 (AXX′X′′, ΣJ = 28.7 Hz, C^4 of phosphinines), 143.6 (s, C^1 of C_6H_5), 156.0 (AXX′X′′, ΣJ = 11.5 Hz, C^3 of phosphinines), 162.0 (AXX′X′′, ΣJ = 51.7 Hz, C^2 of phosphinines) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$, 278 K): δ = 222.3 ppm. $C_{63}H_{69}AgBF_4O_3P_3Si_6$ (1330.33): calcd. C 56.88, H 5.23; found C 57.00, H 5.42.

Synthesis of Complex 10: Macrocycle **4** (50 mg, 0.044 mmol) and [AuCl(SMe2)] (13 mg, 0.044 mmol) were dissolved in CH_2Cl_2 (2 mL) at room temperature. The resulting solution was cooled to −80 °C and a solution of $GaCl_3$ (10 mg, 0.057 mmol) in CH_2Cl_2 (prepared in the glovebox) was added into the mixture by cannula. The resulting solution was warmed to room temperature and then stirred for one hour. After evaporation of the solvent, the solid obtained was washed successively with hexanes and ether (2 × 2 mL). Complex **10** was collected by filtration. After drying under vacuum, **10** was recovered as a yellow powder. Yield: 66 mg (97%).^1H NMR (300 MHz, $CDCl_3$, 278 K): δ = 0.00 [s, 36 H, $Si(CH_3)_3$], 7.2−7.5 (m, 33 H, C_6H_5 and H^4 of phosphinines) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 278 K): δ = 3.90 [s, $Si(CH_3)_3$], 3.95 [s, $Si(CH_3)_3$], 128.7 (s, C_{ipso} of C_6H_5), 128.8 (s, C^3 of C_6H_5), 129.1 (s, C^2 of C_6H_5), 133.1 (AXX′X′′, ΣJ = 34.5 Hz, C^4 of phosphinines), 143.8 (s, C^1 of C_6H_5), 156.6 (AXX′X′′, ΣJ = 14.9 Hz, C^3 of phosphinines), 159.2 (AXX′X′′, ΣJ = 46.0 Hz, C^2 of phosphinines) ppm. ^{31}P NMR (121.5 MHz, CH_2Cl_2, 278 K): δ = 249.5 ppm.

Table 1. Details of X-ray structure determinations

Compound	4	8
Crystal colour	colorless	yellow
Crystal shape	plate	cube
Crystal size [mm]	0.18 × 0.18 × 0.05	0.18 × 0.18 × 0.18
Empirical formula	$C_{63}H_{69}O_3P_3Si_4.C_6H_{14}\cdot 1/2C_7H_8\cdot H_2O$	$C_{63}H_{69}BCuF_4O_3P_3Si_6\cdot 2.5CHCl_3$
Molecular mass	1285.89	1584.40
Temperature [K]	150.0(1)	150.0(1)
Radiation (graphite-monochromated)	Mo-K_α	Mo-K_α
Wavelength [Å]	0.71070	0.71069
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	12.1666(6)	13.775(2)
b [Å]	16.3580(6)	15.894(2)
c [Å]	18.1896(8)	18.550(3)
α [°]	104.944(2)	83.8740(10)
β [°]	98.117(2)	77.0910(10)
γ [°]	92.553(2)	77.2960(10)
V [Å]^3	3450.2(3)	3854.6(10)
Z, calcd. density [g·cm^{-3}]	2, 1.238	2, 1.365
Abs. coefficient [cm^{-1}]	0.238	0.750
$2\Theta_{max}$ [deg]	24.11	27.48
$F(000)$	1370	1630
Index ranges	$-13 \le h \le 11 - 18 \le k \le 18 - 20 \le l \le 20$	$-17 \le h \le 17 - 20 \le k \le 20 - 24 \le l \le 22$
Reflections collected/independent	17022/10952	26536/17590
Reflections used	8052	13531
R_{int}	0.0438	0.0490
Absorption correction	0.9584 min., 0.9882 max.	0.8768 min., 0.8768 max.
Parameters refined	734	794
Reflection/parameter	10	17
Final R1, $wR2$ [$I > 2\sigma(I)$]	0.0478, 0.1265	0.0534, 0.1578
Goodness-of-fit on F^2	1.020	1.103
Diff, peak and hole [e·Å^{-3}]	1.021(0.055)/−0.638(0.055)	1.524(0.076)/−1.233(0.076)

$C_{63}H_{69}AuCl_4GaO_3P_3Si_6$ (1544.15): calcd. C 49.00, H 4.50; found C 48.88, H 4.55.

X-ray Structure Determinations: Single crystals of **4** were obtained by diffusing methanol into a toluene solution of the compound. Crystals of **8** were obtained by diffusing hexane into a chloroform solution of the complex. Data were collected on a Nonius Kappa CCD diffractometer using a Mo-$K\alpha$ (λ = 0.71069 Å) X-ray source and a graphite monochromator. Experimental details are described in Table 1. The crystal structures were solved using SIR 97[14] and Shelxl-97.[15] ORTEP drawings were made using ORTEP III for Windows.[16] In the structure of **8** a 1/2 $CHCl_3$ located near a symmetry center was accounted with SQUEEZE. Analysis of the principal mean square displacements in the structure of complex **8** may indicate a slight libration or long range disorder of the BF_4 anion. CCDC-178617 (for **4**) and -178618 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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