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Selective Formation of Gold(I) Bis-Phospholane Macrocycles, Polymeric Chains, and Nanotubes

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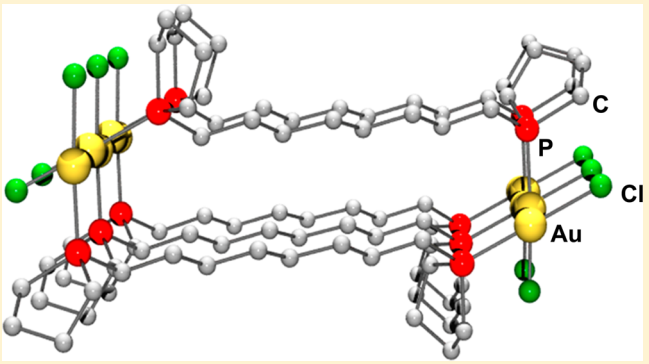
Supporting Information

ABSTRACT: A series of highly flexible bis-phospholane ligands **3a–g** with 5–11 methylene groups in the backbone was synthesized and fully characterized by mass spectrometry and NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy. Gold bis-phospholane macrocycles containing 16 ($[Au_2Cl_2(\mu\text{-}\mathbf{3a})_2]$, **4**), 20 ($[Au_2Cl_2(\mu\text{-}\mathbf{3c})_2]$, **5**), 24 ($[Au_2Cl(\mu\text{-}\mathbf{3e})_2]Cl$, **6**), and 28 ($[Au_2Cl_2(\mu\text{-}\mathbf{3g})_2]$, **7**) atoms in the ring were obtained in one step from [AuCl(tht)] (tht = tetrahydrothiophene) and **3a,c,e,g** in excellent yield. In addition, three polymers resulting from aurophilic interactions, i.e., zigzag chains in $[Au_2Cl_2(\mu\text{-}\mathbf{3b})]_x$ (**8**) and nanotubes in $[Au_2Cl_2(\mu\text{-}\mathbf{3d})]_x$ (**9**) and $[Au_2Cl_2(\mu\text{-}\mathbf{3f})]_x$ (**10**), with Au···Au distances of 309.41(2), 330.24(6), and 335.82(3) pm, respectively, were obtained. Halide abstraction of **4–7** with $AgBF_4$ led to macrocycles $[Au_2(\mu\text{-}\mathbf{3a})_2](BF_4)_2$ (**11**), $[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$ (**12**), $[Au_2(\mu\text{-}\mathbf{3e})_2](BF_4)_2$ (**13**), and $[Au_2(\mu\text{-}\mathbf{3g})_2](BF_4)_2$ (**14**). In **12**, the monomers are connected by strong aurophilic interactions (Au···Au 296.57(1) pm) in the solid state with formation of a polymeric chain. All complexes were fully characterized by NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy, mass spectrometry, and X-ray diffraction.



INTRODUCTION

In supramolecular chemistry, the targeted synthesis of macrocycles, chains, and tubes is of interest for developing new materials with useful optical and electronic properties.[1,2] Gold(I) cations are predestined for predictable molecular assemblies due to their favored linear geometry and the potential for aurophilic interactions.[3] The strength of this closed-shell interaction is similar to that of a hydrogen bond[3d,4] and can be fine-tuned by the choice of counterions[5] or the number of carbon atoms in the backbone of bis-phosphine ligands.[6] Understanding this phenomenon is of importance for the targeted synthesis of gold(I)-rich chains, rings, and tubes. For example, ultrathin gold nanowires were obtained by reducing oleylamine–AuCl complexes formed by aurophilic interaction.[7]

The selective formation of gold(I) bis-phosphine macrocycles is largely unexplored. The majority of the published gold(I) bis-phosphine-containing macrocycles were prepared by a multistep synthesis starting from preorganized dinuclear gold(I) bis-phosphine complexes with mostly linear and rigid bridging ligands. The bis-phosphine ligands $R_2P(CH_2)_nPR_2$ (n = 1, 2; R = phenyl, cyclohexyl) have been intensely studied in the formation of macrocycles with additional bridging ligands, such as bipyridyls,[9] dithiolates,[10] diisocyanides,[11] diacetylides,[11b,12] *trans,trans*-muconates,[13] and a second bis-phosphine.[14] Even though bis-phospholanes are "privileged ligands",[15] gold(I) phospholane complexes are largely unexplored and bis-phospholanes have not been used as bridging ligands for the construction of gold phosphine macrocycles.[16] Furthermore, only a small number of publications deal with long and highly flexible bridging units in bis-phosphine ligands.[17] Pioneering work by Shaw et al. demonstrated the unusual coordination behavior of $(^{t}Bu)_2P(CH_2)_nP(^{t}Bu)_2$ (n = 5–12),[18] and gold bis-phosphine macrocycles with $Ph_2P(CH_2)_nPPh_2$ ($n \geq 5$) have been described by Schmidbaur et al.,[19] Puddephatt et al.,[9a,12b,c,f,i,20] Kelleher et al.,[21] Hill et al.,[22] Alvarez-Falcón et al.,[23] and Balch et al.[24]

We here report the first high-yield one-step synthesis of gold(I) bis-phospholane complexes. Depending on the counterions and the carbon-chain length of the bis-phosphine ligands used, gold(I) bis-phospholane macrocycles, polymeric chains, and nanotubes are selectively formed without using high-dilution techniques.

RESULTS AND DISCUSSION

Synthesis of Bis-Phospholane Ligands. New bis-phospholanes with 5–11 methylene groups in the backbone were synthesized by using a modified strategy published by Haddow et al. in 2009 (Scheme 1).[25] Two equivalents of 1-phenylphospholane[26] was treated with 1,n-dibromoalkanes (n = 5–11) in acetonitrile to give the corresponding bis-phospholanium salts **1a–g** in quantitative yield as white solids. Oxidative cleavage of the P–phenyl bond by aqueous sodium

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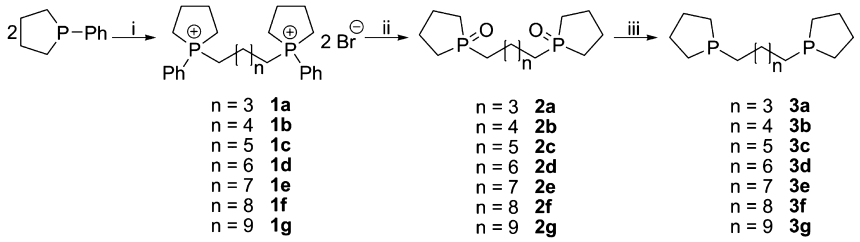
Scheme 1. Synthesis of Bis-Phospholanes 3a–g[a]

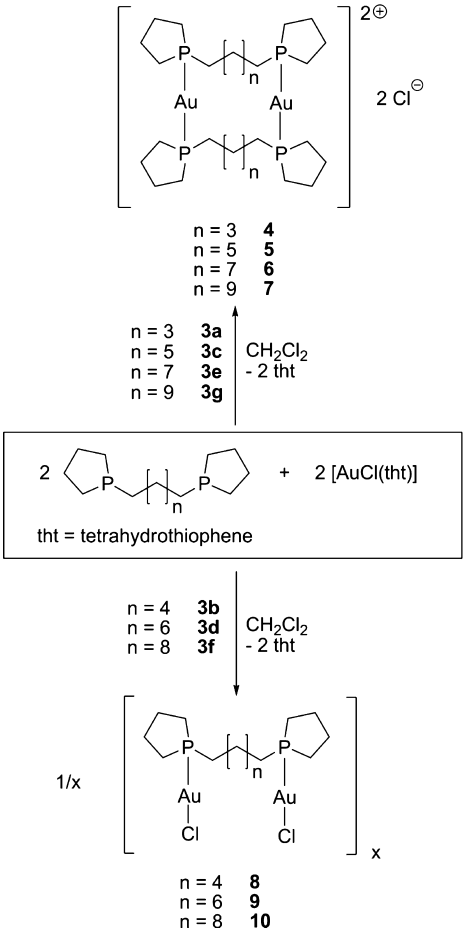


[a](i) 1,(n+2)-Dibromoalkane, MeCN, 80 °C, 48 h; (ii) 20% NaOH(aq), 80 °C, 20 h; (iii) $LiAlH_4/SiMe_3Cl$, THF, room temperature, 10 h.

hydroxide solution led to the bis-phospholane oxides **2a–g**. Reduction to the corresponding bis-phospholanes **3a–g** was carried out with a mixture of lithium aluminum hydride and trimethylsilyl chloride in tetrahydrofuran.[27] Ligands with an even number of carbon atoms in the backbone (**3b,d,f**) were obtained as white solids and those with an odd number (**3a,c,e,g**) as highly viscous oils.

Gold(I) Bis-Phospholane Complexes: Selective Formation of Macrocycles, Chains, and Tubes. Addition of [AuCl(tht)] (tht = tetrahydrothiophene) to a solution of bis-phospholane **3a,c,e,g** in dichloromethane led to 16- (**4**), 20- (**5**), 24- (**6**), and 28-membered (**7**) macrocycles in excellent yield by self-assembly under thermodynamic control (Scheme 2).

Scheme 2. Synthesis of Gold(I) Complexes



All complexes were obtained as white solids and are soluble in common organic solvents such as dichloromethane, chloroform, and acetonitrile. Compounds **4–7** are air and light stable and were fully characterized by NMR and IR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography. In the $^{31}P\{^1H\}$ NMR spectra a downfield shift is observed on coordination, from ca. −27 ppm (free ligands) to sharp signals at ca. 37 ppm (macrocycles). In the mass spectra (ESI^+ mode), $[M - Cl]^+$ peaks are observed. The molecular structures (Figure 1) display a [2 + 1] coordination mode for gold(I). Selected bond lengths and angles are given in Table 1.

Compounds **4**, **5**, and **7** form isolated macrocycles in the solid state. Each gold atom exhibits almost linear coordination by two phospholane moieties (P–Au–P 169.37(8)–175.32(3)°) and additionally weakly coordinating terminal chlorido ligands. The Au–Cl interactions decrease with increasing length of the backbone from 280.7(2) pm in **4** to

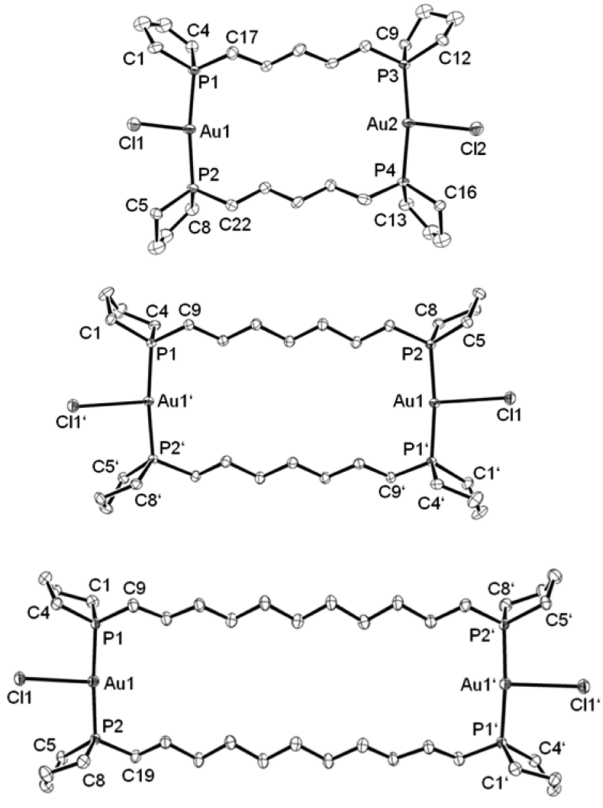


Figure 1. Molecular structures of **4** (top), **5** (middle), and **7** (bottom). Ellipsoids are drawn at the 50% probability level, and H atoms and solvent molecules are omitted for clarity.

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Table 1. Selected Bond Lengths (pm) and Angles (deg) for 4–7[a]

	4	5	6[b]	7
Au1–P1	229.9(2)	229.71(8)	230.0(2) [229.5(2)]	229.2(1)
Au1–P2	229.9(2)	229.40(8)	230.6(2) [230.0(2)]	229.6(1)
Au1–Cl1	280.7(2)	290.26(7)	292.4(2) [304.1(2)]	294.1(2)
Au2–P3	228.7(2)		229.7(2) [229.8(2)]	
Au2–P4	229.4(2)		229.3(2) [230.1(2)]	
Au2–Cl2	284.5(2)			
P1–Au1–P2	169.37(8)	172.77(3)	167.35(6) [167.62(6)]	175.32(3)
P3–Au2–P4	170.14(8)		170.07(6) [167.75(6)]	

[a]Omitted values are generated by symmetry. [b]Values for the second independent molecule are given in brackets.

294.1(2) pm in **7**, resulting in longer Au–Cl bonds (cf. Au–Cl 250 pm in $[AuCl(PPh_3)_2]$)[28] and an increase of the P–Au–P bond angles from **4** (169.37(8)°) to **7** (175.32(3)°). The Au–P bond lengths and P–Au–P bond angles are in agreement with similar structures described in the literature (Au–P 230.7(2) and 231.1(2) pm, P–Au–P 172.1(1) and 174.2(1)° in $[Au_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}_2](SbF_6)_2$).[21] $[Au_2Cl_2(\mu\text{-}Ph_2PCH_2PPh_2)_2]$, reported by Schmidbaur et al. in 1977, exhibits similar bond lengths (P1–Au 232.7(3) pm, P2–Au 228.8(3) pm, Au–Cl 277.1(4) pm) and a smaller P1–Au–P2 bond angle (155.9(1)°), presumably due to strong, supported Au···Au contacts (296.2(1) pm).[14a] The intramolecular Au···Au distances are 850.4 (**4**), 1099.5 (**5**), 1339.0 and 1373.6 (**6**), and 1593.1 pm (**7**).

In compound **6**, the macrocycles are connected by chlorido bridges in the solid state. **6** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit (Figure 2). It forms two polymeric chains along the *b* axis that differ in the position of the chlorido bridges. In one polymer, a symmetrical chlorido bridge (Au–Cl–Au 179.4(2)°; Au–Cl 304.1(2), 304.7(2) pm) is observed, while a nonsymmetrical (Au–Cl 292.4(2), 326.5(2) pm), slightly bent (169.8(2)°) chlorido bridge is observed in the latter. In 1986, Schmidbaur et al. reported the molecular structure of the $[Au_2\{Ph_2PC(CH_2)_2PPh_2\}_2Cl]$ cation, with the second chloride anion as a discrete and isolated anion in the crystal.[29]

The 2:2 reaction of [AuCl(tht)] with **3b,d,f** was carried out under the same conditions as for the ligands **3a,c,e,g** (Scheme 2). The $^{31}P\{^1H\}$ NMR signal of the reaction mixture at ca. 37 ppm suggested the formation of macrocycles. However, instead of the expected macrocycles the X-ray analysis of the crystals obtained showed 2:1 complexes (Au:L) with each phosphorus atom coordinated to an Au–Cl unit in a linear fashion (compounds **8**–**10**, Figures 3 and 4). A solution of the crystals in CD_2Cl_2 gave a signal at ca. 24 ppm in the $^{31}P\{^1H\}$ NMR spectra, which was not observed in the reaction mixture. The $^{31}P\{^1H\}$ NMR spectra of the filtrates showed no signals for the free ligands (ca. −27 ppm) and only one at ca. 34 ppm (see the Supporting Information). The hypothesis that this signal belongs to a four-coordinate gold(I) complex is based on reasons of stoichiometry and the observation that the reaction of 2 equiv of **3g** with 1 equiv of [AuCl(tht)] resulted in the same chemical shift. Crystals of $[Au_2Cl_2(\mu\text{-}\mathbf{3b})]$ (**8**) were obtained as colorless needles from dichloromethane/toluene at room temperature. The monomeric unit of **8** exhibits an *anti* conformation of the AuCl groups. These monomers form zigzag chains through unsupported intermolecular Au···Au interactions (309.41(2) pm) (Figure 3). Aurophilic interactions are common in gold(I)-based polymers.[11b,24,30] The bond lengths and angles of **8** (Table 2) are comparable to those of the related compound $[Au_2\{\mu\text{-}Ph_2P(CH_2)_7PPh_2\}Cl_2]$ (Au–P 219.5(6), 222.0(5) pm, Au–Cl 239.2(6), 232.7(5) pm, Au···Au 326.4(2) pm).[24b]

In **9** and **10** (Figure 4), each gold atom is involved in two aurophilic interactions, one of which is slightly stronger (330.24(6), 335.82(3) pm) than the other (each 351.06(1) pm) (Table 2), with formation of nanotubes in the solid state. It is known that gold atoms can participate in more than one

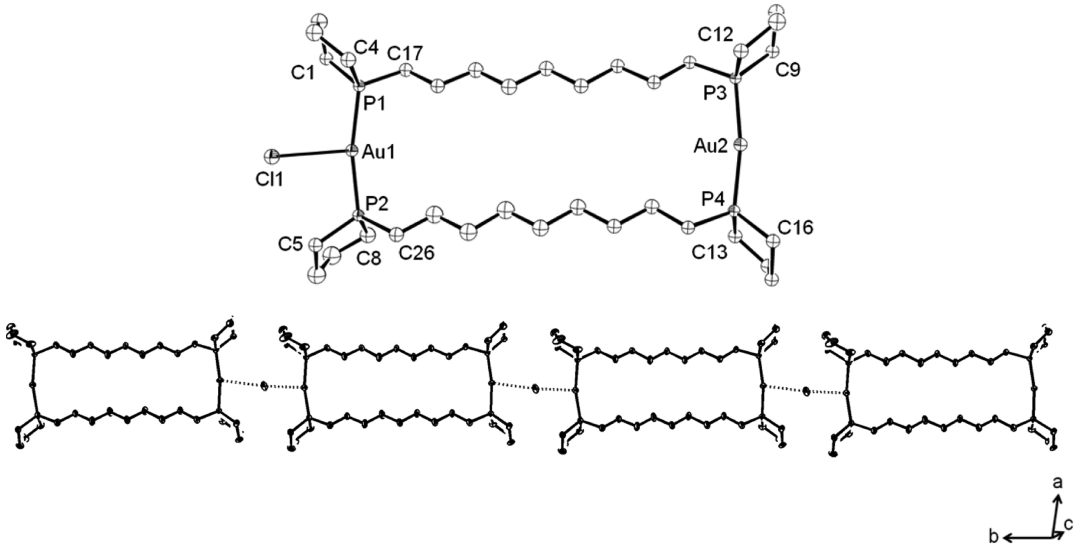

Figure 2. (top) Molecular structure of the cation of **6**. (bottom) View along the *b* axis. Ellipsoids are drawn at the 50% probability level, and H atoms, solvent molecules, and the second counterion are omitted for clarity. Only one of the two independent molecules in the asymmetric unit is shown.

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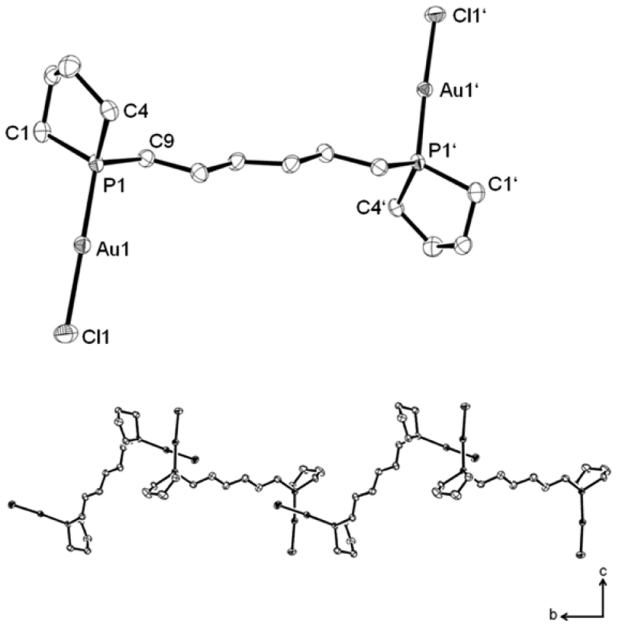

Figure 3. (top) Molecular structure of **8**. (bottom) Polymeric chain formed through aurophilic interactions, viewed along the *b* axis. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

aurophilic interaction,[3e] resulting in longer Au···Au distances. The angles between the two P−Au−Cl axes are 71.27(4)° (**9**) and 67.40(5)° (**10**). Similar complexes, such as $[Au_2(\mu\text{-}Ph_2PCH_2CH_2PPh_2)Cl_2]$, form dimers with Au···Au interactions of 318.9 pm.[31]

Due to the weaker *trans* effect of the chlorido ligand in comparison to phosphorus, the Au−P bonds in **8**−**10** are significantly shorter than those of the macrocycles **4**−**7**.[31] The intramolecular Au···Au distances increase with an increasing number of carbon atoms in the backbone, and the P−Au−Cl bond angle becomes closer to 180° on going from **8** to **10**.

Table 2. Selected Bond Lengths (pm) and Angles (deg) in 8−10

	8	9	10
Au1−P1	223.2(1)	223.6(3)	222.6(1)
Au2−P2	224.0(1)	223.5(3)	223.3(2)
Au1−Cl1	229.9(1)	231.3(3)	229.3(2)
Au2−Cl2	231.2(1)	230.4(3)	230.0(2)
Au1···Au2	309.41(2)	330.24(6)	335.82(3)
Au1···Au2′		351.06(1)	351.06(1)
P1−Au1−Cl1	174.15(4)	175.70(9)	178.67(6)
P2−Au2−Cl2	174.07(4)	178.5(1)	177.30(6)

A similar influence of the number of methylene units in the backbone of flexible bis-phosphine ligands was also observed by others. For $Ph_2P(CH_2)_nPPh_2$ (n = 1−6), crystals of macrocycles $[Au_4\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}_2(\mu\text{-}NC_5H_4C_5H_4N)_2](CF_3CO_2)_4$ were obtained with n = 1, 3, 5, but not in the case of even numbers (n = 2, 4, 6).[9a] Furthermore, Brandys et al. reported formation of macrocycles for $[Au_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}_2](CF_3CO_2)_2$ and $[Au_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}_2](CF_3CO_2)_2$, but a polymeric structure for the complex with 1,4-bis(diphenylphosphino)butane.[20a] This phenomenon is due to the preferred *anti* orientation of the two phosphorus lone pairs of electrons when n is even.[32]

Halide Abstraction. Aurophilic interactions are important tools for creating supramolecular assemblies.[3c−e] Puddephatt and co-workers connected the gold(I) complexes bis[μ-1,3-diphenylphosphinopropane-κ^2-P,P']digold(I) bis(trifluoroacetate) and bis[μ-1,5-diphenylphosphinopentane-κ^2-P,P']digold(I) bis(trifluoroacetate) with $K[Au(CN)_2]$.[20a] As direct gold−gold contacts in gold(I) bis-phosphine complexes have not yet been reported, we replaced the chloride anions in

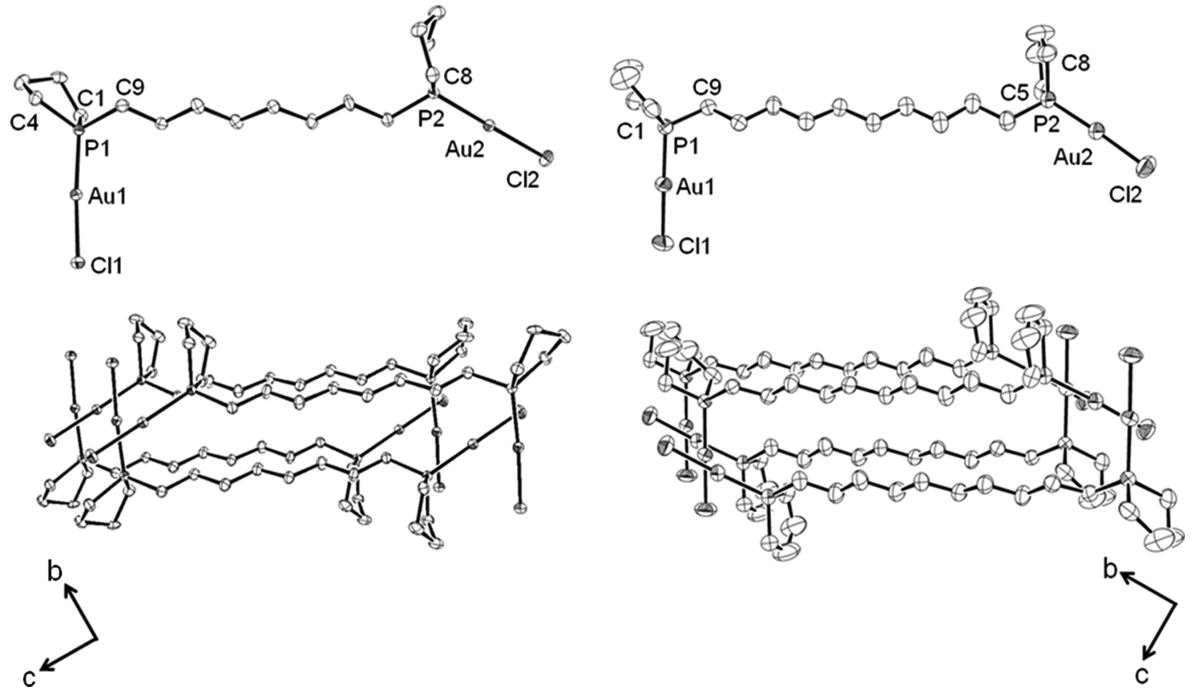

Figure 4. (top) Molecular structures of **9** (left) and **10** (right). (bottom) Nanotubes formed via aurophilic interactions, viewed along the *a* axis. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

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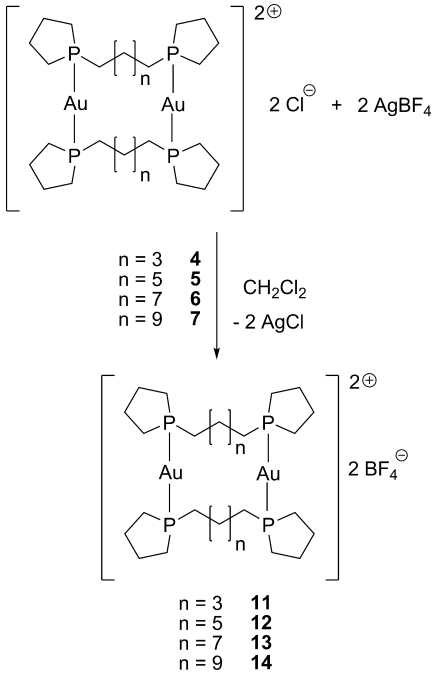
4–7 with weakly coordinating BF_4^- anions (Scheme 3), expecting the formation of gold–gold interactions. Isolated

Scheme 3. Synthesis of Macrocycles 11–14



macrocycles $[Au_2(\mu\text{-}\mathbf{3a})_2](BF_4)_2$ (**11**), $[Au_2(\mu\text{-}\mathbf{3e})_2](BF_4)_2$ (**13**), and $[Au_2(\mu\text{-}\mathbf{3g})_2](BF_4)_2$ (**14**) were formed in the case of n = 3, 7, 9 (Figure 5), while 1,7-bis(phospholano)heptane (**3c**) as ligand gave the first gold(I) bis-phosphine chain based on aurophilic interactions (**12**; Figure 6).

Selected bond lengths and angles for **11–14** are given in Table 3. The Au–P bond lengths and P–Au–P bond angles are in the same ranges as for macrocycles **4–7**. The anion–cation interaction increases from **11** (Au–F 346.1 pm) to **13** (Au–F 317.6 pm) and **14** (Au–P 299.5 pm). The opposite trend was observed for the terminal chlorido ligands in **4–7**. The $^{31}P\{^1H\}$ NMR spectra of complexes **11–14** exhibit singlets at ca. 40 ppm, shifted downfield by ca. 3 ppm in comparison to macrocycles **4–7** due to the more weakly coordinating anions. In the mass spectra, $[M - BF_4]^+$ ions are observed, indicating that the macrocyclic structures are also retained in solution. In contrast to the case for **11**, **13**, and **14**, the single monomers in $[Au_2(\mu\text{-}\mathbf{3c})_2](BF_4)_2$ (**12**) are connected through short Au···Au contacts of 296.61(1) pm to form the first bis-phospholane gold(I) polymeric chain. The P–Au–P axes in each monomer are twisted by 83.3(1)° (Figure 6). The Au–P bond lengths (230.98(7), 231.16(7) pm) are in the same range as in **11**, **13**, and **14**, but the strong intermolecular aurophilic interaction results in smaller P–Au–P angles (169.62(3), 168.21(3)°). As in **11**, **13**, and **14**, the tetrafluoroborate anions are isolated in the solid state.

Intramolecular and intermolecular aurophilic interactions were observed in eight-membered metallacycles of thiouracilate complexes containing bridging bis(diphenylphosphino)-methane (dppm) ligands,[8b] *O*,*O*′-dialkyldithiophosphate ligands,[8c,33] and mixtures of dithiolates and dppm[34] or dithiocarbamates[35] and have also been the focus of theoretical calculations.[36] On the other hand, gold(I) macrocycles bearing only bis-phosphine ligands do not show intermolecular

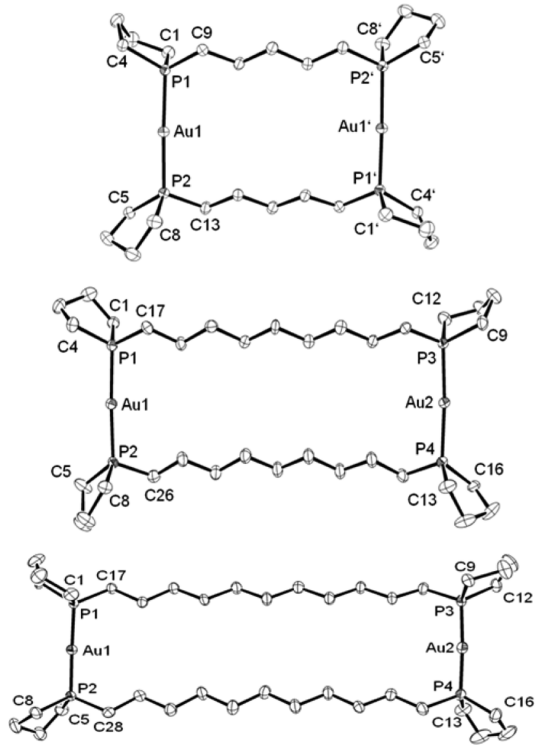


Figure 5. Molecular structures of **11** (top), **13** (middle), and **14** (bottom). Ellipsoids are drawn at the 50% probability level, and H atoms and BF_4^- groups are omitted for clarity.

aurophilic interactions even with weakly coordinating anions such as nitrate,[37] trifluoromethanesulfonate,[38] bis- and tris-(trichlorogermyl)aurate(I),[39] halides and perchlorates,[40] cyanoborohydride,[41] tetrafluoroborate,[42] and hexafluorophosphate.[43] Apparently, the widely used diphenyl-substituted bis-phosphines are sterically too demanding to allow a direct intermolecular aurophilic interaction between single monomers, even with weakly coordinating anions. On the other hand, gold(I) complexes such as $[Au_2\{\mu\text{-}Me_2P(CH_2)_nPMe_2\}_2]X_2$ (n = 1, 2; X = Cl, Br, I, ClO_4) show only an intramolecular aurophilic interaction.[40]

To the best of our knowledge, compound **12** is the first gold(I) macrocycle bearing only bis-phosphine ligands that forms a polymeric chain via aurophilic interactions in the solid state. Twisting of the backbone is necessary to decrease the steric interaction of the phospholane moieties and to allow aurophilic interaction and seems to be preferred with 1,7-bis(phospholano)heptane (**3c**).

CONCLUSION

A new class of highly flexible bis-phospholanes with long alkylene spacers (5–11 methylene groups) was prepared and shown to demonstrate unusual coordination behavior toward gold(I) which is highly dependent on backbone chain length. Ligands **3a,c,e,g** (odd number of carbon atoms in the alkylene spacer) formed macrocycles **4–7** in a one-step reaction with [AuCl(tht)] in excellent yield. Bis-phospholanes **3b,d,f** (even number of carbon atoms in the alkylene spacer) resulted in chains (**8**) or nanotubes (**9** and **10**; Scheme 2). Anion exchange of **4–7** with $AgBF_4$ gave isolated macrocycles (**11**, **13**, **14**) or the first bis-phosphine gold(I) chain based on aurophilic interactions (**12**) and demonstrated the importance of the counterion. The reported results are essential for a deeper

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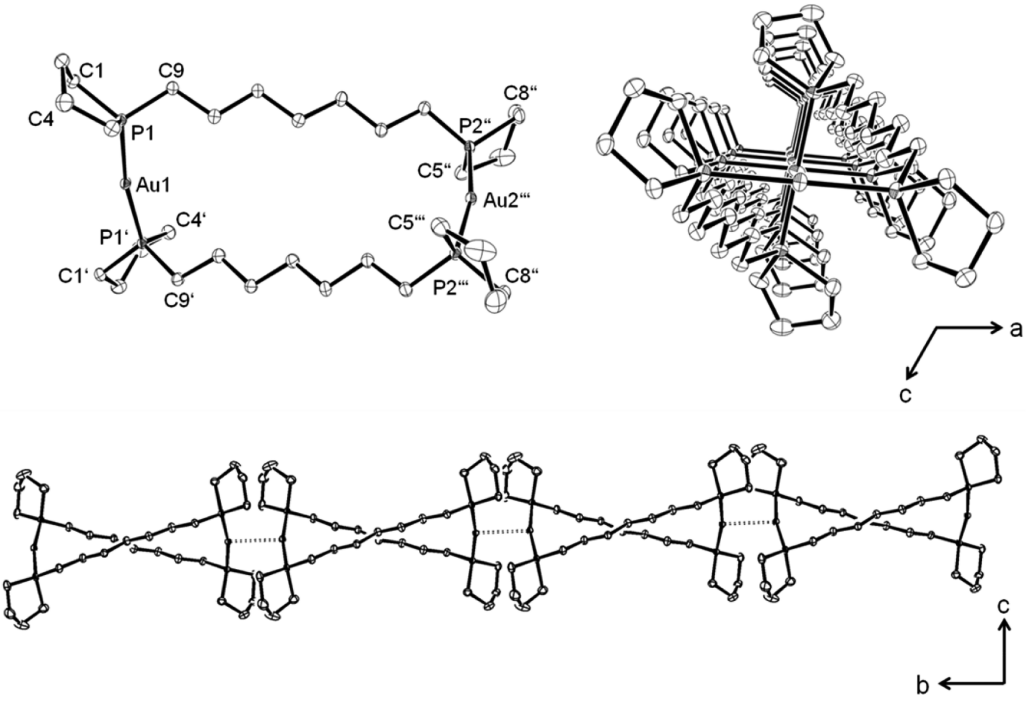

Figure 6. (top left) Monomeric unit of **12**. (top right) View along the *b* axis. (bottom) polymeric structure along the *b* axis in the solid state. Ellipsoids are drawn at the 50% probability level, and H atoms and BF_4^- groups are omitted for clarity.

Table 3. Selected Bond Lengths (pm) and Angles (deg) in 11−14[a]

	11	12	13	14
Au1−P1	231.02(8)	230.98(7)	229.3(1)	229.3(1)
Au1−P2	230.79(8)	231.16(7)	229.9(1)	229.2(1)
Au2−P3			230.4(1)	230.2(1)
Au2−P4			230.4(1)	230.2(1)
Au1···Au2		296.61(1)		
P1−Au1−P2	177.12(3)	169.62(3)	176.46(5)	173.77(4)
P3−Au2−P4		168.21(3)	174.94(6)	176.37(4)

[a]Omitted values are generated by symmetry.

understanding of the influence of the carbon-chain length of bis-phosphine ligands and the anions on aurophilic interactions in gold(I) complexes.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in a nitrogen atmosphere using standard Schlenk techniques[44] and anhydrous solvents. The latter were purified using an MB SPS-800 solvent purification system from MBRAUN or as mentioned in the literature.[45] 1-Phenylphospholane[46,47] and [AuCl(tht)][48] were prepared according to the literature. All other chemicals were used as purchased. NMR spectra were recorded at 298 K on a Bruker AVANCE DRX 400 spectrometer. The chemical shifts of ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR spectra are reported in parts per million at 400.12, 128.38, 162.02, and 100.63 MHz, respectively, and utilizing tetramethylsilane as an internal standard and referencing to the unified scale.[49] FTIR spectra were recorded on a Perkin-Elmer Spectrum 2000 FTIR spectrometer, scanning between 400 and 4000 cm^{-1}, by using KBr pellets. Mass spectra were recorded on an ESQUIRE 3000 plus spectrometer (ESI) or a Finnigan MAT 8200 spectrometer (EI). Elemental analyses were carried out with a Heraeus VARIO EL oven. The melting points were measured in sealed capillaries using a variable heater from Gallenkamp.

X-ray Crystallography and Data Collection. Data for compounds **4**−**14** were collected on an Oxford Diffraction CCD Xcalibur-S diffractometer (data reduction with CrysAlis Pro,[50] including the program SCALE 3 ABSPACK[51] for empirical absorption correction) using Mo Kα radiation (λ = 71.073 pm) and ω-scan rotation. The structures were solved with the SIR tool,[52] and the refinement of all non-hydrogen atoms was performed with SHELXL97.[53] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by constrained methods using the riding model. The refinement was carried out with the least-squares method on F^2. Final R indices were calculated as follows: $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$. The structure figures were drawn with the program ORTEP.[54] In **9**, disordered solvent molecules and counterions were removed by the SQUEEZE command.[55] CCDC 985575 (**4**), 985576 (**5**), 985577 (**6**), 985582 (**7**), 985579 (**8**), 985578 (**9**), 985584 (**10**), 985581 (**11**), 985580 (**12**), 985583 (**13**), 985585 (**14**) contain crystal structures of the compounds in this paper.

Synthesis Procedures. General Synthesis of 1a−g. Dibromoalkane (4.00 mmol) was added to a stirred solution of 1-phenylphospholane (8.00 mmol) in acetonitrile (30 mL). After the mixture was stirred for 2 days at 80 °C, volatile compounds were removed under vacuum. The resulting white solids (**1a**−**g**) were used without further purification.

*1,5-Bis(phenylphospholanium)pentane dibromide (**1a**):* yield 2.2 g (99%); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 50.4 ppm (s); ^{1}H NMR (CD_2Cl_2) δ 8.10 (m, 4H), 7.73 (m, 2H), 7.66 (m, 4H), 3.17 (m, 8H), 2.62 (m, 4H), 2.35 (m, 4H), 2.04 (m, 4H), 1.72 (m, 6H); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 134.2 (d, ^4J(C,P) = 2.8 Hz), 132.3 (d, ^2J(C,P) = 9.6 Hz), 130.1 (d, ^3J(C,P) = 12.1 Hz), 119.9 (d, ^1J(C,P) = 76.2 Hz), 29.8 (t, ^3J(C,P) = 16.8 Hz), 26.3 (d, ^2J(C,P) = 5.9 Hz), 22.9 (d, ^1J(C,P) = 51.2 Hz), 22.7 (d, ^1J(C,P) = 44.6 Hz), 20.7 (d, ^2J(C,P) = 4.0 Hz); IR (KBr disk) $\tilde{\nu}$ 2927 (s), 2361 (m), 1653 (s), 1635 (m), 1438 (w), 1405 (m), 1266 (m), 1120 (s), 1025 (m), 875 (w), 750 (m), 693 (m), 538 cm^{-1} (w); MS (ESI(+), MeOH) m/z 477.1 [M − Br]$^+$, 199.0 [M − 2Br]$^{2+}$; mp 167 °C. Anal. Calcd for $C_{25}H_{36}Br_2P_2$: C, 53.78; H, 6.50. Found: C, 53.72; H, 6.49.

*1,6-Bis(phenylphospholanium)hexane dibromide (**1b**):* yield 2.3 g (99%); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ 50.0 ppm (s); ^{1}H NMR (CD_2Cl_2)

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δ 7.93 (m, 4H), 7.66 (m, 2H), 7.60 (m, 4H), 3.02 (m, 8H), 2.52 (m, 4H), 2.31 (m, 4H), 1.99 (m, 4H), 1.54 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.2 (d, $^4J(C,P)$ = 2.8 Hz), 132.1 (d, $^2J(C,P)$ = 9.4 Hz), 130.0 (d, $^3J(C,P)$ = 12.0 Hz), 119.8 (d, $^1J(C,P)$ = 76.1 Hz), 28.0 (d, $^3J(C,P)$ = 16.8 Hz), 26.3 (d, $^2J(C,P)$ = 5.7 Hz), 23.0 (d, $^1J(C,P)$ = 41.9 Hz), 22.9 (d, $^1J(C,P)$ = 51.4 Hz), 21.1 (d, $^2J(C,P)$ = 4.4 Hz); IR (KBr disk) $\tilde{\nu}$ 3051 (w), 3022 (w), 2932 (m), 2863 (m), 1653 (w), 1436 (s), 1400 (m), 1262 (m), 1122 (s), 1023 (m), 872 (w), 804 (m), 742 (m), 689 (m), 518 cm^{-1} (w); MS (ESI(+), MeCN) m/z 491.1 $[M - Br]^+$, 206.0 $[M - 2Br]^{2+}$; mp 252 °C. Anal. Calcd for $C_{26}H_{38}Br_2P_2$: C, 54.56; H, 6.69. Found: C, 54.63; H, 6.65.

*1,7-Bis(phenylphospholanium)heptanes dibromide (**1c**):* yield 2.3 g (99%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.2 ppm (s); ^1H NMR (CD_2Cl_2) δ 8.01 (m, 4), 7.75 (m, 2H), 7.67 (m, 4H), 3.20−3.02 (m, 8H), 2.69−2.52 (m, 4H), 2.49−2.30 (m, 4H), 2.18−1.99 (m, 4H), 1.70−1.40 ppm (m, 10H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 131.8 (d, $^4J(C,P)$ = 2.8 Hz), 130.3 (d, $^2J(C,P)$ = 9.6 Hz), 128.9 (d, $^3J(C,P)$ = 11.3 Hz), 119.9 (d, $^1J(C,P)$ = 75.8 Hz), 31.4 (d, $^1J(C,P)$ = 41.7 Hz), 31.0 (d, $^3J(C,P)$ = 6.8 Hz), 29.2 (s), 27.5 (d, $^1J(C,P)$ = 64.6 Hz) 24.5 (d, $^2J(C,P)$ = 7.7 Hz), 22.6 ppm (d, $^2J(C,P)$ = 4.1 Hz); IR (KBr disk) $\tilde{\nu}$ 2925 (m), 2855 (m), 2367 (w), 1654 (w), 1636 (w), 1541 (m), 1216 (m), 1120 (m), 872 (w), 806 (m), 669 cm^{-1} (w); MS (ESI(+), MeCN) m/z 507.1 $[M - Br]^+$, 213.0 $[M - 2Br]^{2+}$; mp 218 °C. Anal. Calcd for $C_{27}H_{40}Br_2P_2$: C, 55.31; H, 6.88. Found: C, 55.36; H, 7.16.

*1,8-Bis(phenylphospholanium)octane dibromide (**1d**):* yield 2.4 g (99%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.2 ppm (s); ^1H NMR (CD_2Cl_2) δ 7.99 (m, 4H), 7.75 (m, 2H), 7.68 (m, 4H), 3.07 (m, 8H), 2.61 (m, 4H), 2.38 (m, 4H), 2.08 (m, 4H), 1.60 (m, 4H), 1.50 (m, 4H), 1.37 ppm (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.2 (d, $^4J(C,P)$ = 2.8 Hz), 132.1 (d, $^2J(C,P)$ = 9.4 Hz), 130.0 (d, $^3J(C,P)$ = 12.0 Hz), 119.7 (d, $^1J(C,P)$ = 76.0 Hz), 29.4 (d, $^3J(C,P)$ = 15.9 Hz), 27.4 (s), 26.2 (d, $^2J(C,P)$ = 5.8 Hz), 23.2 (d, $^1J(C,P)$ = 44.1 Hz), 22.9 (d, $^1J(C,P)$ = 51.3 Hz), 21.9 ppm (d, $^2J(C,P)$ = 4.7 Hz); IR (KBr disk) $\tilde{\nu}$ 3022 (w), 2958 (m), 2934 (m), 2906 (m), 2864 (m), 2358 (w), 1438 (m), 1263 (s), 1098 (s), 1021 (s), 878 (m), 803 (s), 696 (w), 508 (w), 477 cm^{-1} (w); MS (ESI(+), MeCN) m/z 519.1 $[M - Br]^+$, 220.0 $[M - 2Br]^{2+}$; mp 214 °C. Anal. Calcd for $C_{28}H_{42}Br_2P_2$: C, 56.01; H, 7.05. Found: C, 56.01; H, 6.63.

*1,9-Bis(phenylphospholanium)nonane dibromide (**1e**):* yield 2.4 g (99%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.2 ppm (s); ^1H NMR (CD_2Cl_2) δ 8.08 (m, 4H), 7.75 (m, 2H), 7.67 (m, 4H), 3.07 (m, 8H), 2.67 (m, 4H), 2.34 (m, 4H), 2.09 (m, 4H), 1.48 (m, 8H), 1.27 ppm (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.2 (d, $^4J(C,P)$ = 2.9 Hz), 132.3 (d, $^2J(C,P)$ = 9.4 Hz), 130.0 (d, $^3J(C,P)$ = 12.0 Hz), 119.7 (d, $^1J(C,P)$ = 76.1 Hz), 29.8 (d, $^3J(C,P)$ = 15.8 Hz), 28.2 (s), 28.1 (s), 26.2 (d, $^2J(C,P)$ = 5.8 Hz), 23.2 (d, $^1J(C,P)$ = 44.1 Hz), 22.9 (d, $^1J(C,P)$ = 51.2 Hz), 22.3 ppm (d, $^2J(C,P)$ = 4.6 Hz); IR (KBr disk) $\tilde{\nu}$ 3058 (w), 2928 (s), 2856 (m), 2362 (s), 2337 (m), 1632 (m), 1438 (m), 1261 (w), 1122 (s), 1025 (w), 875 (w), 751 (m), 691 (w), 669 cm^{-1} (w); MS (ESI(+), MeCN) m/z 533.1 $[M - Br]^+$, 227.0 $[M - 2Br]^{2+}$; mp 103 °C. Anal. Calcd for $C_{29}H_{44}Br_2P_2$: C, 56.69; H, 7.22. Found: C, 56.31; H, 7.28.

*1,10-Bis(phenylphospholanium)decane dibromide (**1f**):* yield 2.5 g (99%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.3 ppm (s); ^1H NMR (CD_2Cl_2) δ 8.02 (m, 4H), 7.76 (m, 2H), 7.68 (m, 4H), 3.08 (m, 8H), 2.64 (m, 4H), 2.37 (m, 4H), 2.10 (m, 4H), 1.48 (m, 8H), 1.28 ppm (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 134.3 (d, $^4J(C,P)$ = 2.9 Hz), 132.1 (d, $^2J(C,P)$ = 9.4 Hz), 130.0 (d, $^3J(C,P)$ = 12.0 Hz), 119.7 (d, $^1J(C,P)$ = 75.9 Hz), 29.8 (d, $^3J(C,P)$ = 15.8 Hz), 28.4 (s), 27.9 (s), 26.2 (d, $^2J(C,P)$ = 5.8 Hz), 23.2 (d, $^1J(C,P)$ = 44.2 Hz), 22.9 (d, $^1J(C,P)$ = 51.4 Hz), 22.3 ppm (d, $^2J(C,P)$ = 4.8 Hz); IR (KBr disk) $\tilde{\nu}$ 3055 (w), 3026 (m), 2931 (s), 2855 (s), 1589 (w), 1466 (m), 1438 (s), 1399 (m), 1266 (w), 1123 (s, CP), 1023 (w), 881 (m), 751 (s), 737 (s), 725 (s), 694 (s), 518 (m), 447 cm^{-1} (m); MS (ESI(+), MeCN) m/z 547.1 $[M - Br]^+$, 234.0 $[M - 2Br]^{2+}$; mp 106 °C. Anal. Calcd for $C_{30}H_{46}Br_2P_2$: C, 57.34; H, 7.38. Found: C, 58.01; H, 7.52.

*1,11-Bis(phenylphospholanium)undecane dibromide (**1g**):* yield 2.6 g (99%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 50.1 ppm (s); ^1H NMR (D_2O) δ 8.03 (m, 4H), 7.91 (m, 2H), 7.83 (m, 4H), 2.87−2.67 (m, 12H), 2.42−2.20 (m, 8H), 1.68−1.40 (m, 8H), 1.33−1.10 ppm (10H); $^{13}C\{^1H\}$ NMR (D_2O) δ 134.4 (d, $^4J(C,P)$ = 3.0 Hz), 131.7 (d, $^2J(C,P)$ = 10.1 Hz), 130.0 (d, $^3J(C,P)$ = 12.0 Hz), 119.2 (d, $^1J(C,P)$ = 76.5 Hz), 29.5 (d, $^3J(C,P)$ = 15.1 Hz), 28.5 (s), 25.3 (s) 28.0 (s), 25.9 (d, $^2J(C,P)$ = 6.0 Hz), 22.2 (d, $^1J(C,P)$ = 45.3 Hz), 22.1 (d, $^1J(C,P)$ = 52.3 Hz), 21.8 ppm (d, $^2J(C,P)$ = 4.0 Hz); IR (KBr disk) $\tilde{\nu}$ 2924 (s), 1628 (s), 1522 (m), 1470 (m), 1440 (m), 1154 (w), 1024 (m), 800 (m), 754 (m), 696 cm^{-1} (m); MS (ESI(+), MeOH) m/z 561.3 $[M - Br]^+$, 241.1 $[M - 2Br]^{2+}$. Anal. Calcd for $C_{31}H_{48}Br_2P_2$: C, 57.77; H, 7.82. Found: C, 57.93; H, 7.76.

General Synthesis of 2a−g. The bis-phenylphospholanium salt **1a−g** (3.5 mmol) was dissolved in an aqueous sodium hydroxide solution (20%, 40 mL) and the mixture stirred for 20 h at 80 °C. The reaction mixture was extracted with chloroform (3 × 50 mL). The combined organic layers were washed with distilled water and brine and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the bis-phospholane oxides **2a−g** as white solids.

*1,5-Bis(1-phospholanooxide)pentane (**2a**):* yield 0.88 g (91%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 70.8 ppm (s); ^1H NMR ($CDCl_3$) δ 2.15−1.45 ppm (m, 26H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 32.1 (t, $^3J(C,P)$ = 13.1 Hz), 30.6 (d, $^1J(C,P)$ = 61.6 Hz), 27.0 (d, $^1J(C,P)$ = 65.0 Hz), 24.5 (d, $^2J(C,P)$ = 7.9 Hz), 21.9 (d, $^2J(C,P)$ = 4.0 Hz); IR (KBr disk) $\tilde{\nu}$ 2922 (m), 2863 (m), 1653 (w), 1636 (w), 1457 (w), 1405 (w), 1266 (m), 1165 (s), 1110 (m), 1060 (w), 1021 (w), 865 (m), 797 (w), 725 (w), 611 cm^{-1} (w); MS (EI) m/z (%) 276 $[M]^+$ (5), 173 $[M - C_4H_8OP]^+$ (95), 159 $[M - C_5H_{10}OP]^+$ (100), 131 $[C_6H_{12}OP]^+$ (40), 118 $[C_5H_{11}OP]^+$ (35), 103 $[C_4H_8OP]^+$ (60); mp 121 °C. Anal. Calcd for $C_{13}H_{26}O_2P_2$: C, 56.51; H, 9.49. Found: C, 55.78; H, 9.72.

*1,6-Bis(1-phospholanooxide)hexane (**2b**):* yield 0.90 g (89%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 70.8 ppm (s); ^1H NMR ($CDCl_3$) δ 2.19−1.28 ppm (m, 28H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.8 (d, $^1J(C,P)$ = 63.7 Hz), 30.5 (d, $^3J(C,P)$ = 12.8 Hz), 27.0 (d, $^1J(C,P)$ = 64.8 Hz), 24.5 (d, $^2J(C,P)$ = 7.7 Hz), 22.0 (d, $^2J(C,P)$ = 3.8 Hz); IR (KBr disk) $\tilde{\nu}$ 2947 (m), 2914 (m), 2866 (m), 2848 (m), 1636 (w), 1474 (w), 1405 (w), 1268 (m), 1169 (s), 857 (w), 786 (m), 700 (m), 516 cm^{-1} (m); MS (EI) m/z (%) 290 $[M]^+$ (15), 187 $[M - C_4H_8OP]^+$ (100), 118 $[C_5H_{11}OP]^+$ (95), 104 $[C_4H_9OP]^+$ (90); mp 131 °C. Anal. Calcd for $C_{14}H_{28}O_2P_2$: C, 57.92; H, 9.72. Found: C, 57.39; H, 9.85.

*1,7-Bis(1-phospholanooxide)heptane (**2c**):* yield 1.05 g (98%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 71.3 ppm (s); ^1H NMR ($CDCl_3$) δ 2.25−1.92 ppm (m, 6H), 1.90−1.55 (m, 18H), 1.51−1.32 ppm (m, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.9 (d, $^1J(C,P)$ = 48.0 Hz), 30.6 (d, $^3J(C,P)$ = 13.2 Hz), 28.7 (s), 27.0 (d, $^1J(C,P)$ = 64.7 Hz), 24.5 (d, $^2J(C,P)$ = 7.4 Hz), 22.1 (d, $^2J(C,P)$ = 2.7 Hz); IR (KBr disk) $\tilde{\nu}$ 2924 (m), 2854 (m), 1409 (w), 1267 (m), 1157 (s), 863 (w), 719 (w), 711 (w), 513 cm^{-1} (w); MS (EI) m/z (%) 304 $[M]^+$ (22), 187 $[M - C_5H_{10}OP]^+$ (99), 173 $[M - C_6H_{12}OP]^+$ (100), 131 $[M - C_7H_{14}OP]^+$ (76), 103 $[C_4H_9OP]^+$ (88); mp 102 °C. Anal. Calcd for $C_{15}H_{30}O_2P_2$: C, 59.15; H, 9.94. Found: C, 58.58; H, 9.61.

*1,8-Bis(1-phospholanooxide)octane (**2d**):* yield 0.97 g (87%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 70.9 ppm (s); ^1H NMR ($CDCl_3$) δ 2.10−1.27 ppm (m, 32H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K) δ 30.9 (d, $^1J(C,P)$ = 61.8 Hz), 30.8 (d, $^3J(C,P)$ = 13.4 Hz), 28.8 (s), 26.9 (d, $^1J(C,P)$ = 64.7 Hz), 24.5 (d, $^2J(C,P)$ = 7.7 Hz), 22.1 (d, $^2J(C,P)$ = 3.9 Hz); IR (KBr disk) $\tilde{\nu}$ 2947 (m), 2930 (m), 2912 (m), 2848 (m), 1636 (w), 1474 (w), 1405 (w), 1268 (m), 1169 (s), 1118 (w), 1012 (w), 877 (w), 864 (m), 773 (w), 701 (m), 514 cm^{-1} (m); MS (EI) m/z (%) 318 $[M]^+$ (10), 215 $[M - C_4H_8OP]^+$ (100), 201 $[M - C_5H_{10}OP]^+$ (65), 187 $[M - C_6H_{12}OP]^+$ (30), 131 $[C_6H_{12}OP]^+$ (25), 103 $[C_4H_9OP]^+$; mp 137 °C. Anal. Calcd for $C_{16}H_{32}O_2P_2$: C, 60.36; H, 10.13. Found: C, 59.90; H, 9.65.

*1,9-Bis(1-phospholanooxide)nonane (**2e**):* yield 1.1 g (93%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 71.1 ppm (s); ^1H NMR ($CDCl_3$) δ 2.12−1.21 ppm (m, 34H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.0 (d, $^3J(C,P)$ = 13.5 Hz), 30.9 (d, $^1J(C,P)$ = 61.8 Hz), 29.1 (s), 27.0 (d, $^1J(C,P)$ = 64.7 Hz), 24.6 (d, $^2J(C,P)$ = 7.7 Hz), 22.2 (d, $^2J(C,P)$ = 4.1 Hz); IR (KBr disk) $\tilde{\nu}$ 2928 (s), 2850 (s), 1635 (m), 1405 (m), 1268 (m), 1169 (s), 860 (w), 726 (w), 700 (w), 483 cm^{-1} (w); MS (EI) m/z (%) 332 $[M]^+$ (10), 229 $[M - C_4H_8OP]^+$ (100), 215 $[M - C_5H_{10}OP]^+$ (100),

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201 [M − $C_6H_{12}OP$]$^+$ (25), 173 [$C_9H_{18}OP$]$^+$ (20), 159 [$C_8H_{16}OP$]$^+$ (30), 118 [$C_5H_{10}OP$]$^+$ (60), 104 [C_4H_8OP]$^+$ (50); MS (ESI(+), $CHCl_3$, MeOH) *m/z* 333 [M + H]$^+$; mp 101 °C. Anal. Calcd for $C_{17}H_{34}O_2P_2$: C, 61.43; H, 10.31. Found: C, 61.31; H, 9.90.

*1,10-Bis(1-phospholanooxide)decane (**2f**):* yield 1.1 g (87%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 70.9 ppm (s); ^1H NMR ($CDCl_3$) δ 2.08−1.28 ppm (m, 36H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.0 (d, ^3J(C,P) = 13.6 Hz), 30.9 (d, ^1J(C,P) = 61.9 Hz), 29.3 (s), 29.1 (s), 27.0 (d, ^1J(C,P) = 64.7 Hz), 24.6 (d, ^2J(C,P) = 7.7 Hz), 22.2 ppm (d, ^2J(C,P) = 4.0 Hz); IR (KBr disk) $\tilde{\nu}$ 2946 (m), 2918 (m), 2848 (m), 1635 (m), 1474 (w), 1404 (w), 1266 (w), 1168 (s), 1118 (w), 1022 (w), 883 (w), 782 (w), 701 (w), 520 cm^{-1} (w); MS (EI) *m/z* (%) 346 [M]$^+$ (15), 243 [M − C_4H_8OP]$^+$ (95), 229 [M − $C_5H_{10}OP$]$^+$ (100), 118 [$C_5H_{11}OP$]$^+$ (100), 104 [C_4H_9OP]$^+$ (70), mp 141 °C. Anal. Calcd for $C_{18}H_{36}O_2P_2$: C, 62.41; H, 10.47. Found: C, 62.21; H, 10.46.

*1,11-Bis(1-phospholanooxide)undecane (**2g**):* yield 1.2 g (98%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 70.8 ppm (s); ^1H NMR ($CDCl_3$) δ 2.02−1.13 ppm (m, 38H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.9 (d, ^3J(C,P) = 13.4 Hz), 30.9 (d, ^1J(C,P) = 61.8 Hz), 29.4 (s), 29.2 (s), 29.1 (s), 27.0 (d, ^1J(C,P) = 64.4 Hz), 24.5 (d, ^2J(C,P) = 8.0 Hz), 22.1 ppm (d, ^2J(C,P) = 4.0 Hz); IR (KBr disk) $\tilde{\nu}$ 2918 (s), 2894 (s), 1268 (m), 1168 (s), 1118 (m), 1059 (m), 865 (m), 724 (m), 700 cm^{-1} (m); MS (EI) *m/z* (%) 360 [M]$^+$ (16), 257 [M − C_4H_8OP]$^+$ (100), 243 [M − $C_5H_{10}OP$]$^+$ (75), 118 [$C_5H_{11}OP$]$^+$ (44); mp 92 °C. Anal. Calcd for $C_{19}H_{38}O_2P_2$: C, 63.31; H, 10.63. Found: C, 63.24; H, 10.78.

General Synthesis of 3a−g. **2a−g** (1.0 mmol) was added to a suspension of lithium aluminum hydride (0.057 mg; 1.5 mmol), and trimethylsilyl chloride (0.16 mg; 1.5 mmol) in thf (20 mL) and stirred for 10 h at room temperature. Degassed methanol was added at 0 °C, volatile compounds were removed under vacuum, and the residue was extracted with *n*-hexane (3 × 10 mL). The *n*-hexane was removed, and the crude product was purified by bulb-to-bulb distillation.

*1,5-Bis(1-phospholano)pentane (**3a**):* yield 0.2 g (82%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.8 ppm (s); ^1H NMR ($CDCl_3$) δ 1.85−1.56 (m, 12H), 1.51−1.18 (m, 14H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 32.8 (t, ^3J(C,P) = 11.6 Hz), 28.8 (d, ^2J(C,P) = 15.5 Hz), 27.8 (d, ^2J(C,P) = 3.8 Hz), 26.6 (d, ^1J(C,P) = 15.4 Hz), 25.9 ppm (d, ^1J(C,P) = 11.4 Hz); IR (KBr disk) $\tilde{\nu}$ 2927 (s), 2857 (s), 1446 (m), 1417 (m), 1302 (w), 1263 (w), 1181 (w), 1110 (m), 1027 (w), 834 (w), 740 (m, CH), 697 (m), 668 (w), 514 cm^{-1} (w); MS (EI) *m/z* (%) 244 [M]$^+$ (5), 157 [M − C_4H_8P]$^+$ (100), 87 [C_4H_8P]$^+$ (10). Anal. Calcd for $C_{13}H_{26}P_2$: C, 63.91; H, 10.73. Found: C, 64.03; H, 10.64.

*1,6-Bis(1-phospholano)hexane (**3b**):* yield 0.2 g (77%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.9 ppm (s); ^1H NMR ($CDCl_3$) δ 1.91−1.13 (m, 28H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 30.9 (d, ^3J(C,P) = 11.6 Hz), 28.8 (d, ^2J(C,P) = 15.3 Hz), 27.7 (d, ^2J(C,P) = 3.8 Hz), 26.6 (d, ^1J(C,P) = 15.1 Hz), 25.8 ppm (d, ^1J(C,P) = 11.2 Hz); IR (KBr disk) $\tilde{\nu}$ 2927 (s), 2856 (m), 2360 (m), 2342 (m), 1700 (w), 1559 (w), 1457 (w), 1419 (w), 1262 (m), 1108 (s), 1023 (s), 803 (m), 669 (w), 459 cm^{-1} (w); MS (EI) *m/z* (%) 258 [M]$^+$ (10), 171 [M − C_4H_8P]$^+$ (100), 87 [C_4H_8P]$^+$ (20); mp 47 °C. Anal. Calcd for $C_{14}H_{28}P_2$: C, 65.09; H, 10.93. Found: C, 65.10; H, 10.75.

*1,7-Bis(1-phospholano)heptane (**3c**):* yield 0.22 g (81%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.9 ppm (s); ^1H NMR ($CDCl_3$) δ 1.78−1.52 (m, 12H), 1.42−1.15 ppm (m, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.1 (d, ^3J(C,P) = 11.5 Hz), 29.1 (s), 28.9 (d, ^2J(C,P) = 15.6 Hz), 27.7 (d, ^2J(C,P) = 3.7 Hz), 26.8 (d, ^1J(C,P) = 15.4 Hz), 25.9 ppm (d, ^1J(C,P) = 11.5 Hz); IR (KBr disk) $\tilde{\nu}$ 2854 (s), 1459 (m), 1448 (m), 1301 (m), 1258 (m), 1110 (m), 1059 (m), 950 (m), 869 (m), 836 (m), 800 (m), 713 (m), 670 (m), 654 cm^{-1} (m); MS (EI) *m/z* (%) 272 [M]$^+$ (10), 185 [M − C_4H_8P]$^+$ (100), 174 [M − C_7H_{14}]$^+$ (68). Anal. Calcd for $C_{15}H_{30}P_2$: C, 66.18; H, 11.11. Found: C, 65.91; H, 11.16.

*1,8-Bis(1-phospholano)octane (**3d**):* yield 0.21 g (72%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.8 ppm (s); ^1H NMR ($CDCl_3$) δ 1.71−1.34 (m, 32H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.2 (d, ^3J(C,P) = 11.1 Hz), 29.3 (s), 28.9 (d, ^2J(C,P) = 15.1 Hz), 27.8 (d, ^2J(C,P) = 3.0 Hz), 26.8 (d, ^1J(C,P) = 15.1 Hz), 25.9 ppm (d, ^1J(C,P) = 11.1 Hz); IR (KBr disk) $\tilde{\nu}$ 2845 (s), 1471 (m), 1445 (m), 1410 (m), 1303 (m), 1255 (m), 1170 (w), 1109 (m), 1069 (m), 977 (m), 865 (m), 844 (m), 770 (w), 732 (m), 648 (s), 509 (w), 459 cm^{-1} (w); MS (EI) *m/z* (%) 286 [M]$^+$ (20), 199 [M − C_4H_8P]$^+$ (80), 174 [M − $C_6H_{15}P$]$^+$ (100); mp 53 °C. Anal. Calcd for $C_{16}H_{32}P_2$: C, 67.11; H, 11.26. Found: C, 66.72; H, 10.91.

*1,9-Bis(1-phospholano)nonane (**3e**):* yield 0.25 g (83%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.8 ppm (s); ^1H NMR ($CDCl_3$) δ 1.82−1.52 (m, 12H), 1.46−1.11 (m, 22H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.2 (d, ^3J(C,P) = 11.6 Hz), 29.3 (s), 28.8 (d, ^2J(C,P) = 14.9 Hz), 27.7 (d, ^2J(C,P) = 3.7 Hz), 26.8 (d, ^1J(C,P) = 15.1 Hz), 25.8 ppm (d, ^1J(C,P) = 11.2 Hz); IR (KBr disk) $\tilde{\nu}$ 2906 (s), 2859 (s), 1462 (s), 1448 (s), 1415 (m), 1301 (m), 1256 (m), 1173 (w), 1110 (s), 1061 (m), 1028 (m), 836 (m), 714 (m), 669 (m), 655 (m), 511 (w), 470 cm^{-1} (w); MS (EI) *m/z* (%) 300 [M]$^+$ (10), 213 [M − C_4H_8P]$^+$ (75), 102 [$C_5H_{11}P$]$^+$ (100). Anal. Calcd for $C_{17}H_{34}P_2$: C, 67.97; H, 11.41. Found: C, 67.84; H, 11.39.

*1,10-Bis(1-phospholano)decane (**3f**):* yield 0.23 g (74%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.8 ppm (s); ^1H NMR ($CDCl_3$) δ 1.86−1.59 (m, 12H), 1.49−1.19 (m, 24H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.3 (d, ^3J(C,P) = 11.6 Hz), 29.5 (s), 29.4 (s), 28.9 (d, ^2J(C,P) = 14.6 Hz), 27.8 (d, ^2J(C,P) = 3.4 Hz), 26.8 (d, ^1J(C,P) = 14.9 Hz), 25.9 ppm (d, ^1J(C,P) = 10.6 Hz); IR (KBr disk) $\tilde{\nu}$ 2915 (s), 2848 (s), 1465 (w), 1262 (s), 1100 (s), 805 (s), 713 (w), 498 cm^{-1} (w); MS (EI) *m/z* (%) 314 [M]$^+$ (10), 227 [M − C_4H_8P]$^+$ (50), 174 [M − $C_8H_{13}P$]$^+$ (100), 157 [M − $C_9H_{18}P$]$^+$ (10), 102 [$C_5H_{11}P$]$^+$ (40); mp 58 °C. Anal. Calcd for $C_{18}H_{36}P_2$: C, 68.76; H, 11.54. Found: C, 68.56; H, 11.08.

*1,11-Bis(1-phospholano)undecane (**3g**):* yield 0.23 g (69%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −26.8 ppm (s); ^1H NMR ($CDCl_3$) δ 1.87−1.58 (m, 12H), 1.50−1.17 ppm (m, 26H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.3 (d, ^3J(C,P) = 12.0 Hz), 29.6 (s), 29.5 (s), 29.4 (s), 28.9 (d, ^2J(C,P) = 15.1 Hz), 27.8 (d, ^2J(C,P) = 3.0 Hz), 26.8 (d, ^1J(C,P) = 15.1 Hz), 25.9 ppm (d, ^1J(C,P) = 11.1 Hz); IR (KBr disk) $\tilde{\nu}$ 2929 (s), 2853 (s), 1173 (w), 1110 (m), 1027 (w). 909 (m), 837 (m), 730 cm^{-1} (m); MS (EI) *m/z* (%) 329 [M]$^+$ (9), 241 [M − C_4H_8P]$^+$ (42), 174 [M − $C_9H_{15}P$]$^+$ (83), 102 [$C_5H_{11}P$]$^+$ (100). Anal. Calcd for $C_{19}H_{38}P_2$: C, 69.48; H, 11.66. Found: C, 69.49; H, 11.71.

General Synthesis of 4−7. [AuCl(tht)] (0.160 g, 0.5 mmol) was added to a stirred solution of the bis-phospholane (**3a,c,e,g**) (0.5 mmol) in CH_2Cl_2 (10 mL). After the mixture was stirred for 1 h at room temperature, volatile compounds were removed under vacuum. The residue was dissolved in CH_2Cl_2 (1 mL), and the products precipitated as white solids by addition of *n*-hexane (20 mL). Suitable crystals for X-ray diffraction could be obtained from saturated dichloromethane−toluene solutions at room temperature as colorless prisms (**4**), needles (**5**, **6**) or plates (**7**).

*Bis[μ-1,5-bis(1-phospholano)pentane-κ^{2}P,P′]digold(I) dichloride (**4**):* yield 226 mg (95%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 37.2 ppm (s); ^1H NMR ($CDCl_3$) δ 2.51 (m, 8H), 2.05 (m, 8H), 1.82 (m, 24H), 1.61 ppm (m, 12H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 32.7 (br s), 28.6 (br s), 27.4 (br s), 26.9 (br s), 26.4 ppm (br s); IR (KBr disk) $\tilde{\nu}$ 2854 (s), 1637 (w), 1458 (w), 1408 (m), 1303 (w), 1260 (w), 1113 (m), 1078 (m), 1023 (m), 858 (m), 790 (w), 697 (w), 514 cm^{-1} (m); MS (ESI(+), MeOH) *m/z* 917.3 [M − Cl]$^+$, 685.3 [Au(**3a**)$_2$]$^+$; MS (ESI(−), MeOH) *m/z* 743.0 [Au_2Cl_3(**3a**)]$^-$; mp 199 °C. Anal. Calcd for $C_{26}H_{52}Au_2Cl_2P_4$: C, 32.75; H, 5.50. Found: C, 32.52; H, 5.62.

*Bis[μ-1,7-bis(1-phospholano)heptane-κ^{2}P,P′]digold(I) dichloride (**5**):* yield 240 mg (95%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 37.3 ppm (s); ^1H NMR (CD_2Cl_2) δ 2.39 (m, 8H), 2.01 (m, 8H), 1.85 (m, 16H), 1.76 (m, 8H), 1.62 (m, 8H), 1.45 (m, 8H), 1.35 ppm (m, 4H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 31.2 (br s), 29.9 (br s), 28.7 (br s), 27.1 (br s), 26.6 ppm (br s); IR (KBr disk) $\tilde{\nu}$ 2922 (s), 2853 (s), 1611 (w), 1466 (m), 1445 (m), 1405 (m), 1302 (w), 1261 (w), 1113 (m), 1082 (s), 1068 (m), 1025 (m), 950 (w), 877 (m), 717 (m), 701 (m), 497 cm^{-1} (m); MS (ESI(+), MeOH) *m/z* 973.1 [M − Cl]$^+$, 773.2 [Au(**3c**)$_2$ + MeOH]$^+$, 469.1 [Au(**3c**)]$^+$; mp 151 °C. Anal. Calcd for $C_{30}H_{60}Au_2Cl_2P_4$: C, 35.69; H, 5.99. Found: C, 35.98; H, 6.22.

*Bis[μ-1,9-bis(1-phospholano)nonane-κ^{2}P,P′]digold(I) dichloride (**6**):* yield 240 mg (90%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 36.3 ppm (s); ^1H NMR (CD_2Cl_2) δ 2.52 (m, 8H), 2.06 (m, 8H), 1.84 (m, 20H), 1.76 (m, 8H), 1.62 (m, 8H), 1.31 ppm (m, 16H); $^{13}C\{^1H\}$ NMR

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(CD_2Cl_2) δ 31.6 (s), 31.0 (s), 30.3 (br s), 28.8 (br s), 28.1 (br s), 26.8 (s), 26.2 ppm (br s); IR (KBr disk) $\tilde{\nu}$ 2919 (s), 2859 (s), 1625 (w), 1467 (m), 1445 (m), 1406 (m), 1302 (w), 1260 (m), 1112 (m), 1073 (s), 1025 (m), 916 (w), 860 (m), 790 (w), 718 (m), 698 (m), 514 (m), 492 cm^{-1} (m); MS (ESI(+), MeOH, $CHCl_3$): m/z 1029.1 [M − Cl]$^+$, 497.1 [Au(**3e**)]$^+$; mp 94 °C. Anal. Calcd for $C_{34}H_{68}Au_2Cl_2P_4$: C, 38.32; H, 6.43. Found: C, 37.71; H, 6.40.

*Bis[μ-1,11-bis(1-phospholano)undecane-κ^{2}P,P′]digold(I) dichloride (**7**):* yield 256 mg (95%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 37.1 ppm (s); ^1H NMR (CD_2Cl_2) δ 3.00−2.60 (m, 4H), 2.55−2.25 (m, 8H), 2.20−1.72 (m, 28H), 1.72−1.22 ppm (m, 36H); IR (KBr disk) $\tilde{\nu}$ 2922 (s), 2851 (s), 1631 (w), 1447 (m), 1109 (m), 1056 (s), 853 (w), 800 (w), 715 (m), 688 cm^{-1} (m); MS (ESI(+), MeOH, CH_2Cl_2): m/z 1085.4 [M − Cl]$^+$, 525.3 [Au(**3g**)]$^+$; mp 127 °C. Anal. Calcd for $C_{38}H_{76}Au_2Cl_2P_4$: C, 40.69; H, 6.83. Found: C, 40.51; H, 6.93.

General Synthesis of 8−10. [AuCl(tht)] (96 mg; 0.30 mmol) was added to the bis-phospholane **3b,d,f** (0.15 mmol) in dichloromethane (10 mL). After the mixture was stirred for 2 h at room temperature, volatile compounds were removed under vacuum. Suitable crystals for X-ray diffraction could be obtained from saturated dichloromethane−toluene solutions at room temperature as colorless needles.

*[μ-1,6-Bis(1-phospholano)hexane-κ^{2}P,P′]digold(I) dichloride (**8**):* yield 103 mg (95%); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 23.5 ppm (s); ^1H NMR ($CDCl_3$) δ 2.19 (m, 4H), 1.94 (m, 10H), 1.80 (m, 4H), 1.61 ppm (m, 10H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 29.7 (s), 27.9 (d, J(C,P) = 33.4 Hz), 26.4 (bs), 26.3 (d, J(C,P) = 37.4 Hz), 25.5 ppm (s); IR (KBr disk) $\tilde{\nu}$ 2925 (s), 2853 (m), 1637 (w), 1446 (m), 1410 (m), 1304 (w), 1260 (w), 1111 (m), 1026 (m), 855 (m), 702 (s), 517 cm^{-1} (w); MS (ESI(+), MeOH) m/z 455.2 [Au(**3b**)]$^+$; MS (ESI(−), MeOH) m/z 757.1 [M + Cl]$^-$; mp 237 °C. Anal. Calcd for $C_{14}H_{28}Au_2Cl_2P_2$: C, 23.25; H, 3.90. Found: C, 22.99; H, 3.93.

*[μ-1,8-Bis(1-phospholano)octane-κ^{2}P,P′]digold(I) dichloride (**9**):* yield 107 mg (95%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 24.6 ppm (s); ^1H NMR (CD_2Cl_2) δ 2.17 (m, 4H), 1.92 (m, 12H), 1.77 (m, 4H), 1.63 (m, 4H), 1.46 (m, 4H), 1.24 ppm (m, 4H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 30.3 (d, J(C,P) = 14.5 Hz), 28.7 (s), 28.2 (d, J(C,P) = 33.4 Hz), 26.4 (s), 26.0 ppm (d, J(C,P) = 10.0 Hz); IR (KBr disk) $\tilde{\nu}$ 2922 (s), 2850 (m), 1636 (m), 1464 (w), 1446 (w), 1413 (w), 1262 (s), 1085 (s), 1027 (s), 856 (m), 804 (s), 715 (w), 516 (w), 459 cm^{-1} (w); MS (ESI(+), CH_2Cl_2, MeCN) m/z 483.3 [Au(**3d**)]$^+$; MS (ESI(−), MeOH) m/z 785.1 [Au_2Cl_3(**3d**)]$^-$; mp 208 °C. Anal. Calcd for $C_{16}H_{32}Au_2Cl_2P_2$: C, 25.58; H, 4.29. Found: C, 25.36; H, 4.47.

*[μ-1,10-Bis(1-phospholano)decane-κ^{2}P,P′]digold(I) dichloride (**10**):* yield 105 mg (90%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 24.5 ppm (s); ^1H NMR (CD_2Cl_2) δ 2.14 (m, 4H), 1.88 (m, 12H), 1.74 (m, 4H), 1.55 (m, 4H), 1.38 (m, 4H), 1.22 ppm (m, 8H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 31.4 (d, J(C,P) = 78.8 Hz), 30.5 (d, J(C,P) = 14.6 Hz), 28.9 (d, J(C,P) = 8.4 Hz), 28.2 (d, J(C,P) = 33.2 Hz), 26.5 (s), 26.4 (s), 26.1 ppm (d, J(C,P) = 11.6 Hz); IR (KBr disk) $\tilde{\nu}$ 2921 (s), 2849 (s), 1637 (w), 1461 (s), 1445 (m), 1411 (s), 1304 (w), 1260 (m), 1115 (s), 1068 (m), 1027 (m), 858 (m), 806 (m), 1072 (m), 858 (m), 717 (m), 529 (m), 517 cm^{-1} (w); MS (ESI(+), CH_2Cl_2, MeOH) m/z 511.1 [Au(**3f**)]$^+$; mp 215 °C. Anal. Calcd for $C_{18}H_{36}Au_2Cl_2P_2$: C, 27.74; H, 4.66. Found: C, 28.50; H, 4.99.

1:2 Reaction (Au:L) of [AuCl(tht)] with 3g. [AuCl(tht)] (48 mg; 0.15 mmol) was added to the bis-phospholane **3g** (98.4 mg 0.3 mmol) in dichloromethane (10 mL). After the mixture was stirred for 2 h at room temperature, all volatile compounds were removed under vacuum. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 34.4 (s); MS (ESI(+), CH_2Cl_2, MeCN) m/z 525.2 [Au(**3g**)]$^+$.

General Synthesis of 11−14. $AgBF_4$ (58.4 mg; 0.30 mmol) was added to **4−7** (0.15 mmol) in dichloromethane (10 mL). After the mixture was stirred for 1 h at room temperature, AgCl was filtered off and all volatile compounds were removed under vacuum. The obtained solid was dissolved in dichloromethane (1 mL) and the product obtained by the addition of *n*-hexane (20 mL). Suitable crystals for X-ray diffraction could be obtained from saturated dichloromethane−toluene or dichloromethane−*n*-hexane solutions at room temperature as colorless prisms (**11**, **12**, **14**) or plates (**13**).

*Bis[μ-1,5-bis(1-phospholano)pentane-κ^{2}P,P′]digold bis(tetrafluoroborate) (**11**):* yield 67 mg (85%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.7 ppm (s); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ −1.2 ppm (s); ^1H NMR (CD_2Cl_2) δ 2.19 (m, 8H), 1.94 (m, 32H), 1.66 (m, 12H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 32.5 (t, J(C,P) = 8.2 Hz), 27.9 (t, J(C,P) = 15.6 Hz), 27.2 (s), 26.7 (s), 25.7 ppm (t, J(C,P) = 17.2 Hz); $^{13}C\{^1H, ^{31}P\}$ NMR (CD_2Cl_2) δ 32.5 (s), 27.9 (s), 27.2 (s), 26.7 (s), 25.7 ppm (s); IR (KBr disk) $\tilde{\nu}$ 2939 (s), 2858 (s), 1447 (m), 1420 (m), 1408 (m), 1262 (m), 1212 (w), 1048 (s), 857 (m), 803 (m), 721 (m), 702 (m), 671 (w), 519 (m), 497 cm^{-1} (m); MS (ESI(+), CH_2Cl_2, MeCN) m/z 969.3 [M − BF_4]$^+$, 441.1 [Au(**3a**)]$^+$; mp 269 °C. Anal. Calcd for $C_{26}H_{52}Au_2B_2F_8P_4$: C, 29.57; H, 4.96. Found: C, 29.04; H, 5.32.

*Bis[μ-1,7-bis(1-phospholano)heptane-κ^{2}P,P′]digold(I) bis(tetrafluoroborate) (**12**):* yield 71 mg (85%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.2 ppm (s); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ −1.2 ppm (s); ^1H NMR (CD_2Cl_2) δ 2.20 (m, 8H), 1.98 (m, 32H), 1.65 (m, 8H), 1.49 (m, 8H), 1.38 ppm (m, 4H); $^{13}C\{^1H, ^{31}P\}$ NMR (CD_2Cl_2) δ 30.9 (br s), 29.5 (br s), 28.0 (br s), 27.0 (br s), 26.7 (br s), 25.8 ppm (br s); IR (KBr disk) $\tilde{\nu}$ 2925 (s), 2888 (s), 2861 (s), 1467 (s), 1444 (m), 1413 (s), 1318 (w), 1302 (w), 1282 (m), 1254 (w), 1183 (m), 1028 (s), 951 (s), 854 (s), 727 (s), 697 (m), 519 (s), 501 cm^{-1} (m); MS (ESI(+), CH_2Cl_2, MeCN) m/z 1025.3 [M − BF_4]$^+$, 469.2 [Au(**3c**)]$^+$; mp 219 °C. Anal. Calcd for $C_{30}H_{60}Au_2B_2F_8P_4$: C, 32.40; H, 5.44. Found: C, 32.53; H, 5.47.

*Bis[μ-1,9-bis(1-phospholano)nonan-κ^{2}P,P′]digold bis(tetrafluoroborate) (**13**):* compound **13** could not be isolated in pure form and was, therefore, only characterized by $^{31}P\{^1H\}$, $^{11}B\{^1H\}$ NMR, and ESI-MS; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 40.4 ppm (s); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ −1.1 ppm (s); MS (ESI(+), MeOH) m/z 1081.5 [M − BF_4]$^+$.

*Bis[μ-1,11-bis(1-phospholano)undecane-κ^{2}P,P′]digold(I) bis(tetrafluoroborate) (**14**):* $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 39.4 ppm (s); $^{11}B\{^1H\}$ NMR (CD_2Cl_2) δ −1.2 ppm (s), ^1H NMR (CD_2Cl_2) δ 2.30−2.14 (m, 8H), 2.08−1.81 (m, 32H), 1.68−1.20 ppm (m, 36H); IR (KBr disk) $\tilde{\nu}$ 2919 (s), 2850 (s), 1468 (m), 1447 (m), 1409 (m), 1305 (w), 1259 (w), 1083 (s), 949 (w), 858 (m), 757 (w), 721 (m), 699 (s) 520 cm^{-1} (m), MS (ESI(+), CH_2Cl_2, MeCN) m/z 1137.3 [M − BF_4]$^+$, 525.2 [Au(**3g**)]$^+$; mp 201 °C. Anal. Calcd $C_{40}H_{80}Au_2B_2Cl_4F_8P_4$: C, 34.46; H, 5.57. Found: C, 34.95; H, 5.64.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures, tables, and CIF files giving X-ray crystallographic details and ^1H, ^{11}B, ^{13}C, and ^{31}P NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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