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Gold and platinum benzenehexathiolate complexes as large templates for the synthesis of 12-coordinate polyphosphine macrocycles

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Abstract

A general strategy for the synthesis of large-ring, poly-donor macrocycles using multi-metal ion templates is outlined. This strategy is illustrated in the design and synthesis of the hexanuclear (divinyl)(phenyl)phosphine gold complex of benzenehexathiolate, $\{[(C_2H_3)_2(Ph)P]Au\}_6(C_6S_6)$ (**1**), which undergoes macrocycle formation upon reaction with $PhPH_2$ in the presence of AIBN (Scheme 1). NMR spectra (^1H and ^{31}P) and elemental analyses indicate that the resulting macrocycle is a 36-membered ring containing 12 phosphorus donors, six of which are coordinated to the six Au atoms in the $Au_6(C_6S_6)$ core. A series of tri-platinum complexes, $[(P^{\frown}P)Pt]_3(C_6S_6)$ (**16**–**19**), where $(P^{\frown}P)$ is a bidentate phosphine ligand, with three $(P^{\frown}P)Pt^{II}$ units coordinated to a $C_6S_6^{6-}$ core, were also prepared as models for templated formation of other poly-phosphorus macrocycles.

Keywords: Benzenehexathiolate complexes; Templated synthesis; Phosphine macrocycle; Gold complexes; Platinum complexes

1. Introduction

Since Pederson's [1] discovery of crown ethers in 1967, much research has been dedicated to the development of other cyclic ligands with cation-specific binding abilities. Through the years exceedingly complex macrocycles have been prepared, which include donor atoms other than oxygen; these include nitrogen, sulfur, phosphorus and arsenic [2–8].

Generally, methods for the preparations of large ring compounds (containing more than six heteroatoms) are highly inefficient with the success depending strongly on the preorganization of reactants prior to macrocycle assembly. Preorganization is often accomplished by using metal ions as templates [9,10]. In many cases, the size of the metal ion template controls the number of heteroatoms and size of the resulting macrocycle [11–17]. Since Cs^+ is the largest non-radioactive metal ion, the size of macrocycles that can be prepared using metal ion templates is limited by the size of this metal ion [18,19].

In this paper, we initiate studies of the design of templates containing several metal ions that will permit the synthesis of much larger macrocycles. Although many designs for such templates can be conceived, Fig. 1 illustrates a template that is based on a benzene core with donor atoms (X) that bind to six metal ions (M). These metal ions serve as sites at which macrocycle precursors with donor groups (A) can be organized prior to linking to give the macrocycle in Fig. 1. As illustrated in this Figure, the resulting macrocycle has 12 donor atoms (A); however, one can imagine that different numbers of donor atoms (A) could be incorporated depending on the coordination numbers and geometries of the metal ions (M). In principle, the donor atoms (A) could be O, S, N, P and other typical ligand atoms.

Although there are numerous reports of macrocycles in the literature [2–8], comparatively few phosphine macrocycles are among them [20–44], and there are no examples of phosphacrowns that have more than four

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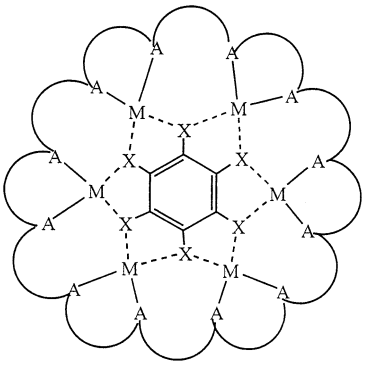


M = metal ion
X = donor group (O, S, N, P) in template.

Fig. 1. Generalized strategy for the synthesis of large macrocycles around a template consisting of six metal ions (M).

phosphorus atoms in the ring. This is surprising since acyclic phosphines form numerous transition metal complexes, many of which are homogeneous catalysts [45–48]. Complexes with multidentate phosphacrowns containing more than four phosphorus atoms might be expected to give complexes with unusual structures and catalytic activities. Several of the known tri- and tetradentate phosphacrowns were prepared using transition metal templates to control the synthetic outcome [20,21,25,28,31,32]. However, as noted above, the use of a single metal ion template limits the size of the phosphine macrocycle that can be synthesized.

Our approach to the synthesis of polyphosphine ligands uses benzenehexathiolate ($C_6S_6^{6-}$) as the arene core of the multi-metal ion template in the structure in Fig. 1. Schmidbaur and co-workers [49] showed that $C_6S_6^{6-}$ forms a 'golden wheel' (Fig. 2) when 6 equiv. of $(Ph_3P)AuCl$ react with benzenehexathiol and triethylamine in chloroform. The X-ray-determined structure of the hexanuclear (triphenylphosphine)gold benzenehexathiolate compound, $[(Ph_3P)Au]_6(C_6S_6)$, shows that the arene carbon, sulfur, Au, and P atoms are nearly co-planar with a slight puckering of the sulfur and gold hexagons.

For the synthesis of 12-coordinate phosphine macrocycles, our approach was to make the (divinyl)(phenyl)phosphine analog of the 'golden wheel' and then link the neighboring vinyl groups with $PhPH_2$ as shown in Scheme 1. Free-radical addition of P–H bonds across alkenes has been used to prepare several tri- [25–27] and tetradentate [32] phosphine macrocycles; Norman and co-workers first used this approach to prepare *fac*-$(CO)_3Mo(PHC_3H_6)_3$ [25] by heating *fac*-$(CO)_3Mo(H_2PCH_2CH{=}CH_2)_3$ in the presence of AIBN.

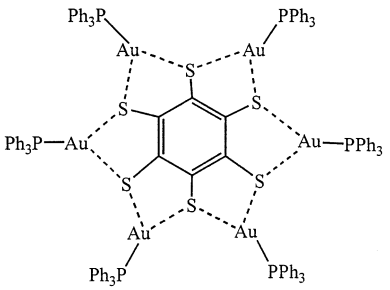


Fig. 2. Schmidbaur's 'golden wheel' [49].

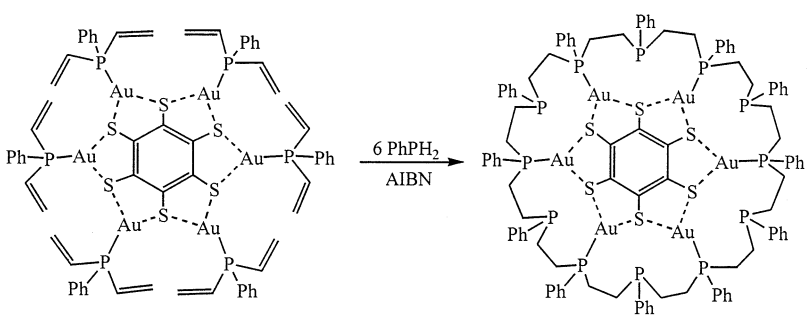
In our second approach to the synthesis of a polyphosphine macrocycle, we again made use of the $C_6S_6^{6-}$ core, but incorporated three square-planar Pt(II) ions, which also bind to bidentate phosphine ligands with P–H groups at each phosphorus donor (Scheme 2). Molecular models indicate that these P–H groups, when reacted with (divinyl)(phenyl)phosphine, $(C_2H_3)_2(Ph)P$, using an AIBN catalyst [50], should give a stable 30-atom macrocycle ring with nine phosphorus donor groups.

In this paper, we describe syntheses of the Au and Pt templates $\{[(C_2H_3)_2(Ph)P]Au\}_6(C_6S_6)$ (**1**) and $[(P^{\frown}P)Pt]_3(C_6S_6)$ and the use of **1** in the subsequent cyclization reaction described in Scheme 1.

2. Experimental

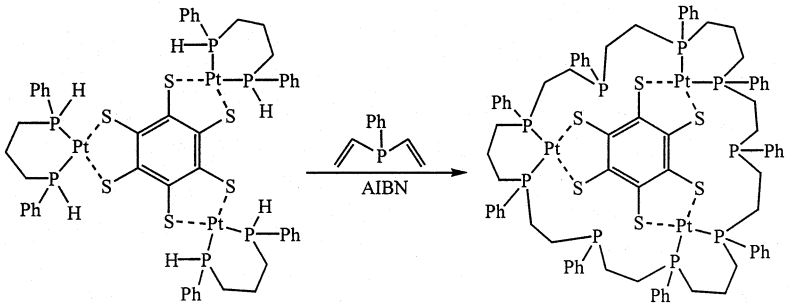
2.1. Materials and methods

All preparative reactions and manipulations were carried out under an atmosphere of N_2 or Ar using



(**1**) (**2**)

Scheme 1. Cyclization reaction of template (**1**) with $PhPH_2$ to produce templated macrocycle **2**.



Scheme 2. Cyclization reaction of **3** with (divinyl)(phenyl)phosphine.

standard Schlenk techniques [51]. Anhydrous platinum dichloride, *cis*-dichlorobis(triphenylphosphine)platinum(II), 1,2-bis(dimethylphosphino)ethane (dmpe), 1,3-bis(phenylphosphino)propane (ppp), and phenylphosphine were purchased from Strem Chemical Co., Newburyport, MA. All other materials were purchased from Aldrich Chemical Co., Milwaukee, WI. Benzenehexathiol was prepared using a literature procedure [49,52] modified as described below. Solvents were purified under nitrogen using standard methods [53]. Dichloromethane, benzene, hexanes, and ethyl sulfide were refluxed over CaH_2 and then distilled. THF was distilled from sodium benzophenone. CD_2Cl_2, $CDCl_3$, CD_3CN and CD_3OD were stored over 4 Å molecular sieves under nitrogen.

^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz spectrometer using the residual solvent peak as an internal reference (^1H NMR: δ 5.32 (CD_2Cl_2), 7.26 ($CDCl_3$), 1.94 (CD_3CN), 4.78 (CD_3OD); ^{13}C NMR: δ 53.1 (CD_2Cl_2), 77.00 ($CDCl_3$), 1.32 (CD_3CN), 49.0 (CD_3OD)). $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 MHz spectrometer using 85% phosphoric acid ($\delta = 0.00$) as the external reference. Electron ionization mass spectra (EIMS, 70 eV), chemical ionization mass spectra (CIMS), using NH_3 as the ionizing gas, and electrospray mass spectra (ESMS) were run on a Finnigan 4000 spectrometer. All ESMS samples were dissolved in methanol or CH_2Cl_2, as noted below. Elemental microanalyses were performed on a Perkin–Elmer 2400 series II C, H, N, S analyzer.

As previously described by Schmidbaur and co-workers [49], triethylammonium chloride, $Et_3N{\cdot}HCl$, co-crystallizes in the lattice of the (phosphine)-gold(I)-benzenehexathiolate compounds along with the reaction solvent, chloroform, to give an overall composition of $[(PPh_3)Au]_6(C_6S_6){\cdot}2Et_3NHCl{\cdot}4CHCl_3$. The solid gold(I) and platinum(II) templates described in this paper also contain Et_3NHCl and the solvent CH_2Cl_2. The presence of Et_3NH^+ and CH_2Cl_2 was established by elemental analyses and ^1H NMR spectra of the compounds, which exhibit peaks with proper intensities for these species: δ 3.06 (q) and δ 1.39 (t) for the Et_3NH^+ cation, δ 5.30 (s) for CH_2Cl_2 and δ 1.56 (s) for H_2O.

2.2. Preparation of benzenehexathiol, $C_6(SH)_6$

2.2.1. Synthesis of hexakis(benzylthio)benzene, $C_6(SCH_2Ph)_6$ (**5**)

In an atmosphere of nitrogen, 4.8 g (120 mmol) of a 60% NaH suspension in mineral oil was washed with dry hexanes 3 × 10 ml, followed by 2 × 10 ml of DMF. Then 50 ml of DMF was added to the flask. The suspension was cooled to 0°C and 14.1 ml (120 mmol) of benzyl mercaptan was slowly added to avoid foaming. Then 2.85 g (10 mmol) of C_6Cl_6 was added in three portions. The reaction was stirred for 10 min at 0°C and allowed to warm to room temperature (r.t.). The mixture congealed and was left under N_2. After 1 h the solvent was removed under reduced pressure leaving behind a yellow residue, which was dissolved in chloroform and precipitated with methanol. Yield 75%. ^1H NMR: ($CDCl_3$, δ) 7.19 [30H, m], 4.00 [12H, s]. ^{13}C NMR: ($CDCl_3$, δ) 146.88, 137.28, 129.19, 128.34, 127.18, 42.32. EIMS: 810.2 (M^+), 718 ($M^+ - CH_2Ph$), 628 ($M^+ - 2CH_2Ph$), 536 ($M^+ - 3CH_2Ph$), 446 ($M^+ - 4CH_2Ph$), 354 ($M^+ - 5CH_2Ph$). $C_{48}H_{42}S_6$ *Anal.* Found: C, 70.58; H, 5.12. Calc. for $C_{48}H_{42}S_6$: C, 71.07; H, 5.22%.

2.2.2. Synthesis of hexasodium benzenehexathiolate, $C_6(SNa)_6$ (**6**)

To 10 ml of anhydrous liquid ammonia at −78°C was added 0.68 g (0.84 mmol) of **5** with stirring. Then 0.23 g (10 mmol) of elemental sodium was added in three portions. A blue–green color appeared as the sodium dissolved. The solution was stirred for 0.5 h at −78°C. Degassed methanol was then added cautiously to the flask until the blue color was discharged. The flask was warmed to r.t. over 2 h. Afterwards, 10 ml of degassed, deionized water was added and the aqueous layer was extracted with ethyl ether (3 × 20 ml). The

yellow aqueous layer was evaporated under reduced pressure leaving behind **6** as an air-sensitive yellow residue.

2.2.3. Synthesis of benzenehexathiol, $C_6(SH)_6$ (7)

To 3 ml of degassed, deionized water was added the residue (0.25 g, 0.62 mmol) of **6** obtained in the above procedure. Then 10 ml of a degassed 5% HCl solution was added dropwise. The color changed from yellow to red–brown, and a yellow solid precipitated from solution. The solid was filtered and dried under vacuum. Yield 55%. ^{1}H NMR: (CD_3CN, δ) 2.19 [6H, s]. ^{13}C NMR: (CD_3CN, δ) 118.40. EIMS: 270 (M^+), 236 ($M^+ - H_2S$), 202 ($M^+ - 2H_2S$).

2.3. Gold-based template syntheses

To avoid decomposition to elemental gold, all reactions of **9**, **10**, and **1** were carried out in the dark at 0°C.

2.3.1. Synthesis of (divinyl)(phenyl)phosphine, $(C_2H_3)_2(Ph)P$ (8)

(Divinyl)(phenyl)phosphine was prepared using a previously reported procedure [54]. Yield 60%. ^{1}H NMR: ($CDCl_3$, δ) 7.44 [2H, m], 7.29 [3H, m], 6.39 [2H, m], 5.74 [4H, m]. ^{13}C NMR: ($CDCl_3$, δ) 137.19, 136.61, 132.44, 128.66, 128.44. ^{31}P{^{1}H} NMR: ($CDCl_3$, δ) −15.66. EIMS: 162 (M^+), 135 ($M^+ - C_2H_3$), 108 ($M^+ - 2C_2H_3$).

2.3.2. Synthesis of diethylsulfide gold(I) chloride $(Et_2S)AuCl$ (9)

(Et_2S)AuCl was prepared by a modified procedure analogous to that reported for (Me_2S)AuCl [55]. To a solution of 1.0 g (2.94 mmol) of $HAuCl_4$ in 25 ml of deionized water at 0°C was slowly added 0.95 ml (8.82 mmol) ethyl sulfide in 2 ml of acetone. The solution was stirred at r.t. in the dark for 1.5 h. After this time the yellow color had discharged and a flocculant white precipitate had formed. The solution was concentrated to 15 ml under reduced pressure to ensure complete precipitation. The white solid was filtered and dried under vacuum with the flask in an ice water bath to avoid decomposition. Yield 94%. ^{1}H NMR: ($CDCl_3$, δ) 3.10 [2H, q], 1.45 [3H, t]. ^{13}C NMR: ($CDCl_3$, δ) 32.09, 14.31. EIMS: 322 (M^+), 62 (Et_2S). *Anal.* Found: C, 13.72; H, 3.44; S, 9.07. Calc. for $C_4H_{10}SAuCl \cdot H_2O$: C, 14.10; H, 3.55; S, 9.41%.

2.3.3. Synthesis of [(divinyl)(phenyl)phosphine)]gold(I) chloride, $[(C_2H_3)_2(Ph)P]AuCl$ (10)

To 0.95 g (2.9 mmol) of **9** in 5 ml of CH_2Cl_2 at 0°C in the dark was added 0.49 g (3.0 mmol) of **8** in 1 ml of CH_2Cl_2. The solution was stirred at 0°C in the dark for 0.5 h. After this time, the CH_2Cl_2 was evaporated until a yellow–white precipitate began to form. Then 20 ml of hexanes were added to completely precipitate the product. Yield 61%. ^{1}H NMR: ($CDCl_3$, δ) 7.69 [2H, m], 7.49 [3H, m], 6.28 [6H, m]. ^{13}C NMR: ($CDCl_3$, δ) 136.55 [d, $J_{C-P} = 30$ Hz], 133.43 [d, $J_{C-P} = 54$ Hz], 131.92 [d, $J_{C-P} = 9$ Hz], 129.23 [d, $J_{C-P} = 45$ Hz], 128.32, 127.57. ^{31}P{^{1}H} NMR: ($CDCl_3$, δ) 26.16. ESMS: 394 (M^+), 360 (PhPAuCl), 252 (AuCl).

2.3.4. Synthesis of $\{[(C_2H_3)_2(Ph)P]Au\}_6(C_6S_6)$ (1)

To 0.71 g (1.8 mmol) of **10** in 5 ml of CH_2Cl_2 was added 0.080 g (0.30 mmol) of **7** and 25 μl (1.8 mmol) of Et_3N. The reaction was stirred at r.t. for 2 h. After this time, the solution was filtered and the solvent was removed under reduced pressure leaving behind a red–brown residue. The residue was recrystallized at r.t. from CH_2Cl_2 and hexanes. Yield 80%. ^{1}H NMR: ($CDCl_3$, δ) 7.65 [2H, m], 7.47 [3H, m], 6.16 [6H, m]. ^{13}C NMR: ($CDCl_3$, δ) 136.91, 133.65, 133.36, 132.28, 129.67, 128.34. ^{31}P{^{1}H} NMR: ($CDCl_3$, δ) 22.59. ESMS (MeOH): 2452 (M^+ + MeOH), 2291 ($M^+ - (C_2H_3)_2(Ph)P$ + MeOH + H), 2128 ($M^+ - 2(C_2H_3)_2$-Ph)P + MeOH), 1967 ($M^+ - 3(C_2H_3)_2(Ph)P$ + MeOH + H). *Anal.* Found: C, 35.27; H, 4.16; N, 1.90. Calc. for $C_{66}H_{66}P_6Au_6S_6 \cdot 3(CH_3CH_2)_3NHCl$: C, 35.62; H, 4.06; N, 1.48%.

2.3.5. Cyclization reaction of (1)

In a 5-mm glass NMR tube was placed 5.0 mg (2.0×10^{-3} mmol) of **1**, 0.6 ml of THF, 0.3 mg (1.9×10^{-3} mmol) of AIBN (α-azoisobutylnitrile) and 10 μl (9.1×10^{-2} mmol) of $PhPH_2$. The tube was heated at 60°C in a hot water bath for 4.5 h. The yellow solution was filtered and evaporated under reduced pressure to give a red residue of the template macrocycle **2**, which was recrystallized at r.t. from CH_2Cl_2 and hexanes to give a red solid. ^{1}H NMR: (CD_2Cl_2, δ) 7.78–7.40 [5H, m], 1.25 [4H, m]. ^{13}C NMR: (CD_2Cl_2, δ) 134.83, 131.08 [m], 129.04 [m], 122.88, 31.14, 26.12. ^{31}P{^{1}H} NMR: (CD_2Cl_2, δ) 19.10, 14.36. ESMS (CH_2Cl_2): 3062 (M^+ − 18, very weak peak). *Anal.* Found: C, 35.79; H. 3.94; N, 0.93. Calc. for $C_{102}H_{108}Au_6S_6P_{12} \cdot 2(CH_3CH_2)_3$-$NHCl \cdot 8CH_2Cl_2$: C, 36.31; H, 3.90; N, 0.69%.

2.3.6. Reaction of (2) with KCN

In a 5-mm glass NMR tube was placed product **2** (approximately 0.3 mg, 1 equiv.), 1.5 ml of D_2O and 5.0 mg (33 equiv.) of KCN. The solution was heated at 50°C for 12 h in a hot water bath. Deuterated chloroform (1 ml) was then added and the tube was shaken vigorously. After the layers had separated, the $CDCl_3$ layer was removed, dried over anhydrous $MgSO_4$ and evaporated to give $[P(Ph)CH_2CH_2]_{12}$ (**11**) as a yellow oily solid, which in CD_2Cl_2 gave a single ^{31}P{^{1}H} NMR signal at δ 1.55.

2.4. Platinum-based template syntheses

2.4.1. Preparation of $(P^{\frown}P)PtCl_2$ complexes

All $(P^{\frown}P)PtCl_2$ complexes were prepared by stirring 0.20 mmol of bis(benzonitrile)dichloroplatinum(II) and 0.20 mmol of the chelating phosphine in 5 ml of methylene chloride at r.t. according to a previously reported procedure [56,57]. Compounds **12**–**15** have been previously prepared by other methods [58]. Abbreviations used for the $P^{\frown}P$ phosphines are dppp = 1,2-bis(diphenylphosphino)propane, dmpe = 1,2-bis(dimethylphosphino)ethane, dppm = bis(diphenylphosphino)-methane, *cis*-dppv = *cis*-1,2-bis(diphenylphosphino)-ethylene, and ppp = 1,3-bis(phenylphosphino)propane.

(dmpe)$PtCl_2$ (**12**): Yield 88%. ^{1}H NMR: (CD_3OD, δ) 2.24 [4H, t], 1.95 [12H, t]. ^{13}C NMR: (CD_3OD, δ) 28.44 [m], 13.19 [m]. $^{31}P\{^1H\}$ NMR: ($CDCl_3$, δ) 34.19, Pt satellites at 47.75, 20.65, $J_{Pt-P} = 2708$ Hz. EIMS: 416 (M^+, ^{195}Pt), 150 (dmpe).

(dppm)$PtCl_2$ (**13**): Yield 58%. ^{1}H NMR: ($CDCl_3$, δ) 7.96 [8H, d], 7.47 [12H, m], 4.45 [2H, t]. $^{31}P\{^1H\}$ NMR: ($CDCl_3$, δ) -63.66, Pt satellites at -44.54, -82.70, $J_{Pt-P} = 3808$ Hz. EIMS: 650 (M^+, ^{195}Pt), 614 ([(dppm)PtCl]$^+$), 384 (dppm). *Anal.* Found: C. 45.98; H, 3.39. Calc. for $C_{25}H_{22}P_2PtCl_2$: C, 46.17; H, 3.41%.

(*cis*-dppv)$PtCl_2$ (**14**): Yield 72%. ^{1}H NMR: ($CDCl_3$, δ) 7.50 [22H, m]. ^{13}C NMR: ($CDCl_3$, δ) 134.12 [m], 133.41 [m], 132.96, 132.16, 129.76 [m], 129.12 [m]. $^{31}P\{^1H\}$ NMR: ($CDCl_3$, δ) 55.77, Pt satellites at 70.78, 40.76, $J_{Pt-P} = 3002$ Hz. CIMS: 662 (M^+, ^{195}Pt), 397 (*cis*-dppv).

(ppp)$PtCl_2$ (**15**): Yield 72%. ^{1}H NMR: ($CDCl_3$, δ) 7.37 [10H, m], 2.80 [1H, s], 2.40 [1H, s], 1.53 [6H, m]. ^{13}C NMR: ($CDCl_3$, δ) 134.11, 131.78, 128.82, 123.20, 19.83, 19.68. $^{31}P\{^1H\}$ NMR: ($CDCl_3$, δ) -29.47, Pt satellites at -15.49, -43.98, $J_{Pt-P} = 2848$ Hz.

2.4.2. Synthesis of $[(P^{\frown}P)Pt]_3(C_6S_6)$ complexes

All $[(P^{\frown}P)Pt]_3(C_6S_6)$ compounds were prepared by stirring 0.025 mmol (3 equiv.) of $(P^{\frown}P)PtCl_2$, 8.4×10^{-3} mmol (1 equiv.) of **7** and 7 μl (5.0×10^{-2} mmol, 6 equiv.) of Et_3N in 5 ml of CH_2Cl_2 (or 0.034 mmol of Na_2CO_3 in 5 ml of MeOH for $[(dmpe)Pt]_3(C_6S_6)$) at r.t. for 2 h according to a procedure [49] similar to that reported for the synthesis of $[(PPh_3)Au]_6(C_6S_6)$. After the 2 h period, the solvent was removed under reduced pressure leaving behind a solid yellow residue that was dissolved in CH_2Cl_2 and precipitated with hexanes at r.t.

$[(dmpe)Pt]_3(C_6S_6)$ (**16**): Yield 70%. ^{1}H NMR: (CD_3OD, δ) 2.23 [4H, t], 1.93 [12H, t]. $^{31}P\{^1H\}$ NMR: (CD_3OD, δ) 36.33, Pt satellites at 49.82, 22.85, $J_{Pt-P} =$ 2696 Hz. ESMS (MeOH): 1299 (M^+). *Anal.* Found: C, 20.24; H, 4.98. Calc. for $C_{24}H_{43}S_6Pt_3P_6{\cdot}7H_2O$: C, 20.21; H, 4.38%.

$[(dppm)Pt]_3(C_6S_6)$ (**17**): Yield 69%. ^{1}H NMR: (CD_2Cl_2, δ) 8.01 [8H, m], 7.54 [10H, m], 7.39 [2H, m], 4.54 [2H, t]. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, δ) -63.96, Pt satellites at -44.92, -82.91, $J_{Pt-P} = 3790$ Hz. ESMS (CH_2Cl_2): 2001 ($M^+ - 1$).

$[(cis\text{-dppv})Pt]_3(C_6S_6)$ (**18**): Yield 70%. ^{1}H NMR: ($CDCl_3$, δ) 7.81 [4H, m], 7.47 [16H, m], 7.23 [1H, s], 6.99 [1H, s]. ^{13}C NMR: ($CDCl_3$, δ) 134.21, 133.51 [t], 132.20, 129.87, 129.12 [t]. $^{31}P\{^1H\}$ NMR: ($CDCl_3$, δ) 56.18, Pt satellites at 71.02, 41.33, $J_{Pt-P} = 2968$ Hz. ESMS (CH_2Cl_2): 2038 (M^+). *Anal.* Found: C, 46.32; H, 3.84; N, 0.87. Calc. for $C_{84}H_{66}S_6P_6Pt_3{\cdot}(CH_3CH_2)_3NHCl{\cdot}3CH_2Cl_2$: C, 45.94; H, 3.65; N. 0.58%.

$[(PPh_3)_2Pt]_3(C_6S_6)$ (**19**): Yield 80%. ^{1}H NMR: ($CDCl_3$, δ) 7.49 [6H, t], 7.33 [3H, t], 7.15 [6H, t]. $^{31}P\{^1H\}$ NMR: (CD_2Cl_2, δ) 14.89, Pt satellites at 37.97, -7.91, $J_{Pt-P} =$ 4616 Hz. ESMS (CH_2Cl_2): 2422 ($M^+ - 1$), 2160 ($M^+ -$ PPh_3), 1896 ($M^+ - 2PPh_3$). *Anal.* Found: C, 52.55; H, 4.07; N, 0.36. Calc. for $C_{114}H_{90}P_6S_6Pt_3{\cdot}(CH_3CH_2)_3$-$NHCl{\cdot}3CH_2Cl_2$: C, 52.46; H, 4.01; N, 0.50%.

3. Results and discussion

3.1. Gold-based template syntheses

For the purpose of constructing the 12 phosphorus-donor macrocycle (**2**) in Scheme 1, the precursor hexanuclear [(divinyl)(phenyl)phosphine]gold(I) benzenehexathiolate template (**1**) was easily prepared in one step by stirring 6 equiv. of [(divinyl)(phenyl)phosphine]-gold(I) chloride (**10**), 1 equiv. of benzenehexathiol (**7**) and 6 equiv. of triethylamine in CH_2Cl_2 for 2 h at r.t. (Eq. (1)).

$$6\underset{(\mathbf{10})}{[(C_2H_3)_2(Ph)P]AuCl} + 1\underset{(\mathbf{7})}{C_6(SH)_6} \xrightarrow[6Et_3N]{CH_2Cl_2} \underset{(\mathbf{1})}{\{[(C_2H_3)_2(Ph)P]Au\}_6(C_6S_6){\cdot}3Et_3NHCl} + 3Et_3NHCl \quad (1)$$

The resulting template product (**1**) is a red–brown solid that contains 3 equiv. of Et_3NHCl. The analogous compound, $[(Ph_3P)Au]_6(C_6S_6)$, prepared by Schmidbaur and co-workers [49] also crystallized with 3 equiv. of Et_3NHCl. The presence and amount of triethylammonium chloride in **1** was established by C, H, and N elemental analyses, as well as correct integration values for ^{1}H NMR peaks ($\delta = 3.06$ (q) and $\delta = 1.39$ (t)) corresponding to the ethyl groups in the Et_3NH^+ cation. Additionally, diagnostic peaks for the ethyl groups in the Et_3NH^+ cation are observed in the ^{13}C NMR spectrum ($\delta = 46.94$ and $\delta = 11.17$). The $^{31}P\{^1H\}$ NMR spectrum of **1** shows one signal at $\delta = 22.59$, which is shifted only slightly from that of the [(divinyl)-(phenyl)phosphine]gold(I) chloride precursor **10** ($\delta =$ 26.16). A multiplet at $\delta = 6.16$ ppm (6H) in the ^{1}H NMR spectrum of **2** is characteristic of the vinyl protons of the phosphine ligand, while the multiplets at $\delta = 7.47$ and $\delta = 7.65$ (5H) may be assigned to the phenyl group.

The formation of the polyphosphorus macrocycle (**2**) was performed according to Scheme 1 by heating **1** at 60°C with excess $PhPH_2$ and AIBN in THF for 4.5 h. The templated macrocycle (**2**) was isolated as a red solid by recrystallization from CH_2Cl_2 and hexanes. As expected from the structure of **2**, the $^{31}P\{^1H\}$ NMR spectrum shows only two signals $\delta = 19.10$ and $\delta = 14.36$ in CD_2Cl_2 in a 1:1 ratio. These two signals correspond to the six phosphorus atoms directly coordinated to gold and the six phosphorus atoms that lie between the coordinated phosphorus atoms (Scheme 1). There exists the possibility of multiple isomers resulting from different stereochemistries at each of the 12-phosphorus atoms. The presence of such isomers is supported by the fact that each of the two $^{31}P\{^1H\}$ NMR signals is a broad singlet. The ^1H NMR spectrum, which exhibits no signals for the vinyl groups of the precursor (**1**), shows a multiplet for the phenyl protons at 7.78–7.40 ppm and another multiplet for the methylene protons at 1.25 ppm; their relative integrations (5:4) are correct for the proposed structure of **2**.

Elemental analyses (C, H, and N) indicate that solid **2** contains two moles of Et_3NHCl and 8 moles of CH_2Cl_2. The presence and amount of Et_3NHCl and CH_2Cl_2 is confirmed by integrations of the ^1H NMR peaks corresponding to the protons in these compounds. Despite several attempts to grow crystals for X-ray analysis, no crystals of suitable size were obtained.

In a preliminary attempt to isolate the free macrocycle, $[P(Ph)CH_2CH_2]_{12}$ (**11**), a small amount of **2** was heated (50°C) in an aqueous solution of KCN for 12 h. The $^{31}P\{^1H\}$ NMR spectrum of the $CDCl_3$-soluble product of this reaction shows only one signal at $\delta = 1.55$, which is consistent with the free macrocycle (**11**) that was present in **2**. This chemical shift is in good agreement with that ($\delta = 4.1$) reported for cyclic tetra(phenylphosphino)methylene $[P(Ph)CH_2]_4$ [59]. More thorough investigations of the macrocycle (**11**) will be undertaken in the future.

3.2. Platinum-based template syntheses

Although the goal was to prepare **3** (Scheme 2) as the precursor to macrocycle **4**, the secondary phosphine groups in the $Ph(H)PCH_2CH_2CH_2P(H)Ph$ (ppp) ligand were expected to be air-sensitive and pose a challenge to the synthesis of **3**. In order to demonstrate that templates similar to **3** are synthetically accessible, we prepared (Eq. (2)) analogs of **3** that contain the more stable bidentate P⌒P phosphines: $Ph_2P(CH_2)_3PPh_2$ (dppp), $Me_2P(CH_2)_2PMe_2$ (dmpe), $Ph_2PCH_2PPh_2$ (dppm), *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-dppv) and $(Ph_3P)_2$.

$$\underset{(\mathbf{12}-\mathbf{15})}{3(P\frown P)PtCl_2} + \underset{(7)}{1C_6(SH)_6} \xrightarrow[6Et_3N]{CH_2Cl_2} \underset{(\mathbf{16}-\mathbf{19})}{[(P\frown P)Pt]_3(C_6S_6)\cdot x Et_3NHCl\cdot y CH_2Cl_2\cdot z H_2O} \quad (2)$$

12, **16** P⌒P = dmpe, $x = 0$, $y = 0$, $z = 7$
13, **17** P⌒P = dmpe, $x = 1$, $y = 3$, $z = 0$
14, **18** P⌒P = *cis*-dppv, $x = 1$, $y = 3$, $z = 0$
15, **19** P⌒P = $2PPh_3$, $x = 1$, $y = 3$, $z = 0$

Three equivalents of the $(P\frown P)PtCl_2$ complexes were stirred with 1 equiv. of benzenehexathiol and 6 equiv. of Et_3N in CH_2Cl_2 for 2 h to give **16**–**19**. As for the gold-based system, $Et_3N{\cdot}HCl$ and CH_2Cl_2 co-crystallize in **17**–**19** as is evident from their elemental analyses and ^1H NMR spectra. Compound **16** contains H_2O whose origin is unknown but is likely to be the solvents or atmosphere. The ^{31}P NMR chemical shifts and $^{31}P-^{195}Pt$ coupling constants in **16**–**19** are very similar to those of their precursor complexes **12**–**15**. Electrospray mass spectra of compounds **16**–**19** show peaks for the $[(P\frown P)Pt]_3(C_6S_6)$ parent ions (M^+) or ($M^+ - 1$). Attempts to grow single crystals of **16**–**19** were unsuccessful. All spectroscopic data are consistent with the general formula $[(P\frown P)Pt]_3(C_6S_6)$ and confirm the 3:1 $(P\frown P)Pt{:}C_6S_6$ stoichiometry of the product.

In order to accomplish the cyclization in Scheme 2, we also attempted the preparation of **3** containing the bidentate secondary phosphine $Ph(H)PCH_2CH_2CH_2P(H)Ph$ (ppp), by the method (Eq. (2)) that was successful for the synthesis of the other $[(P\frown P)Pt]_3(C_6S_6)$ complexes. However, when 3 equiv. of $(ppp)PtCl_2$ (**15**) were reacted with 1 equiv. of benzenehexathiol (**7**) and 6 equiv. of Et_3N, the desired template (**3**) was not obtained. Since Et_3N is known to react with secondary phosphines [60], which may have complicated the present reaction, we used Na_2CO_3 as the base, but again **3** was not detected despite the fact that Na_2CO_3 was used successfully in place of Et_3N to prepare $[(dmpe)Pt]_3(C_6S_6)$ (**16**). At present, we do not understand why we have not been able to prepare $[(ppp)Pt]_3(C_6S_6)$ (**3**), while all of the related $[(P\frown P)Pt]_3(C_6S_6)$ complexes (**16**–**19**) are easily synthesized. However, as a result, it was not possible to attempt the macrocyclization reaction in Scheme 2.

4. Conclusions

For the purpose of using it as a template for the formation of large-ring, polyphosphorus macrocycles, the Au complex $\{[(divinyl)(phenyl)phosphine]Au\}_6(C_6S_6)$ (**1**) with a benzenehexathiolate core was prepared and characterized. Its reaction (Scheme 1) with the primary phosphine $PhPH_2$ in the presence of AIBN yielded the complex $[P(Ph)CH_2CH_2]_{12}Au_6(C_6S_6)$ (**2**), whose NMR spectra and elemental analyses are consistent with the proposed structure which contains a 36-membered ring with 12 phosphorus atoms, six of which are coordinated to the six Au atoms. Although it was possible to prepare a series of related platinum complexes $[(P\frown P)Pt]_3(C_6S_6)$ (**16**–**19**), we were unable to

obtain a key precursor that was designed to lead to macrocycle **4** (Scheme 2). Despite the lack of success using the platinum-based templates, the Au-based system shows that large-ring, multi-donor macrocycles can be constructed around a multi-metal ion template, a general approach that may be useful for the synthesis of other large macrocyclic ligands.

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