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ARTICLE

Selective formation of a two-dimensional coordination polymer based on a tridentate phospholane ligand and gold(I)†‡

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The tridentate phosphine ligand 1,3,5-tris[(E)-(4-phospholano-2,6-diethyl)styryl]benzene (**1**) reacts with [AuCl(tht)] independent of the stoichiometry employed with selective formation of a two-dimensional coordination polymer (ratio 1:1) with the gold(I) cations in a trigonal-planar [3 + 1] coordination geometry. Each of the three coordinating phosphine units originates from another ligand, thus forming a polymeric structure.

Introduction

Supramolecular Coordination Complexes (SCCs) have been defined by Cohen as "clusters, which combine polydentate organic ligands and transition metals to form elegant assemblies held together by reversible metal-ligand bonds".[1] These compounds are of special interest for applications in sensing, inclusion and transformation of small molecules as well as catalysis.[2,3] Even though extensive research has been conducted over the past decades, examples for SCCs containing phosphine ligands are scarce. Phosphines are prone to oxidation and therefore require more synthetic effort and careful handling. Furthermore, due to rotation around the P–C bond, different orientations of the lone pairs of electrons of the phosphines with respect to each other and to the orientation of the ligand are possible, resulting in a lower predictability and selectivity of the formed SCC.[4] Examples for selectively formed SCCs include macrocycles,[5–9,9–20] tetrahedra,[1,21,22] helicates,[1,8,23,24] and polymeric structures[8,25] based on phosphines and gold(I).

Results and discussion

Recently, we have reported the systematic investigation of flexible bis-phospholane ligands of different chain lengths and the selective formation of dimetallamacrocycles, nanotubes and polymeric chain structures.[26] In order to extend the ring structure of the dimetallamacrocycles to the third dimension, a new tridentate ligand **1** with a semi-rigid backbone allowing a certain degree of flexibility was developed (Scheme 1) and expected to coordinate in a similar fashion as the bidentate ligands, forming sandwich-type structures (Fig. 1).

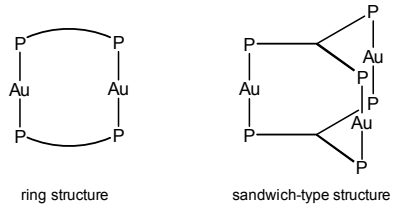
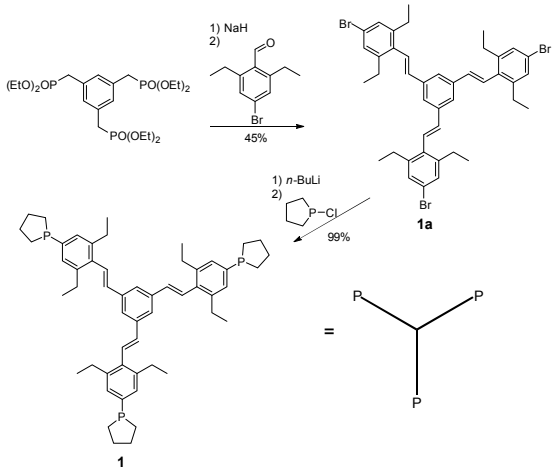


Fig. 1 Schematic representation of a dimetallamacrocycle (left)[26] and the intended sandwich-type structure (right) based on gold(I). Counterions are omitted for clarity.

Since conjugated polyaromatic systems often suffer from solubility issues, ethyl groups were incorporated in the backbone. For compound **1a**, a crystal structure could be obtained (Table 1), confirming the intended geometry of an almost perfect isosceles triangle with the bromine atoms at the edges (distances Br(1)···Br(2) 1.67 nm, Br(2)···Br(3) 1.71 nm, Br(3) ···Br(1) 1.74 nm; Br(2)-Br(1)-Br(3) angles 57.83 to 61.80°). In order to obtain a sandwich-type structure, **1** was reacted with [AuCl(tht)][27] in a 3:2 [M:L] molar ratio in dichloromethane.



Scheme 1 Synthesis of 1,3,5-tris[(*E*)-(4-phospholano-2,6-diethyl)styryl]benzene (**1**).

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† Dedicated to Professor Werner Uhl on the occasion of his 65th birthday.

‡ Electronic Supplementary Information (ESI) available: Assigned NMR spectra of all new compounds, crystallographic details for **1a** and **2**, and TGA/DSC measurements of **2**. See DOI: 10.1039/x0xx00000x.

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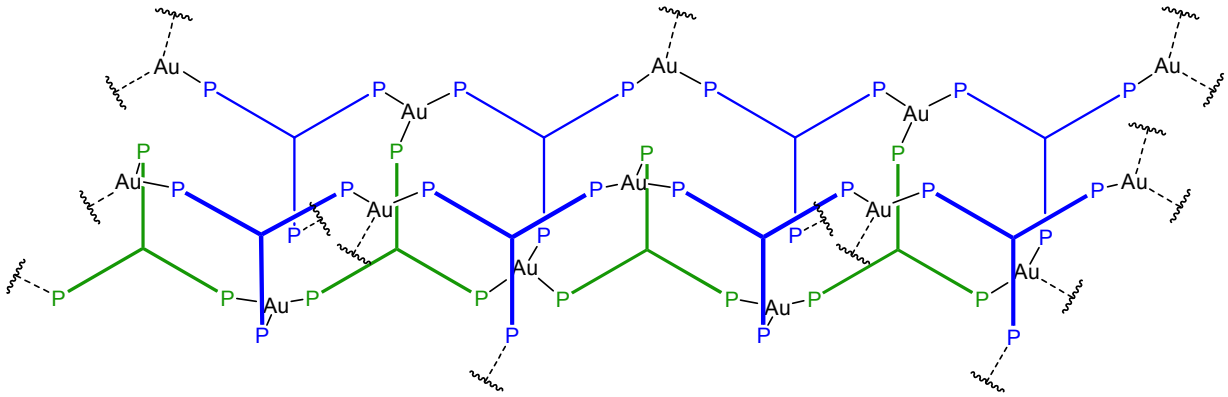

Fig. 2 Schematic representation of the two-dimensional coordination polymer **2**. Chains of different orientation (blue and green) are connected to each other by alternating coordination of the third phospholane to the gold(I) cations in the chains in front and behind, respectively. Counterions (chloride) and the zigzag structure of the chains are omitted for clarity.

The $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture showed two broad signals at δ = 35.4 and 33.2 ppm in a ratio of 5:1, giving evidence for the presence of at least two species in solution. Single crystals suitable for X-ray diffraction were obtained by gas diffusion of *n*-hexane into a saturated solution of the product in *o*-difluorobenzene (Table 1). The resulting structure revealed the formation of a 1:1 [M:L] complex, regardless of the applied stoichiometry. In **2**, a chain is formed (blue) in which gold(I) cations are bridged by two phospholane moieties of ligand **1**, while the third phospholane group is not included in the formation of the chain. In

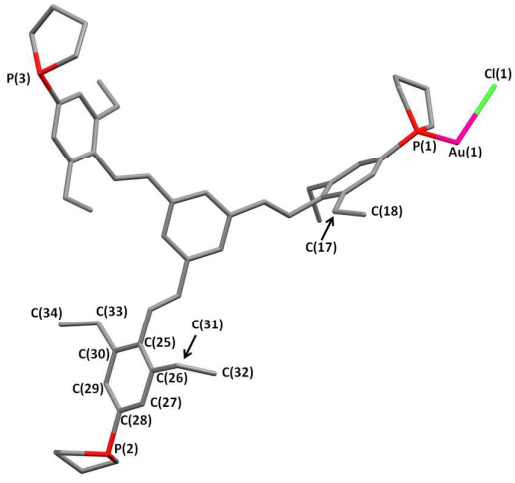

Fig. 3 Asymmetric unit of the coordination polymer **2.**

The next, parallel, chain (green) is rotated by 180° relative to the first chain (blue). The third chain (blue) has the same orientation as the first, and so on (Fig. 2).The phospholane moieties, which are not included in the chain formation, are alternatingly coordinated to the gold(I) cations of the chains in front and behind, respectively, thus forming a two-dimensional polymer. The asymmetric unit of **2** (Fig. 3) shows a different conformation of the ligand compared to **1a** (P(1)···P(2) 1.78 nm, P(2)···P(3) 1.63 nm, and P(3)···P(1) 1.62 nm; P(2)-P(1)-P(3) 56.98°, P(3)-P(2)-P(1) 56.53°, and P(1)-P(3)-P(2) 66.49°). A view along the crystallographic *a* axis shows the polymeric structure (Fig. 4).

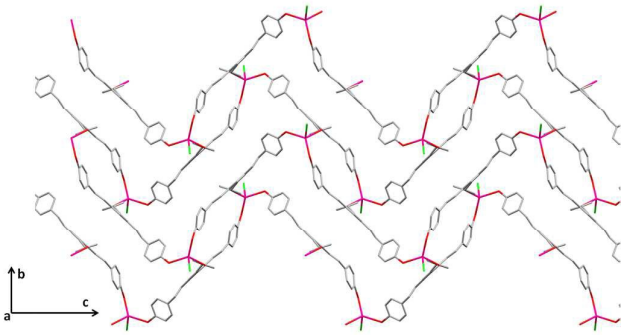

Fig. 4 View of **2** along the *a* axis, illustrating the zigzag structure and connectivity of the chains. Only four chains are shown. Ethyl groups and the carbon atoms of the phospholane rings are omitted for clarity.

Gold(I) cations, phospholane moieties and the weakly coordinating terminal chlorido ligands form the rims of the polymeric chains, while the inner layer of **2** is composed of the organic backbone of the ligands **1** forming hydrophobic channels (200 x 400 pm) along the *b* axis (Fig. 5), in which disordered solvent molecules (*o*-difluorobenzene) are located.

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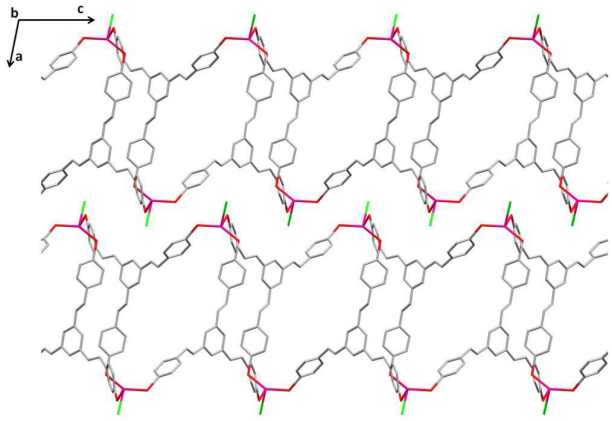

Fig. 5 View of **2** along the *b* axis showing channels. Only two layers are shown. Ethyl groups and the carbon atoms of the phospholane rings of the ligands are omitted for clarity.

The gold(I) cations in **2** are coordinated in an unusual trigonal [3 + 1] fashion (Fig. 6). The sum of P–Au–P bond angles is close to 360°, and the gold(I) cation is located only 11 pm above the plain formed by the three phosphorus atoms. The phospholane rings are oriented in the shape of a bowl, in which the weakly coordinating chlorido ligand is located (Fig. 6).

Table 1 Selected crystallographic data for **1a** and **2**.

	1a	**2**
Formula	$C_{42}H_{45}Br_3$	$C_{54}H_{69}AuClP_3 \cdot 2.75\ C_6H_4F_2$
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	$P2_1/c$
Z	8	4
a [pm]	2861.00(8)	1800.76(2)
b [pm]	1558.71(3)	1336.91(2)
c [pm]	1621.90(3)	2686.19(3)
β [deg]	96.537(2)	98.503(1)
V [nm^3]	7.1858(3)	6.3958(1)

The long Au(1)–Cl(1) 283.1(1) pm bond is almost perfectly perpendicular to P_3 triangle. A similar coordination geometry was reported by Schmidbaur for $[AuCl(PPh_3)_3]$,[28] in which the Au–Cl bond (279.6(1) pm) is slightly shorter and the sum of P–Au–P bond angles (355.35°) also slightly smaller than in **2**. As this structure was discussed as an intermediate between a covalent ($[AuCl(PPh_3)_3]$) and an ionic structure ($[Au(PPh_3)_3]Cl$),[28] the description as a trigonal-planar [3 + 1] coordination in **2** seems reasonable. Only a few examples of complexes with related AuP_3Cl core structures have been reported: $[Au(DHP)(PEt_3)]Cl$ (DHP = o-phenylenebis(diisopropylphosphane, Au–Cl 307.3(2) pm, sum of P–Au–P bond angles 354.8(1)°),[29] $[Au_2Cl_2L]_n$ (L = *p-tert*-butyl-calix[4]-$(OCH_2PPh_2)_4$; Au–Cl 301.2(6) pm),[30] $[Au(DPPP)(PPh_3)]Cl$ (DPPP = 1,3-bis(diphenylphosphino)propane, Au–Cl 292.8(2) pm, sum of P–Au–P bond angles 356.15(7)°),[31] and $[(Au_2Cl)L_3Cl]$ (L = bis(5-diphenylphosphinopyrazol-1-yl)methane, Au–Cl 284.9(4) pm and 281.9(3) pm, sum of P–Au–P bond angles 352.2(1)°)[32]. These structures indicate that an elongation of the Au–Cl bond correlates with formation of a (trigonal)-planar environment of gold(I) by the phosphine ligands; thus, the structures should not be discussed as distorted tetrahedral complexes. Tetra-coordinated complexes with shorter Au–Cl bond are known[33–42] and can be discussed as distorted tetrahedra, even though an intermediate or a trigonal [3 + 1] species could be considered in some cases. An almost ideal trigonal-planar environment has been observed for $Cs_8[Au(TPPTS)_3]\cdot 5.25\ H_2O$ (TPPTS = tris(*meta*-sulfonatophenyl)phosphine), where no counterion is coordinated at gold(I).[43] In the one-dimensional coordination polymer $[AuCl(MandyPhos)]_n$ (MandyPhos = (S_P,S'_P)-1,1′-Bis(diphenylphosphino)-2,2′-bis[(*R*)-α-(dimethylamino)benzyl]ferrocene), gold(I) is coordinated in distorted trigonal-planar fashion by bridging bidentate MandyPhos ligands and a terminal chlorido ligand (av. Au–Cl 258.1(6) pm).[44]

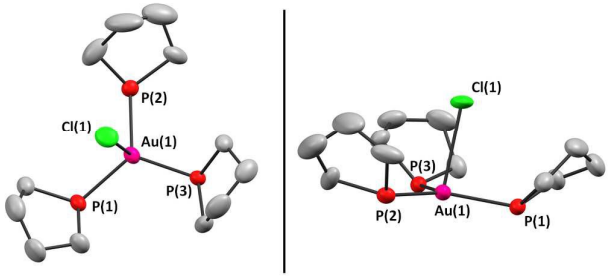

Fig. 6 Coordination environment of the gold(I) cations in **2**, top view (left) and side view (right). Ellipsoids are drawn at 50% probability; H atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: Au(1)–P(1) 233.3(1), Au(1)–P(2) 233.7(1), Au(1)–P(3) 235.9(1), Au(1)–Cl(1) 283.1(1), P(1)–Au(1)–P(2) 125.98(3), P(1)–Au(1)–P(3) 118.78(3), P(2)–Au(1)–P(3) 114.57(3), P(1)–Au(1)–Cl(1) 88.15(3), P(2)–Au(1)–Cl(1) 96.76(3), P(3)–Au(1)–Cl(1) 93.39(3).

Trigonal-planar [3 + 1] gold(I) complexes with other weakly coordinating ligands than chloride are known but were not included. Furthermore, gold(I) complexes with ambiphilic donor-acceptor ligands and a quasi trigonal-bipyramidal environment have been reported,[45–47] but will not be discussed here in detail.

After crystallisation, polymer **2** is almost completely insoluble in common organic solvents as dichloromethane and acetonitrile and can, therefore, be considered as the thermodynamically favoured product.[42] TGA/DSC measurements of crystalline **2** in a range of 35–1100 °C (see ESI) showed a first mass loss of about 20% at 100 °C corresponding to loss of 2.75 co-crystallised *o*-difluorobenzene molecules (also confirmed by mass spectrometry). The second mass loss (about 40%) occurs at 400 °C and corresponds to degradation of the backbone (detection of a species with m/z 26, which can be attributed to ethyne). No further degradation is observed.

While a linear coordination is typically preferred in gold(I) phosphine complexes, in polymer **2**, which is formed selectively independent of the stoichiometry employed, gold(I) exhibits an usually [3 + 1] coordination as a linear sandwich-type arrangements is sterically hindered.

Conclusion

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A straight-forward synthetic route to the tridentate phosphine ligand 1,3,5-tris[(*E*)-(4-phospholano-2,6-diethyl)styryl]benzene (**1**) was developed. The complexation of gold(I) is unusual, resulting in an almost perfect trigonal-planar coordination and formation of a two-dimensional polymeric structure in **2**, regardless of the stoichiometry employed. Our studies indicate that the ligand geometry has a significant impact on the coordination properties; therefore, an extraordinary coordination chemistry of other metal cations can also be expected.

Experimental section

All reactions were carried out in a nitrogen atmosphere by using standard Schlenk techniques and anhydrous solvents, which were purified with an MB SPS-800 solvent purification system from MBRAUN or as mentioned in the literature. 1,3,5-Tris[(methylene)diethylphosphonato]benzene[48] and [AuCl(tht)][27] were prepared according to the literature. All other chemicals were used as purchased. NMR spectra were recorded at 298 K with a Bruker AVANCE DRX 400 spectrometer. The chemical shifts δ of ^{1}H, ^{13}C, ^{31}P are reported in parts per million (ppm) at 400.12, 100.63 and 162.02 MHz, respectively, with tetramethylsilane as an internal standard and referencing to the unified scale. Coupling constants *J* are given in Hz. NMR spectra with detailed signal assignment are given in the ESI. FTIR spectra were recorded between 400 and 4000 cm^{-1} with a PerkinElmer Spectrum 2000 FTIR spectrometer by using KBr pellets, and ATR spectra were recorded on a THERMOFISCHER NICOLET iS5 ATR spectrometer. Mass spectra were recorded on a BRUKER-DALTONICS ESQUIRE 3000 Plus spectrometer (ESI) and on a THERMO FISCHER SCIENTIFIC MAT 8230 spectrometer (EI). Elemental analyses were carried out with a Heraeus VARIO EL oven. Melting points were measured in sealed capillaries by using a variable heater from Gallenkamp.

Crystallographic data for compounds **1a** and **2** were collected with an Oxford Diffraction CCD Xcalibur-S diffractometer (data reduction with CrysAlis Pro,[49] including the program SCALE3 ABSPACK[50] for empirical absorption correction) by using MoK_α irradiation (λ = 71.073 pm) and ω-scan rotation. The structure solution was performed with SHELXS-2013[51] (**1a**) and SHELXT-2014[52] (**2**). Refinement was performed with SHELXL-2018[53]. Figures were drawn with Mercury. CCDC 1861124 (**1a**) and 1860064 (**2**) contain the supplementary crystallographic data for this paper.

Synthesis and characterisation

4-Bromo-2,6-diethylaniline. 25 g (167.5 mmol; 1.0 eq) 2,6-Diethylaniline were dissolved in 200 ml dimethyl sulfoxide and cooled to 0 °C. 200 ml of an aqueous HBr solution (40%) was added and the mixture was allowed to warm to room temperature. The mixture was stirred for 7 days at room temperature, neutralised with aqueous NaOH solution and extracted with diethyl ether (3 x 80 ml). The collected organic phases were dried over $MgSO_4$ and the solvent removed under reduced pressure.

Yield: 36.8 g (96%), slightly brown oil. Found C, 53.06; H, 6.15; N, 6.33. Calc. for $C_{10}H_{14}BrN$: C, 52.65; H, 6.19; N, 6.14. IR: $\tilde{\nu}$ = 3923 (w), 3485 (s), 3402 (s), 3234 (w), 2966 (s), 2935 (m), 2875 (s), 2732 (w), 2429 (w), 2175 (w), 1739 (m), 1622 (s), 1578 (m), 1451 (s), 1378 (m), 1344 (m), 1303 (w), 1284 (m), 1247 (w), 1210 (s), 1137 (w), 1056 (m), 986 (w), 970 (w), 867 (s), 853 (m), 796 (m), 759 (w), 740 (m), 723 (w), 586 (w), 548 (m), 523 (w), 488 (w), 413 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.03 (s, 2H), 3.56 (s, 2H), 2.41 (q, $^{3}J_{HH}$ = 7.5, 4H), 1.19 ppm (t, $^{3}J_{HH}$ = 7.6, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 140.7 (s), 129.6 (s), 128.4 (s), 110.1 (s), 24.1 (s), 12.7 ppm (s). MS (ESI(+), MeCN): *m/z* = 228.1 $[M+H]^+$.

5-Bromo-1,3-diethyl-2-iodobenzene. 73.0 g (320.0 mmol; 1.0 eq) 4-Bromo-2,6-diethylaniline were suspended in 1.1 l H_2O, 200 ml acetonitrile and 350 ml concentrated aqueous HCl and cooled to –10 °C. 40 g (580 mmol; 1.8 eq) $NaNO_2$ in 200 ml H_2O were added dropwise, giving a pink precipitate, followed by formation of a clear red solution. After the addition, the solution was stirred for further 60 min at –10 °C, followed by dropwise addition of a solution of 184 g (902 mmol; 2.8 eq) KI in 300 ml H_2O. The formation of a yellowish foam was observed. Afterwards, the mixture was carefully allowed to warm to room temperature. The mixture was stirred overnight, heated to 60 °C for 30 min, cooled to room temperature, and extracted with *n*-hexane (4 x 50 ml). The collected organic phases were stirred over saturated aqueous Na_2SO_3 solution, until the organic phase had a light yellow colour. The organic phase was then dried over $MgSO_4$ and the solvent removed under reduced pressure.

Yield: 100.0 g (92%), slightly yellow oil. Found C, 35.97; H, 3.55. Calc. for $C_{10}H_{12}BrI$: C, 35.46; H, 3.57. IR (KBr): $\tilde{\nu}$ = 2968 (s), 2931 (m), 2873 (m), 2382 (w), 2347 (w), 1734 (w), 1558 (m), 1460 (s), 1427 (m), 1417 (m), 1397 (w), 1373 (m), 1327 (m), 1271 (w), 1241 (m), 1128 (m), 1075 (w), 1051 (m), 1004 (s), 862 (s), 813 (m), 784 (w), 726 (w), 709 (w), 661 (w), 600 (w), 568 (w), 530 (w), 421 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.15 (s, 2H), 2.73 (q, $^{3}J_{HH}$ = 7.5, 4H), 1.18 ppm (t, $^{3}J_{HH}$ = 7.4, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 148.8 (s), 128.7 (s), 122.6 (s), 105.4 (s), 35.3 (s), 14.5 ppm (s). MS (ESI(+), CH_2Cl_2/MeOH): *m/z* = 374.9 $[C_{10}H_{10}BrI+K]^+$.

4-Bromo-2,6-diethylbenzaldehyde. 10.0 g (29.5 mmol; 1.0 eq) 5-Bromo-1,3-diethyl-2-iodobenzene were dissolved in 100 ml diethyl ether and cooled to –78 °C. 21.9 ml (33.9 mmol; 1.1 eq) of a 1.55 M *n*-butyllithium solution in *n*-hexane were added in one portion and the solution stirred for 90 min at a temperature below –45 °C. A white precipitate was formed. Afterwards, 10.3 ml (132.8 mmol; 4.5 eq) dimethylformamide were added dropwise and the precipitate dissolved. The mixture was allowed to warm to room temperature and was stirred overnight, resulting in a white precipitate. 20 ml of an aqueous NH_4Cl solution were added carefully, and then the mixture was extracted with diethyl ether (2 x 25 ml). The collected organic phase was dried over $MgSO_4$ and the solvent removed using a rotary evaporator. The raw product was

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filtered over silica using *n*-hexane/EtOH (20:1; R_f = 0.7) and subsequently distilled at $2.6 \cdot 10^{-2}$ mbar and 100 °C.

Yield: 6.2 g (87%), colourless oil. Found C, 54.82; H, 5.57. Calc. for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. IR (KBr): $\tilde{\nu}$ = 3373 (w), 2970 (s), 2934 (m), 2874 (m), 2767 (m), 1740 (m), 1695 (s), 1574 (s), 1457 (s), 1401 (m), 1377 (m), 1324 (w), 1298 (w), 1264 (m), 1234 (s), 1184 (m), 1158 (m), 1114 (s), 1061 (m), 968 (w), 893 (m), 867 (s), 844 (s), 799 (w), 737 (m), 590 (w), 442 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 10.52 (s, 1H), 7.28 (s, 2H), 2.93 (q, $^3J_{HH}$ = 7.5, 4H), 1.24 ppm (t, $^3J_{HH}$ = 7.6, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 192.3 (s), 149.1 (s), 131.0 (s), 130.3 (s), 127.8 (s), 26.4 (s), 16.1 ppm (s). MS (ESI(+), MeCN): *m/z* = 298.3.

1,3,5-Tris[(*E*)-(4-bromo-2,6-diethyl)styryl]benzene (1a). 1.00 g (1.89 mmol; 1.0 eq) 1,3,5-Tris[(methylene)diethylphosphonato]benzene were dissolved in 25 ml of tetrahydrofuran. 0.15 g NaH in mineral-oil (60%, 3.8 mmol; 2.0 eq) were added, the mixture was stirred for 3 h and subsequently 0.59 g (2.46 mmol; 1.3 eq) 4-bromo-2,6-diethylbenzaldehyde in 10 ml *n*-hexane were added. The mixture was stirred for 3 h at room temperature and the addition sequence was repeated twice, followed by stirring overnight. 5 ml H_2O were added carefully and all volatiles were removed in vacuo. The remaining solid was dissolved in 30 ml dichloromethane, washed with brine and water (15 ml each) and dried over $MgSO_4$. The raw product was purified via column chromatography using *n*-hexane (R_f = 0,4).

Yield: 0.67 g (45%), white solid. Mp = 133 °C. Found C, 63.89; H, 5.91. Calc. for $C_{42}H_{45}Br_3$: C, 63.89; H, 5.74. IR (KBr): $\tilde{\nu}$ = 3021 (m), 2964 (s), 2930 (s), 2871 (s), 1782 (w), 1735 (w), 1637 (m), 1588 (s), 1574 (s), 1455 (s), 1407 (m), 1372 (m), 1329 (s), 1266 (m), 1239 (m), 1187 (m), 1164 (w), 1115 (w), 1058 (m), 971 (s), 862 (s), 839 (m), 822 (m), 797 (s), 766 (m), 726 (w), 684 (s), 629 (w), 594 (w), 549 (w), 418 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.53 (s, 3H), 7.25 (s, 6H), 7.16 (d, $^3J_{HH}$ = 16.0, 3H), 6.62 (d, $^3J_{HH}$ = 16.0, 3H), 2.70 (q, $^3J_{HH}$ = 8.0, 12H), 1.20 ppm (t, $^3J_{HH}$ = 8.0, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 144.6 (s), 138.1 (s), 135.0 (s), 133.9 (s), 128.8 (s), 126.5 (s), 123.6 (s), 121.2 (s), 26.8 (s), 15.9 ppm (s). MS (ESI(–), CH_2Cl_2/MeOH): *m/z* = 825.0 $[M+Cl]^-$.

1,3,5-Tris[(*E*)-(4-phospholano-2,6-diethyl)styryl]benzene (1). 1.00 g (1.27 mmol; 1.0 eq) 1,3,5-Tris[(*E*)-(4-bromo-2,6-diethyl)styryl]benzene were dissolved in 60 ml tetrahydrofuran and cooled to –78 °C. 3.7 ml (5.08 mmol; 4.0 eq) of a 1.38 M *n*-butyllithium solution in *n*-hexane were added dropwise, resulting in a yellow-greenish colour of the reaction mixture. The mixture was stirred for 3 h at –70 °C and subsequently, 0.67 g (5.46 mmol; 4.3 eq) 1-chlorophospholane were added. The colour faded and a white precipitate formed, which dissolved upon warming to room temperature. The mixture was stirred for 1 h at room temperature. Then all volatiles were removed in vacuo and the remaining solid was dissolved in 15 ml dichloromethane. The suspension was filtered over a silica (3 cm). Evaporation of the solvent in vacuo gave the pure product.

Yield: 1.03 g (99%), slightly yellow oil. IR (KBr): $\tilde{\nu}$ = 2963 (s), 1771 (m), 1634 (w), 1585 (s), 1548 (m), 1455 (s), 1419 (m), 1393 (w), 1372 (m), 1322 (w), 1302 (w), 1261 (s), 1202 (w), 1179 (w), 1107 (s), 1046 (s), 1026 (s), 968 (s), 868 (m), 801 (s), 687 (m), 668 (m), 600 (m), 533 (m), 465 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.42 (s, 3H), 7.15 (d, $^3J_{HH}$ = 16.8, 3H), 7.05 (d, $^3J_{HP}$ = 6.8, 6H), 6.56 (d, $^3J_{HH}$ = 16.8, 3H), 2.66 (q, $^3J_{HH}$ = 7.5, 12H), 1.97 – 1.68 (m, 24H), 1.40 ppm (t, $^3J_{HH}$ = 7.5, 18H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 142.1 (d, $^3J_{CP}$ = 5.2), 140.7 (d, $^1J_{CP}$ = 21.9), 138.3 (s), 135.2 (s), 133.4 (s), 128.1 (d, $^2J_{CP}$ = 15.6), 127.0 (s), 123.3 (s), 27.9 (d, $^2J_{CP}$ = 3.5), 27.1 – 27.0 (m), 15.4 ppm (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –16.8 ppm (s). MS (EI): *m/z* = 693.6 (100.0%) $[M–(C_4H_8)P–C_2H_6]^+$, 723.7 (44.1%) $[M–(C_4H_8)P]^+$, 810.7 (5.1%) $[M]^+$.

Poly[μ-1,3,5-tris[(*E*)-(4-phospholano-2,6-diethyl)styryl]-benzene-κ^3P,P',P'']gold(I) chloride (2). 164 mg (202 µmol; 1.0 eq) 1,3,5-Tris[(*E*)-(4-phospholano-2,6-diethyl)styryl]benzene were dissolved in 10 ml dichloromethane followed by the dropwise addition of 65 mg (202 µmol; 1.0 eq) [AuCl(tht)] in 5 ml dichloromethane, resulting in the formation of a white precipitate, which dissolved again, after the addition was completed. The mixture was stirred for 30 min at room temperature, filtered and all volatiles were removed in vacuo. Suitable crystals of **2** for single-crystal X-ray crystallography were obtained by dissolving the solid in 30 ml *o*-difluorobenzene, followed by filtration and subsequent gas diffusion of *n*-hexane into the solution at room temperature. ^1H NMR and $^{31}P\{^1H\}$ NMR and mass spectra were recorded of the solid before crystallisation, while IR spectra and elemental analysis were obtained from crystalline **2**.

Found C, 61.91; H, 6.19. Calc. for $C_{54}H_{69}AuClP_3 \cdot 2.5\ C_6H_4F_2$: C, 62.37; H, 5.99. IR (ATR): $\tilde{\nu}$ = 3336 (w), 2962 (s), 2931 (s), 2870 (s), 2361 (w), 1617 (w), 1587 (m), 1505 (s), 1455 (m), 1414 (w), 1265 (s), 1192 (w), 1101 (m), 1059 (m), 1024 (m), 969 (m), 875 (w), 842 (m), 753 (s), 687 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 7.53 (s, 3H), 7.40 (d, $^3J_{HP}$ = 13.2, 6H), 7.27 (d, $^3J_{HH}$ = 16.7, 3H), 6.67 (d, $^3J_{HH}$ = 16.6, 3H), 2.79 (q, $^3J_{HH}$ = 7.5, 12H), 2.54 – 2.02 (m, 24H), 1.22 ppm (t, $^3J_{HH}$ = 7.5, 18H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 26.5 ppm (s). MS (ESI(+), CH_2Cl_2): L = $C_{54}H_{69}P_3$, *m/z* = 1471.3 $[Au_3Cl_2L]^+$, 1705.2 $[Au_4Cl_3L]^+$, 1937.2 $[Au_5Cl_4L]^+$. Details for TGA/DSC measurements of **2** are given in the ESI.

References

1. S. H. Lim and S. M. Cohen, *Inorg. Chem.*, 2013, **52**, 7862.
2. T. R. Cook and P. J. Stang, *Chem. Rev.*, 2015, **115**, 7001.
3. A. J. McConnell, C. S. Wood, P. P. Neelakandan and J. R. Nitschke, *Chem. Rev.*, 2015, **115**, 7729.
4. S. L. James, *Chem. Soc. Rev.*, 2009, **38**, 1744.
5. H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber.*, 1977, **110**, 2751.
6. J. Shain and J. P. Fackler, *Inorg. Chim. Acta*, 1987, **131**, 157.
7. L. S. Liou, C. P. Liu and J. C. Wang, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1994, **50**, 538.
8. S. Al-Baker, W. E. Hill and C. A. McAuliffe, *Dalton Trans.*, 1985, 2655.
9. P. A. Bates and J. M. Waters, *Inorg. Chim. Acta*, 1985, **98**, 125.
10. E. J. Fernández, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna and J. M. Lopez-de-Luzuriaga, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 87.

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11. G. Ferguson, E. J. Gabe, T. R. Spalding and A. M. Kelleher, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **52**, 768.
12. J. Yau and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1997, 1103.
13. C. A. Wheaton, M. C. Jennings and R. J. Puddephatt, *Z. Naturforsch., B: Chem. Sci.*, 2009, **64**, 1469.
14. T. M. Dau, B. D. Asamoah, A. Belyaev, G. Chakkaradhari, P. Hirva, J. Jänis, E. V. Grachova, S. P. Tunik and I. O. Koshevoy, *Dalton Trans.*, 2016, **45**, 14160.
15. Q. Xu, F. Zhang, M. C. Jennings and R. J. Puddephatt, *Polyhedron*, 2017, **131**, 46.
16. M. N. I. Khan, R. J. Staples, C. King, J. P. Fackler and R. E. P. Winpenny, *Inorg. Chem.*, 1993, **32**, 5800.
17. J. H. K. Yip and J. Prabhavathy, *Angew. Chem. Int. Ed.*, 2001, **40**, 2159.
18. R. Lin, J. H. K. Yip, K. Zhang, L. L. Koh, K.-Y. Wong and K. P. Ho, *J. Am. Chem. Soc.*, 2004, **126**, 15852.
19. S.-Y. Yu, Z.-X. Zhang, E. C.-C. Cheng, Y.-Z. Li, V. W.-W. Yam, H.-P. Huang and R. Zhang, *J. Am. Chem. Soc.*, 2005, **127**, 17994.
20. T. M. Dau, Y.-A. Chen, A. J. Karttunen, E. V. Grachova, S. P. Tunik, K.-T. Lin, W.-Y. Hung, P.-T. Chou, T. A. Pakkanen and I. O. Koshevoy, *Inorg. Chem.*, 2014, **53**, 12720.
21. S. H. Lim, Y. Su and S. M. Cohen, *Angew. Chem. Int. Ed.*, 2012, **51**, 5106.
22. J. R. Shakirova, E. V. Grachova, A. J. Karttunen, V. V. Gurzhiy, S. P. Tunik and I. O. Koshevoy, *Dalton Trans.*, 2014, **43**, 6236.
23. I. O. Koshevoy, M. Haukka, S. I. Selivanov, S. P. Tunik and T. A. Pakkanen, *Chem. Commun.*, 2010, **46**, 8926.
24. J. R. Shakirova, E. V. Grachova, V. V. Sizov, G. L. Starova, I. O. Koshevoy, A. S. Melnikov, M. C. Gimeno, A. Laguna and S. P. Tunik, *Dalton Trans.*, 2017, **46**, 2516.
25. P. M. van Calcar, M. M. Olmstead and A. L. Balch, *J. Chem. Soc., Chem. Commun.*, 1995, **29**, 1773.
26. M. Streitberger, A. Schmied and E. Hey-Hawkins, *Inorg. Chem.*, 2014, **53**, 6794.
27. G. R. Bourret, P. J. G. Goulet and R. B. Lennox, *Chem. Mater.*, 2011, **23**, 4954.
28. A. Hamel, A. Schier and H. Schmidbaur, *Z. Naturforsch., B: Chem. Sci.*, 2002, **57**, 877.
29. A. Houlton, D. M. P. Mingos, D. M. Murphy and D. J. Williams, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 30.
30. C. B. Dieleman, D. Matt and A. Harriman, *Eur. J. Inorg. Chem.*, 2000, **2000**, 831.
31. F. Caruso, M. Rossi, J. Tanski, C. Pettinari and F. Marchetti, *J. Med. Chem.*, 2003, **46**, 1737.
32. S. A. Bhat, J. T. Mague and M. S. Balakrishna, *Dalton Trans.*, 2015, **44**, 17696.
33. G. Lübbe, R. Fröhlich, G. Kehr and G. Erker, *Inorg. Chim. Acta*, 2011, **369**, 223.
34. J. L. Dempsey, A. J. Esswein, D. R. Manke, J. Rosenthal, J. D. Soper and D. G. Nocera, *Inorg. Chem.*, 2005, **44**, 6879.
35. D. E. Jenkins, R. E. Sykora and Z. Assefa, *Inorg. Chim. Acta*, 2013, **406**, 293.
36. G. Agbeworvi, Z. Assefa, R. E. Sykora, J. Taylor and C. Crawford, *J. Mol. Struct.*, 2016, **1108**, 508.
37. V. Rampazzi, J. Roger, R. Amardeil, M.-J. Penouilh, P. Richard, P. Fleurat-Lessard and J.-C. Hierso, *Inorg. Chem.*, 2016, **55**, 10907.
38. S. Attar, W. H. Bearden, N. W. Alcock, E. C. Alyea and J. H. Nelson, *Inorg. Chem.*, 1990, **29**, 425.
39. P. G. Jones, G. M. Sheldrick, J. A. Muir, M. M. Muir and L. B. Pulgar, *J. Chem. Soc., Dalton Trans.*, 1982, 2123.
40. J. Zank, A. Schier and H. Schmidbaur, *J. Chem. Soc., Dalton Trans.*, 1999, 415.
41. M. Bardají, Teresa de la Cruz, M., P. G. Jones, A. Laguna, J. Martínez and M. Dolores Villacampa, *Inorg. Chim. Acta*, 2005, **358**, 1365.
42. V. J. Catalano, M. A. Malwitz, S. J. Horner and J. Vasquez, *Inorg. Chem.*, 2003, **42**, 2141.
43. Z. Assefa, J. M. Forward, T. A. Grant, R. J. Staples, B. E. Hanson, A. A. Mohamed and J. P. Fackler, *Inorg. Chim. Acta*, 2003, **352**, 31.
44. C. Khin, A. S. K. Hashmi and F. Rominger, *Eur. J. Inorg. Chem.*, 2010, **2010**, 1063.
45. H. Kameo, T. Kawamoto, D. Bourissou, S. Sakaki and H. Nakazawa, *Organometallics*, 2015, **34**, 1440.
46. M. Sircoglou, M. Mercy, N. Saffon, Y. Coppel, G. Bouhadir, L. Maron and D. Bourissou, *Angew. Chem. Int. Ed.*, 2009, **48**, 3454.
47. S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov and D. Bourissou, *Angew. Chem. Int. Ed.*, 2008, **47**, 1481.
48. S. M. F. Vilela, D. Ananias, A. C. Gomes, A. A. Valente, L. D. Carlos, J. A. S. Cavaleiro, J. Rocha, J. P. C. Tomé and F. A. Almeida Paz, *J. Mater. Chem.*, 2012, **22**, 18354.
49. Oxford Diffraction Ltd, *CrysAlis Pro*, Oxfordshire, UK, 2014.
50. Oxford Diffraction Ltd, *SCALE3 ABSPACK*, Oxfordshire, UK, 2014.
51. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.
52. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2015, **71**, 3.
53. G. M. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3.