Preparation, Structure and Gold(I) Complexation of *p*-Xylylene-1,4-diphosphines

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Dedicated to Professor Alfred Schmidpeter on the occasion of his 75th birthday

1,4-Dimethyl-2,5-di(phosphinyl)benzene (**1**) was prepared in high yield in a four-step synthesis from 1,4-dibromo-2,5-dimethyl-benzene. The intermediates with $(Et_2N)_2P$ and Cl_2P groups (**2**, **3**) with the corresponding substitution pattern have been isolated and structurally characterized. All three compounds (**1** – **3**) adopt a centrosymmetrical conformation with one of the P-X bonds of each X_2P group located in the ring plane while the other reaches out from this plane in a roughly perpendicular orientation. Distortions of the ring and its substituents from a standard planar hexagonal geometry are readily explained by invoking steric and inductive effects. The crystal structure of 1,4-dibromo-2,5-dimethyl-benzene has also been determined for reference purposes. Compound **1** was employed as a substrate for auration by tri(gold)oxonium salts of the type $\{[(R_3P)Au]_3O\}BF_4$. Hexanuclear complex salts of the type $\{[(R_3P)Au]_3P(C_6H_2Me_2)P[Au(PR_3)]_3\}(BF_4)_2$ were obtained in almost quantitative yield with $R_3P = {}^tBu_3P$ (**4**) and Ph_3P (**5**). The former (**4**) has the higher thermal stability, it could be crystallized and its structure determined. It features a conformation in which the xylene plane bisects one of the Au-P-Au angles at both tetrahedrally coordinated central phosphorus atoms placing its methyl groups in sterically least hindered positions. Compound **5** is labile in solution and shows rapid ligand exchange on the NMR time scale. The limited stability has also been confirmed by mass spectrometry. Similar structural details and differences in stability were observed in the related trinuclear gold complexes based on 1-naphthyl-phosphine, which were prepared as reference materials using the same preparative procedure. Of the two compounds $\{(1\text{-}C_{10}H_7)\text{-}P[Au(PR_3)]_3\}BF_4$, with $R_3P = {}^tBu_3P$ (**6**) and Ph_3P (**7**), the former is the more stable species. In the solid state the cation approaches mirror symmetry in a conformation comparable to that of **4**. Compound **7** is thermally labile and shows a rapid ligand exchange in solution.

Key words: Primary Phosphines, Phenylene-1,4-diphosphines, Gold Complexes

Introduction

Primary phosphines RPH_2 are attracting current interest [1] owing to their synthetic potential a) for the preparation of new types of functional or chiral ligands [2], b) as substrates for hydrophosphination reactions [3] and c) for the construction of multidimensional frameworks [4]. Regarding the latter aspect, polyfunctional primary *aryl*phosphines with a rigid skeleton are particularly useful for the design of chain-like polymers or sheet-like layer structures with a variety of connectivity motifs which depend on the substitution pattern of the parent aromatic hydrocarbon.

In our own previous studies, work had focused on the chemistry of representative examples like 1,3,5-tri(phosphinyl)benzene, 1,8-di(phosphinyl)naphthalene and 2,5-di(phosphinyl)-thiophene and -furan [5 – 7]. In the course of these studies it has been noted that there is still a paucity of information on the efficient preparation and the properties of 1,4-di(phosphinyl)benzenes (**A**) with the most simple and obvious structural pattern for α,ω-ligation of benzene rings *via* phosphorus atoms [8, 9].

Ring-unsubstituted 1,4-di(phosphinyl)benzene was first prepared by Wagner *et al.* in 1962, but for quite some time its chemistry remained largely unexplored [8]. The compound is a distillable liquid, which could not be crystallized. Through the preparation and structural characterization of hexa- and even octa-nuclear gold(I) complexes it could be demonstrated that the *p*-phenylene group of the substrate can act as a rigid plate-like unit connecting triangular or

square gold clusters by capping them with the phosphorus atoms [10]. In the absence of steric hindrance by additional ring substituents, there is no conformational preference for the orientation of the phenylene plane relative to the Au_3 triangle or Au_4 square as shown by NMR spectroscopy in solution.

The present study therefore was initiated in order to prepare a symmetrically substituted molecule, specifically the *p*-xylylene homologue, *vic*. 1,4-dimethyl-2,5-di(phosphinyl)benzene (**1**). It was hoped that owing to the reduced mobility of the $-PH_2$ groups this homologue should crystallize more readily than the parent compound and allow the determination of its crystal structure. It was further expected that its polynuclear gold(I) complexes will exhibit a localized conformation of the xylylene unit.

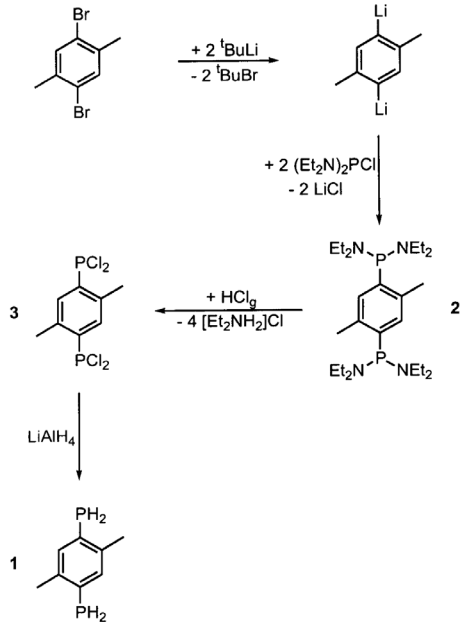
The above structural expectations were based on observations with the corresponding *p*-phenylene compounds with $-SiH_3$ substituents [11 – 16].

For the auration of the new diprimary phosphine **1**, established methods could be employed which were already used successfully in previous studies with phenyl-, *o*-tolyl-, mesityl- and [2,4,6-tri(*t*butyl)phenyl]-phosphine, as well as 1,2- and 1,4-di(phosphinyl)- and 1,3,5-tri(phosphinyl)-benzene [17 – 21].

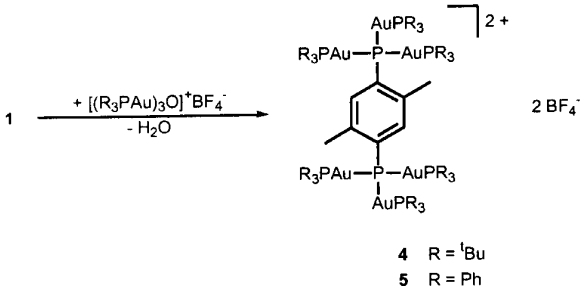
In a complementary investigation *1-naphthylphosphine*, obtained in a parallel study [6], was also triaurated and the product structurally characterized in order to provide a reference compound with a more pronounced steric effect of the aryl group (1-naphthyl).

Preparative Results

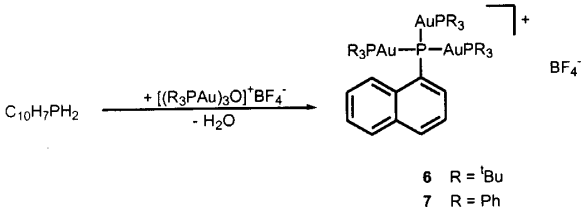
The preparation of compound **1** is outlined in Scheme 1. 1,4-Dibromo-2,5-dimethyl-benzene was lithiated with four equivalents of ^{t}BuLi in a tetrahydrofuran/pentane mixed solvent and the reaction mixture subsequently treated with two equivalents of bis(diethylamino)chlorophosphine. The product **2** was isolated by crystallization from pentane in 59% yield (m.p. 89 °C). Its conversion into the tetrachloride **3** was achieved in 93% yield by passing a stream of dry hydrogen chloride into its solution in hexane. A crystalline material (m.p. 66 °C) was obtained upon crystallization from dichloromethane at −30 °C. In the last step, compound **3** was reduced by an excess of $LiAlH_4$ in diethylether to give a 92.5% yield of the target phosphine **1** which was isolated as a crystalline solid (from diethylether at −30 °C, m. p. 51 °C).



Scheme 1. Synthetic pathway to 1,4-dimethyl-2,5-di(phosphinyl)benzene (**1**).



Scheme 2. Synthesis of the hexanuclear complexes **4** and **5**.



Scheme 3. Synthesis of the trinuclear complexes **6** and **7**.

The diprimary arylphosphine **1** was aurated by treating it with two different oxonium reagents $\{[(R_3P)Au]_3O\}BF_4$ in dichloromethane at −78 °C (R = ^{t}Bu, Ph), (Scheme 2). The product **4** with the ^{t}Bu$_3$P ligands could be crystallized from diethylether/acetone in 98.5% yield (m.p. 204 °C with decomposition). The analogous complex with Ph_3P

ligands (**5**) was also obtained in high yield as a pale yellow powder (m.p. 144 °C with decomposition), but could not be crystallized.

1-Naphthyl-phosphine [6, 22 – 27] was converted into the corresponding trinuclear gold complexes (**6**, **7**) using the same procedures (Scheme 3). While **6** (with the $^{t}Bu_3P$ ligands) was again readily crystallized (98.3% yield, m.p. 142 °C with decomposition), compound **7** was received as a yellow powder (97.9% yield, m. p. 123 °C with decomposition).

Analytical and Spectroscopic Data

Compounds **1** – **3** were characterized by microanalysis, mass spectrometry and NMR spectroscopy. In the EI mass spectra, the molecular ions were observed with high intensity. The peaks featured the expected isotope patterns (**3**) and the fragments originating from the consecutive loss of hydrogen atoms (**1**). The $^{31}P\{^{1}H\}$ NMR spectra showed singlet resonances in the expected shift ranges, with the tetrachloride (**3**) in the low-field region at $\delta = 159.8$ ppm, the tetraamide (**2**) at $\delta = 93.0$ ppm, and the tetra-hydride (**1**) up-field at $\delta = -131.8$ ppm (all in CD_2Cl_2 at 25 °C). The ^{1}H and ^{31}P resonances of the $-PH_2$ groups of compound **1** appear as the A and X parts of an $A_2XX'A'_2$ multiplet, respectively, (with additional fine-structure arising from weak couplings with the aryl hydrogen atoms), which were not fully analyzed.

The gold complexes **4** – **7** gave satisfactory elemental analysis data. In the FAB mass spectra the mono- (**6**) and dications (**4**) of the salts were detected as the parent ions or with low intensity (**7**), while for **5** only fragment ions could be registered. The ^{31}P NMR spectra showed significant differences for the complexes with the $^{t}Bu_3P$ and Ph_3P ligands, in that only the former featured the expected AX_3 multiplicities (d, q) for the $P_A(AuP_X)_3$ groups in CD_2Cl_2 at 25 °C. In these spectra it was unnecessary to treat the coupling pattern as based on an extended $X_3AA'X'_3$ spin system, because the A-A' coupling appears to be almost negligible. For **5** cooling to −80 °C was required to obtain the doublet/quartet pattern. This phenomenon indicated an exchange broadening of $AuPR_3$ or PR_3 groups in solution, which is slow for $^{t}Bu_3P$, but rapid for Ph_3P ligands on the NMR time scale. In this context it should be noted that complexes **5** and **7** were found to have lower thermal stability than **4** and **6** both as solids and in solution. However, there was no NMR evidence for inequivalence of $(AuPR_3)$ groups in solution which would have indicated hindered rotation of $P(AuP)_3$ groups about the C-P(Au_3) bonds. The ^{1}H and $^{13}C\{^{1}H\}$ NMR signals show no anomalies. No efforts were made to completely analyze or assign all phenyl and naphthyl resonances. The data are listed in the Experimental Section.

Crystal and Molecular Structures

1,4-Dibromo-2,5-dimethyl-benzene: The structure of this precursor molecule (Scheme 1) was determined in order to have reference data for the phosphines derived thereof. Crystals (from ethanol) are monoclinic (space group $P2_1/n$) with the unit cell containing Z = 4 molecules with no crystallographically imposed symmetry (Fig. 1). Except for the methyl hydrogen atoms all atoms are largely coplanar with the representative torsional angles all deviating less than 1° from 180°. Relative to the 120° standard, the endocyclic angles at C2/C5 and C1/C4 are smaller by 3° and larger by 2° (average), respectively, as expected for electron-donating methyl and electron-withdrawing bromo substituents [12, 16, 28 – 31]. The exocyclic angles indicate a slight repulsion of neighbouring methyl and bromo substituents (Caption to Fig. 1). The packing of the molecules in the crystal shows no π-π stacking or hydrogen phenyl embrace and appears to be governed by intermolecular Br···Br contacts.

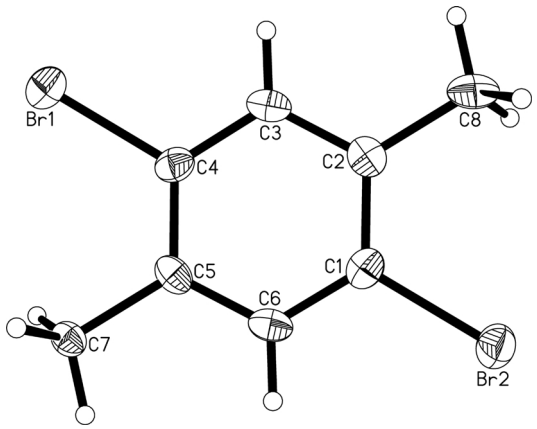


Fig. 1. Molecular structure of 1,4-dibromo-2,5-dimethylbenzene (ORTEP, 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Br1-C4 1.908(7), Br2-C1 1.892(7), C2-C8 1.560(10), C5-C7 1.549(9); C1-C2-C3 116.9(6), C2-C3-C4 120.3(6), C2-C1-C6 121.9(6), C3-C4-C5 122.3(6), C4-C5-C6 117.0(6), C5-C6-C1 121.7(7), Br1-C4-C5 120.5(5), Br1-C4-C3 117.2(5), Br2-C1-C2 119.8(5), Br2-C1-C6 118.3(5), C7-C5-C4 121.9(6), C7-C5-C6 121.1(6), C8-C2-C1 122.4(6), C8-C2-C3 120.7(6). All dihedral angles C-C-C-C/Br are very close to 0 or 180°.

1,4-Bis[bis(diethylamino)phosphinyl]-2,5-dimethyl-benzene (**2**): Crystals (from pentane at −30 °C) are monoclinic (space group $P2_1/c$), with Z = 2 centrosymmetrical molecules in the unit cell (Fig. 2). One of the four independent ethyl groups was found disordered over two positions. The endocyclic C-C-C angles are large at C3, but small and equal at C1 and C2 reflecting the similarity of the electronegativities of C and P substituents. One of the two P-N bonds (P1-N2), and thus the nitrogen atom N2, lie roughly in the molecular plane [torsional angle N2-P1-C1-C3 = 9.30(12)°], while the second P-N bond (P1-N1) reaches out from this plane [with a torsional angle N1-P1-C1-C3 = 122.63(11)°] (Fig. 2). The methyl carbon atoms deviate more strongly from the benzene plane than in the dibromo precursor (above). These distortions are clearly necessary to relieve steric crowding. It is probably due to the proximity of the hydrogen atom at C3 to the Et_2N group which has its N atom in the molecular plane (N2) that causes an unexpected tilting of the C1-P1 bond *towards* the methyl group [C3-C1-P1 = 122.17(10)°].

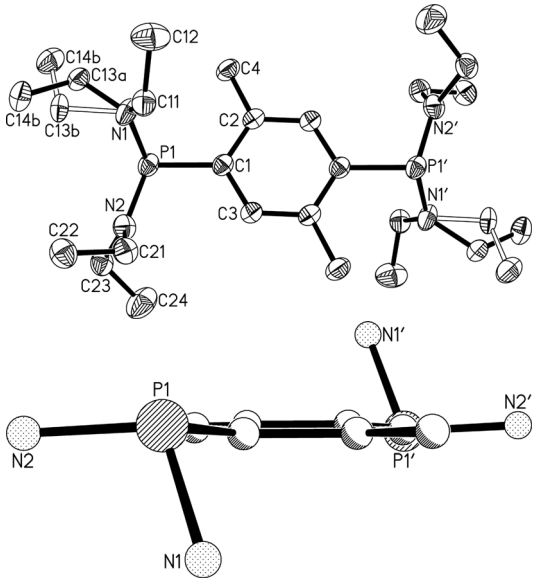


Fig. 2. *Top:* Molecular structure of compound **2** projected onto the xylene plane (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted; one ethyl group is disordered over two positions). *Bottom:* Projection parallel to the xylene plane (arbitrary radii, ethyl groups and hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: P1-C1 1.8422(13), P1-N1 1.6939(12), P1-N2 1.6956(13), C2-C4 1.5127(18); P1-C1-C2 119.46(10), P1-C1-C3 122.17(10), C1-C2-C4 122.31(12), C3'-C2-C4 118.89(12). The center of the xylene ring is a center of inversion.

1,4-Bis(dichlorophosphinyl)-2,5-dimethyl-benzene (**3**): Crystals (from dichloromethane at −30 °C) are monoclinic (space group $P2_1/c$), with Z = 2 centrosymmetrical molecules in the unit cell (Fig. 3). The conformation resembles that of compound **2**. The endocyclic angles show only minor deviations from 120°, but the exocyclic angles P1-C2-C1 = 124.16(12)° and P1-C2-C3 = 115.91(12)° are significantly different and indicate again (*c.f.* **2**) a leaning over of the PCl_2 groups *towards* the methyl group owing to the proximity of the hydrogen atom at C1 and the in-plane chlorine atom Cl2 (the dihedral angles Cl2-P1-C2-C1 and P1-C2-C3-C4 are only 4.22(14)° and −4.9(2)°, respectively).

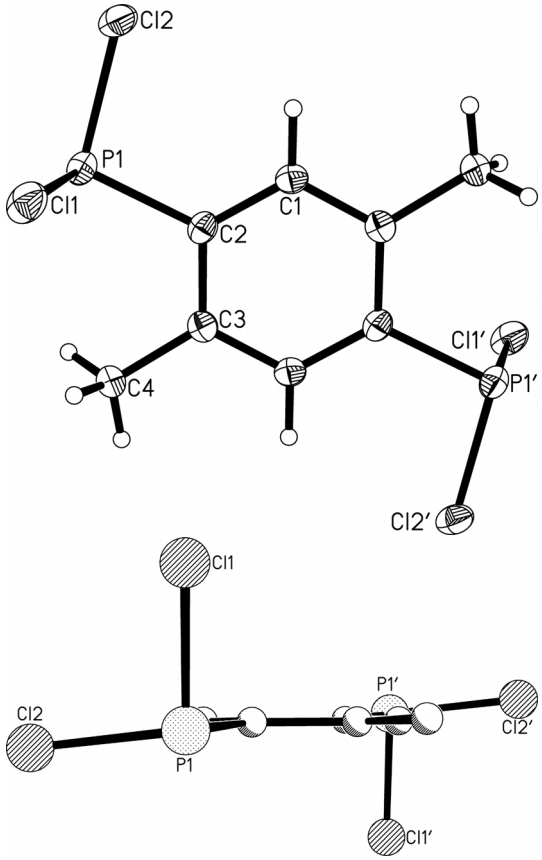


Fig. 3. *Top:* Molecular structure of compound **3** projected perpendicular to the xylene plane (ORTEP, 50% probability ellipsoids). *Bottom:* Projection parallel to the xylene plane (arbitrary radii, hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: P1-C2 1.8309(17), P1-Cl1 2.0726(6), P1-Cl2 2.0553(6), C3-C4 1.514(2); P1-C2-C1 124.16(12), P1-C2-C3 115.91(12), C1'-C3-C4 119.67(14), C2-C3-C4 122.03(15). The center of the xylene ring is a center of inversion.

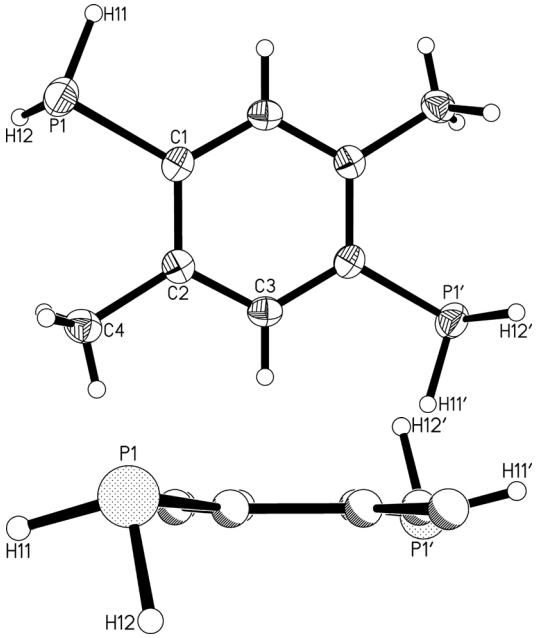


Fig. 4. *Top:* Molecular structure of compound **1** projected perpendicular to the xylene plane (ORTEP, 50% probability ellipsoids). *Bottom:* Projected parallel to the xylene plane (arbitrary radii, xylene and methyl hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: P1-C1 1.8361(15), P1-H11 1.28(2), P1-H12 1.29(3), C2-C4 1.533(2); P1-C1-C2 119.66(12), P1-C1-C3' 121.08(12), C1-C2-C4 121.03(14), C3-C2-C4 120.51(14). The center of the xylene ring is a center of inversion.

1,4-Dimethyl-2,5-di(phosphinyl)benzene (**1**): Crystals (from diethylether at −30 °C) are monoclinic (space group $P2_1/n$) with $Z = 2$ centrosymmetrical molecules in the unit cell (Fig. 4). The overall conformation of molecule **1** resembles that of **2** and **3**, but there are only minor signs of steric crowding. The methyl carbon atoms reside in the molecular plane and only the phosphorus atoms are slightly offset. Within the molecular plane, the angles C1-C2-C4 and C2-C1-P1 deviate from the 120° standard by only 1°. The leaning over of the (dichloro)phosphinyl group towards the methyl group observed in **3** is not discernible in **1**, probably owing to the negligible steric effect of the hydrogen atoms. The endocyclic angles are a little larger at C3, but smaller and virtually equal at C1 and C2. The packing of the molecules in the unit cell shows no evidence for hydrogen bonding or other non-standard van der Waals interactions. This observation is in agreement with previous findings.

1,4-Dimethyl-2,5-bis{tris[(tri(^{t}*butyl)phosphine)-gold(I)]phosphonio}benzene bis(tetrafluoroborate)* (**4**): Crystals (from diethylether/acetone at −30 °C) are monoclinic (space group $P2_1/n$) with two formula units of the salt, four acetone and four diethylether molecules in the unit cell: $(\mathbf{4})_2(Me_2CO)_4(Et_2O)_4$. The structure of the centrosymmetrical dication is shown in Fig. 5. There are no unusual intermolecular contacts between these dications and the anions or solvent molecules. The phosphorus atoms of the precursor molecule **1** are seen to be triply aurated attaining a quasi-tetrahedral configuration with average Au-P-Au and C-P-Au angles of 105.3° and 113.4°, respectively. The gold atoms are linearly two-coordinate with conventional Au-P bond lengths. These structural details are in agreement with results of structural studies of other triply aurated primary phosphines. No significant aurophilic bonding can be invoked due to the large intermetallic distances [17–19].

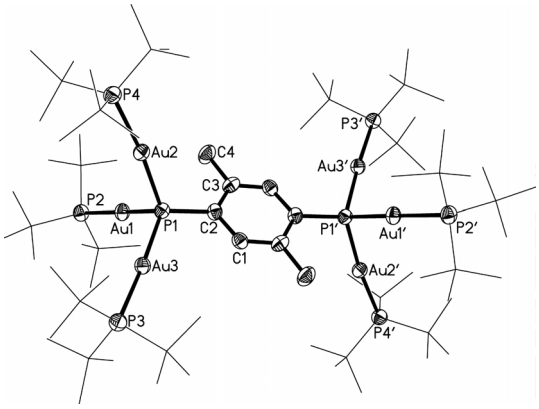


Fig. 5. Structure of the dication of compound **4** in the $\mathbf{4}\cdot(Et_2O)_2(Me_2CO)_2$ solvate (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: P1-Au1 2.3085(16), P1-Au2 2.3123(16), P1-Au3 2.3129(15), P1-C2 1.822(6), C3-C4 1.519(8), C2-C3 1.421(8); C2-P1-Au1 113.3(2), C2-P1-Au2 114.4(2), C2-P1-Au3 112.4(2), Au1-P1-Au2 103.91(6), Au2-P1-Au3 105.37(6), Au1-P1-Au3 106.60(6), C2-C3-C4 121.8(6), P1-C2-C3 122.7(4), P1-C2-C1 119.6(4), C4-C3-C1' 119.8(6). The center of the xylene ring is a center of inversion.

The central xylene plane roughly bisects the angle Au1-P1-Au2 thus placing each of its methyl substituents between a pair of [(^{t}Bu$_3$P)Au] groups in order to minimize steric pressure. As shown by NMR studies in solution (above), this conformation is not fixed and rapid rotation of the components about the P1-C2 axes is possible (on the NMR time scale).

1-Naphthyl-tris{[tri(^{t}*butyl)phosphine]gold(I)}phosphonium tetrafluoroborate*, (**6**): Crystals (from diethylether/acetone at −30 °C) are monoclinic (space

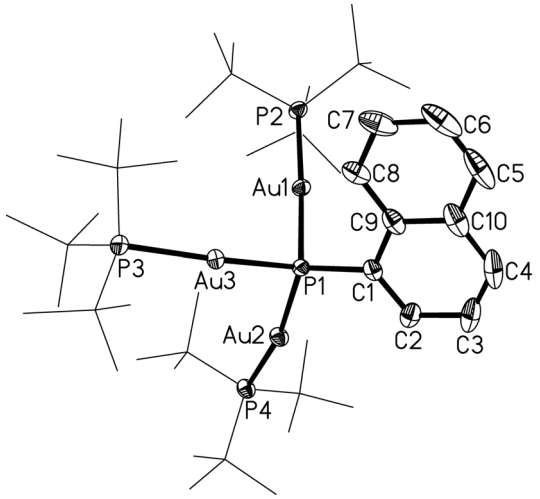


Fig. 6. Structure of the cation of compound **6** (ORTEP, 50% probability ellipsoids, hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: P1-Au1 2.3188(9), P1-Au2 2.2971(9), P1-Au3 2.3145(9), P1-C1 1.836(4); C1-P1-Au1 106.14(11), C1-P1-Au2 118.35(13), C1-P1-Au3 119.61(12), Au1-P1-Au2 103.37(4), Au2-P1-Au3 103.03(3), Au1-P1-Au3 104.45(3).

group $P2_1/c$) with Z = 4 formula units in the unit cell. The structure of the cation is shown in Fig. 6. The geometry of the environment of the phosphonium center is very similar to that in compound **4** and needs no further comment. The plane of the naphthyl group almost exactly bisects the angle Au1-P1-Au3 with dihedral angles C9-C1-P1-Au1/Au3 of 58.7(3) and −58.9(3)°, respectively. This conformation places the annealed benzene ring C5-C10 between two of the three bulky [(^{t}Bu$_3$P)Au] groups, very similar to the conformation observed in compound **4** with respect to the xylylene methyl groups. Neglecting the orientation of the ^{t}Bu groups, the structure of the cation in compound **6** thus approaches very closely mirror symmetry. However, in solution the three [(^{t}Bu$_3$P)Au] groups are NMR-equivalent and only one ^{31}P signal is observed for the tertiary phosphine ligands (in CD_2Cl_2 at 25 °C), suggesting free rotation of the naphthyl "flag" around the P1-C1 "pole".

Conclusions

In the preparative part of this work it has been demonstrated that diprimary phosphines based on the *p*-xylylene skeleton can readily be prepared in high yield from 1,4-Br$_2$-2,5-Me$_2$-C$_6$H$_2$ following the four-step procedure shown in Scheme 1. The target compound **1** is obtained as a stable, colourless, crystalline solid (m. p. 51 °C), which is soluble in most low-polarity solvents. Upon reaction with tri[gold(I)]oxonium salts, it is converted in almost quantitative yield into the corresponding hexanuclear diquaternary phosphonium salts **4** and **5** (Scheme 2). The complex **4** with the extremely bulky auxiliary ligand ^{t}Bu$_3$P shows significantly higher thermal stability than complex **5** with the smaller Ph$_3$P ligand, probably due to the efficient steric protection of the sensitive parts of the dication. The analogous reactions with 1-naphthyl-phosphine afford the trinuclear phosphonium salts **6** and **7** (Scheme 3), of which the former – with its ^{t}Bu$_3$P ligands – again shows higher thermal stability.

NMR spectroscopic studies at room temperature have indicated that in dichloromethane solutions of the more labile complexes **5** and **7** there is ligand mobility which probably opens the decomposition pathway. By contrast, no such process is observed for the robust complexes **4** and **6**. For all four complexes (**4**–**7**) there is no NMR-evidence for hindered rotation of the [(R$_3$P)Au]$_3$P units (with their local C_{3v} symmetry) about the P-C(arene) bonds connecting them to the flat xylylene or naphthyl units (with local C_s symmetry).

Single crystal X-ray diffraction studies of compounds **1**–**3** and their dibromo precursor have shown that all four molecules have a center of inversion, either imposed by crystal symmetry (**1**–**3**) or to a good approximation (C$_6$H$_2$Me$_2$Br$_2$). Significant distortions of the standard geometry are observed only for **2** with its bulky P(NEt$_2$)$_2$ substituents. The PH$_2$ groups in **1** are not sterically hindered and give freely access for extensive complexation. The minor distortions of the endocyclic angles of the central benzene ring in molecules **1**–**3** show that carbon and phosphorus have very similar electronegativity ("phosphorus, the carbon copy" [32]).

The structures of the complexes **4** and **6** have also been determined, for the former from a diethylether/acetone solvate **4**·(Et$_2$O)$_2$(Me$_2$CO)$_2$. The [(R$_3$P)Au]$_3$P groups have a pseudo-tetrahedral configuration attached to the flat xylylene and naphthyl groups, respectively. The xylene plane bisects two of the six Au-P-Au angles establishing inversion and mirror symmetry for the dication of **4**, while the naphthyl plane bisects one of the three Au-P-Au angles generating approximate mirror symmetry for the cation of **6**.

The two structures show efficient steric shielding of the core units of the cations which explains the robust nature of the two poly(gold)phosphonium salts.

Experimental Section

General: All experiments were carried out in an atmosphere of dry nitrogen. Solvents were dried, distilled and saturated with nitrogen; glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. The starting materials were commercially available except for $(Et_2N)_2PCl$ and the two oxonium salts which were prepared following literature procedures [33 – 36]. *MS*: Finnigan MAT 90 (FAB, 4-nitro-benzyl alcohol); HP 5971A (EI, 70 eV). *NMR*: JEOL JNM-GX-270/400. Standards: TMS (^{1}H, ^{13}C), H_3PO_4 (85%, ^{31}P), $BF_3{\cdot}OEt_2$ (^{11}B), $CFCl_3$ (^{19}F).

Compound ***2***: A solution of $C_6H_2Me_2Br_2$ (12.0 g, 45 mmol) in THF (360 ml) was cooled to −78 °C and treated dropwise with a solution of ^{t}BuLi in pentane (135 ml, 1.5 M, 203 mmol). The reaction mixture was allowed to warm to 0 °C and stirred for 1 h at this temperature. The yellow solution turned into a pale yellow suspension, which was again cooled to −78 °C and treated with $(Et_2N)_2PCl$ (30.1 g, 143 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. Thereafter all volatiles were removed in a vacuum and the residue extracted with 3 × 150 ml of pentane. The pentane extracts were concentrated in a vacuum to a volume of 100 ml and cooled to −30 °C to crystallize the product; colourless crystals, 12.2 g (59.2% yield), m.p. 89 °C. $C_{24}H_{48}N_4P_2$ (454.61): calcd. C 63.41, H 10.64, P 13.63; found C 62.98, H 10.66, P 13.26. MS(EI): *m/z* 454 [M^+]. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: $\delta = 93.0$ (s); $^{13}C\{^1H\}$: 139.9 (d, $J = 4.6$, *C*P), 136.8 (d, $J = 25.4$, *C*Me), 133.2 (m, AXX', *C*H), 44.0 (d, $J = 16.9$, CH_2), 20.8 (d, $J = 13.9$, *Me*C), 15.0 (s, *Me*CH_2). ^{1}H: 7.16 (m, AA'XX', 2H, *H*C), 3.07 (m, 16H, CH_2), 2.32 (s, 6H, *Me*C), 1.09 (t, $J = 7.0$, 24H, *Me*CH_2).

Compound ***3***: A solution of **2** (11.45 g, 25.2 mmol) in hexane (500 ml) was cooled to 0 °C and saturated with a stream of gaseous HCl. The reaction mixture was stirred for 1 h and again saturated with HCl gas. This procedure was repeated until the supernatant solution remained clear upon further addition of HCl. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h before the precipitate was removed by filtration and washed with 2 × 100 ml of hexane. The filtrate and the extracts were combined and the solvent evaporated in a vacuum. From a solution of the residue in dichloromethane the product separated upon cooling to −30 °C; colourless crystals sensitive to oxidation and hydrolysis, 7.21 g (93% yield), m.p. 66 °C. $C_8H_8Cl_4P_2$ (307.91): calcd. C 31.21, H 2.62, P 20.12; found C 31.21, H 2.69, P 19.90. MS(EI): *m/z* 308 [M^+]. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: $\delta = 159.8$ (s); $^{13}C\{^1H\}$: 142.5 (d, $J = 59.2$, *C*P), 139.1 (d, $J = 34.8$, *C*Me), 132.3 (d, $J = 13.0$, *C*H), 19.7 (d, $J = 25.4$, C*Me*); ^{1}H: 7.89 (m, AA'XX', 2H, *H*C), 2.67 (d, $J = 3.3$, 6H, *Me*C).

Compound ***1***: A solution of **3** (6.44 g, 20.9 mmol) in diethylether (50 ml) was added slowly to a stirred suspension of $LiAlH_4$ (6.35 g, 167.3 mmol) in diethylether (200 ml) at −78 °C. The reaction mixture was then allowed to warm to room temperature and subsequently stirred for 12 h. After cooling to 0 °C the mixture was treated with degassed water (40 ml), stirred for 1 h and filtered. The residue was extracted with 2 × 50 ml of diethylether, the filtrate combined with the extracts and dried over $MgSO_4$. Evaporation of the solvents in a vacuum left a residue which could be crystallized from diethylether at −30 °C; colourless, air-sensitive crystals, m.p. 51 °C, 3.29 g (92.5% yield). $C_8H_{12}P_2$ (170.13): calcd. C 56.48, H 7.11, P 36.41; found C 56.36, H 7.10, P 36.32. MS(EI): *m/z* 170 [M^+]. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: $\delta = -131.8$ (s); $^{13}C\{^1H\}$: 138.9 (dd, $J = 11.5$ and 4.6, *C*Me), 136.4 (dd, $J = 13.1$ and 2.3, *C*H), 129.6 (d, $J = 10.0$, *C*P), 21.4 (d, $J = 10.0$, *Me*); ^{1}H: 7.29 (m, AA'XX', 2H, *H*C), 3.82 (d, $J = 204.3$, 4H, H_2P), 2.31 (s, 6H, *Me*).

Compound ***4***: A solution of the phosphine **1** (8.4 mg, 0.05 mmol) in dichloromethane (10 ml) was added slowly to a solution of $\{[(^tBu_3P)Au]_3O\}BF_4$ (128.4 mg, 0.10 mmol) in the same solvent (20 ml) at −78 °C with stirring. After 2 h the reaction mixture was warmed to room temperature, concentrated to a volume of 5 ml in a vacuum, and pentane (50 ml) was added to precipitate the product. The compound crystallized as the solvate **4**·$(Et_2O)_2(Me_2CO)_2$ from acetone solution upon layering with diethylether at −30 °C. The solvent can be removed in a vacuum; 133 mg (98.5% yield), m.p. 204 °C with decomposition. $C_{80}H_{170}Au_6B_2F_8P_8$ (2735.40): calcd. C 35.13, H 6.26, P 9.06; found C 34.78, H 6.16, P 9.17. MS(FAB) *m/z* 1282.0 (100%) [M^{2+}]. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: $\delta = 99.3$ (d, $J = 235.8$, *P*Au), −7.0 (q, $J = 235.8$, PAu_3); ^{31}P: 99.3 (2 × 28, 18 lines resolved, $^2J_{PP}$ 235.8 and $^3J_{PH}$ 13.9, *P*Au), −7.0 (qd, $^2J_{PP}$ 235.8 and $^3J_{PH}$ 13.9, PAu_3); $^{13}C\{^1H\}$: 141.0 (d, $J = 22.3$, *C*P), 140.4 and 138.4 (2xm, AXX', *C*-2,5 / *C*-3,6), 40.0 (d, $J = 13.8$, CMe_3), 32.7 (s, *Me*), 24.5 (d, $J = 9.2$, Me_{xyl}); ^{1}H: 7.95 (m, AA'XX', 2H, C*H*), 2.64 (s, 6H, Me_{xyl}), 1.53 (d, $J = 13.5$, 162H, *Me*); ^{11}B: −2.1 (s); ^{19}F: −153.3 (s).

Compound ***5***: The preparation followed the procedure given for **4** with 11.8 mg (0.07 mmol) of **1** and 205.6 mg (0.14 mmol) of $\{[(Ph_3P)Au]_3O\}BF_4$; 204.6 mg (95.3% yield) of a yellow solid, m. p. 144 °C with decomposition. $C_{116}H_{98}Au_6B_2F_8P_8$ (3095.22): calcd. C 45.01, H 3.19, P 8.01; found C 44.86, H 3.15, P 8.22. MS(FAB): *m/z* 720.4 [$Au(PPh_3)_2^+$]. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: $\delta = 46.5$ (br. s, *P*Au), −19.1 (br. s, PAu_3); [at −80 °C: 45.7 (d, $J = 258.1$) / −20.4 (q, $J = 258.1$)]; $^{13}C\{^1H\}$: 141.0 and 138.9 (2xm, AXX', C_{xyl}), 139.4 (d, $J = 24.6$, *C*P), 134.5 (d, $J = 13.1$), 132.3 (s), 129.9 (d, $J = 51.9$), and 129.8 (d, $J =$ 10.8, all *Ph*), 25.5 (d, $J = 8.5$, *Me*). ^{1}H: 8.19 (m, AA'XX', 2H, H_{xyl}), 7.68 – 7.32 (m, 90H, *Ph*), 2.78 (s, 6H, *Me*); ^{11}B: −2.1; ^{19}F: −153.3.

Table 1. Crystal data, data collection and structure refinement of 1,4-Br_2-2,5-Me_2-C_6H_2 and compounds **1** – **4**, and **6**.

	$C_6H_2Me_2Br_2$	**1**	**2**	**3**	**4**	**6**
Empirical formula	$C_8H_8Br_2$	$C_8H_{12}P_2$	$C_8H_8Cl_4P_2$	$C_{24}H_{48}N_4P_2$	$C_{94}H_{202}Au_6B_2F_8O_4P_8$	$C_{46}H_{88}Au_3BF_4P_4$
M	263.96	170.12	307.88	454.60	2999.74	1442.75
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	6.2838(2)	6.2217(2)	7.4772(1)	7.9661(1)	13.2321(2)	12.1358(1)
b [Å]	7.7186(3)	11.0937(3)	11.2813(2)	9.9005(2)	17.2175(2)	23.9766(2)
c [Å]	17.3959(7)	6.4939(2)	7.5360(1)	17.5714(3)	26.4908(4)	19.4960(2)
β [°]	95.368(1)	98.032(1)	110.257(1)	102.729(1)	102.5490(7)	104.6056(4)
V [Å^3]	840.04(5)	443.82(2)	596.36(2)	1351.77(4)	5891.1(1)	5489.53(9)
ρ_{calc} [g cm^{-3}]	2.087	1.273	1.715	1.117	1.691	1.746
Z	4	2	2	2	2	4
$F(000)$	504	180	308	500	2948	2808
T [K]	143(2)	143(2)	143(2)	143(2)	143(2)	143(2)
Refls. measured	31213	10140	15954	40221	152951	124856
Refls. unique	1932	808	1218	3101	9384	10400
Parameters	93	70	65	161	582	550
$R1$ $[I \geq 2\sigma(I)]$	0.058	0.035	0.031	0.041	0.031	0.022
$wR2$[a]	0.148	0.096	0.080	0.11	0.078	0.054
Weighting	$a = 0.0349$	$a = 0.0652$	$a = 0.0503$	$a = 0.0551$	$a = 0.0255$	$a = 0.0194$
scheme	$b = 11.6627$	$b = 0.1866$	$b = 0.3455$	$b = 0.4837$	$b = 32.7801$	$b = 13.2669$
σ_{fin}(max/min) [eÅ^{-3}]	1.451 / −0.832	0.259 / −0.363	0.282 / −0.459	0.305 / −0.405	1.772 / −1.180	1.495 / −0.956

[a] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

Compound ***6***: The preparation followed the procedure given for **4** with 16.7 mg (0.10 mmol) of 1-naphthyl-phosphine and 135.6 mg (0.10 mmol) of $\{[(^tBu_3P)Au]_3O\}BF_4$; 147.9 mg (98.3% yield) of colourless crystals, m.p. 142 °C with decomposition. $C_{46}H_{88}Au_3BF_4P_4$ (1442.79): calcd. C 38.29, H 6.15, P 8.59; found C 38.08, H 6.18, P 8.47. MS(FAB): *m/z* 1356.7 (100%) [M^+]. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: δ = 99.5 (d, J = 236.0, *P*Au), −9.3 (q, J = 236.0, *P*Au_3); $^{13}C\{^1H\}$: 139.9 – 125.1 (naphthyl carbon atoms), 40.0 (d, J = 14.5, *C*Me_3), 32.7 (d, J = 3.1, *Me*); ^1H: 9.24 – 7.32 (m, naphthyl hydrogen atoms), 1.52 (d, J = 13.5, *Me*); ^{11}B: −2.1 (s); ^{19}F: −153.5 (s).

Compound ***7***: The preparation followed the procedure given for **4** with 20.5 mg (0.13 mmol) of 1-naphthyl-phosphine and 189.5 mg (0.13 mmol) of $\{[(Ph_3P)Au]_3O\}BF_4$; 203.3 mg (97.9% yield) of a yellow solid, m.p. 123 °C with decomposition. $C_{64}H_{52}Au_3BF_4P_4$ (1622.70): calcd. C 47.37, H 3.23, P 7.64; found C 46.98, H 3.41, P 7.48. MS(FAB) *m/z* 1535.1 (21%) [M^+]. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: δ = 46.2 (br. s, *P*Au), −21.3 (br. s, *P*Au_3); $^{13}C\{^1H\}$: 134.6 (d, J = 13.1), 132.3 (s), 129.9 (d, J = 52.3), and 129.8 (d, J = 10.8) for *Ph*; 138 – 125.4 (naphthyl carbon atoms); ^1H: 9.42 – 7.32 (m, phenyl and naphthyl); ^{11}B: −2.1 (s); ^{19}F: −153.4 (s).

Crystal structure determination: Specimens of suitable quality and size of $C_6H_2Me_2Br_2$, **1**, **2**, **3**, **4** and **6** were mounted on the ends of quartz fibers in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K_α radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97) [37]. The thermal motion was treated anisotropically for all non-hydrogen atoms.

One ethyl group in the structure of **2** is disordered over two sites with site occupation factors of 0.79 and 0.21, respectively.

The hydrogen atoms of **1** were located and refined with isotropic displacement parameters, those in $C_6H_2Me_2Br_2$, **2**, **3**, **4** and **6** were calculated in ideal positions and refined after a riding model.

Absorption corrections were carried out for $C_6H_2Me_2Br_2$, **4** and **6** using DELABS, as part of the PLATON suite of programs [38]. Further information on crystal data, data collection and structure refinement is summarized in Table 1.

Displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC 264182 – 264187.

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