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Synthesis and auration of primary and di-primary heteroaryl-phosphines

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Received 5th October 2004, Accepted 12th November 2004
First published as an Advance Article on the web 7th December 2004

Convenient high-yield syntheses of the primary and di-primary heteroaryl-phosphines R–PH$_2$ and H$_2$P–R′–PH$_2$ (with R = 2-thienyl, 2-furyl, and R′ = 2,5-thiophenediyl, 2,5-furandiyl, respectively) are presented. The products and a set of precursor molecules have been characterized by analytical and spectral data, and the crystal structures of selected molecules have been determined: 2-C$_4$H$_3$O–PCl$_2$, 2,5-(Cl$_2$P)$_2$C$_4$H$_2$O, 2,5-[(Et$_2$N)$_2$P]$_2$C$_4$H$_2$E (with E = O, S). In the crystals, the two molecules with –PCl$_2$ substituents adopt *trans* conformations, while the other two have the –P(NEt$_2$)$_2$ groups rotated into a *twist* conformation. The reaction of the thienyl compounds with tris[(*tert*-phosphine)gold]oxonium tetrafluoroborates gave almost quantitative yields of the tri- and hexanuclear gold complexes, respectively: {2-C$_4$H$_3$S–P[Au(PR$_3$)]$_3$}$^+$BF$_4$$^-$ and [2,5-{[(R$_3$P)Au]$_3$P}$_2$C$_4$H$_2$S]$^{2+}$(BF$_4$$^-$)$_2$, (R = ^{t}Bu, Ph). The structures of the compounds with R$_3$P = ^{t}Bu$_3$P ligands have been determined. In both cases the [2-C$_4$H$_{3/2}$S–P] units cap triangles of gold atoms in an array that can be described as three [Au(PR$_3$)]$^+$ cations bridged by a phosphido dianion (RP)$^{2-}$.

Introduction

There is currently a rapidly growing interest in primary phosphines RPH$_2$.[1] Owing to the two P–H reaction sites, not available in tertiary phosphines R$_3$P, molecules of this type can be used as synthons for the preparation of phosphines with mixed substituents R^{1}R^{2}R^{3}P as chiral ligands for coordination chemistry.[2] Moreover, primary phosphines can be employed as reagents for many chemical transformations, in which the P–H functions are added to unsaturated substrates. This "hydrophosphination" reaction is the analogue of the "hydrosilylation" reaction well established in organosilicon chemistry. It may be carried out in many catalytic variants leading to a large variety of products.[3]

RPH$_2$ compounds can also be considered important precursors for phosphinidenes of the type RP,[4] which are phosphorus analogues of carbenes: With a similar set of frontier orbitals and a sextet of electrons at the functional site, RP units can perform as terminal, bridging or capping ligands to single metal atoms, pairs of metal atoms or multi-atom clusters, respectively. Phosphinidenes are generally prepared by reductive elimination from suitable precursors such as 7-phosphanorbornadienes[5] or phosphacyclopropenes.[6] Alternative methods are based on the metallation and reduction of dihalogenophosphines RPX$_2$ with suitable (metallic) reductants, or on halogeno(organo)phosphines RP(H)X which can undergo reductive elimination of hydrogen halide. For their synthesis, primary phosphines RPH$_2$ are required.[1,3,7,8] Finally, primary phosphines can be metallated with electropositive metals (or metal hydrides) to give phosphides RP(M)H and RPM$_2$, and the products can be used as reagents *e.g.* for metal halides to give again the RP-bridged dinuclear compounds or the RP-capped metal triangles or clusters.[4,7–9]

Primary phosphines thus are key starting materials for phosphinidene chemistry. Though direct elimination of molecular hydrogen from RPH$_2$ compounds to leave RP units has not yet been observed on a preparative scale, there is evidence for dehydrogenative P–P coupling of di-primary phosphines.[10]

However, as compared to the plethora of *tertiary* phosphines R$_3$P available in the literature, the collection of RPH$_2$ compounds is still very limited.[1,11,12] This is particularly true for compounds with substituents R other than alkyl or aryl. In the present study we therefore explored the synthesis of a few simple *heteroaryl* compounds, with R = 2-furyl and 2-thienyl. Tertiary phosphines R$_3$P with these two substituents have been explored extensively in an effort to accomplish fine-tuning of ligand properties for transition metal catalysis. In these studies, the thienyl substituent was found to resemble most closely the conventional phenyl substituent, while the furyl group exhibits stronger electron-withdrawing character.[12]

Our studies are also an extension of previous work[13–15] on 2-thienyl-/2-furyl-*silanes* and *-germanes*, which are precursors for the preparation of substituted poly(thiophenes) with interesting photophysical properties. Phosphorus analogues of these materials were investigated much less.[16]

Preparative results

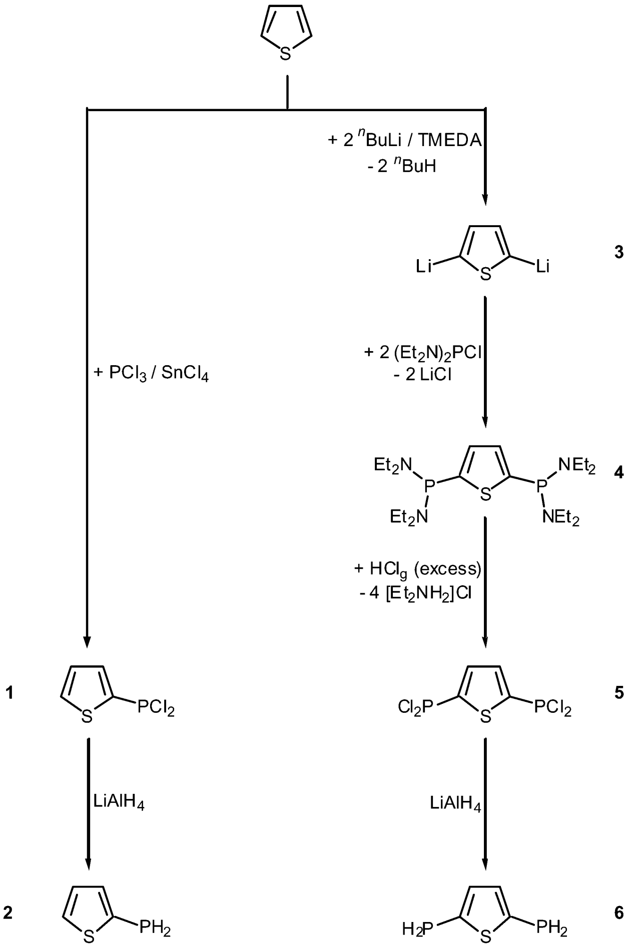
2-Phosphinyl- and 2,5-di(phosphinyl)thiophene (2, 6)

(Dihalogenophosphinyl)thiophenes are the most obvious precursors for the preparation of the corresponding primary phosphines **2** and **6** (Scheme 1). It is fortunate that several synthetic pathways have been reported at least for the compounds mono-substituted in the 2-position, including the particularly convenient direct "phosphination" of thiophene under Friedel–Crafts conditions, using *e.g.* a mixture of PCl$_3$ and SnCl$_4$, which affords good yields of compound **1**.[17–19]

In the present study it was found, however, that for the "di-phosphination" of thiophene a procedure following the three-step metallation route is necessary (Scheme 1). The 2,5-dilithiation of thiophene (to give compound **3**) requires a slight excess of ^{n}BuLi along with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as an auxiliary base.[20–22] After reaction of **3** with two equivalents of bis(diethylamino)chlorophosphine high yields (83.5%) of the product **4** could be isolated by crystallization (from hexane or dichloromethane, mp 61 °C). This compound was converted into the tetrachloride **5** (95% yield, mp −1 °C) by passing a stream of HCl gas through a solution of **4** in hexane.

The chlorides **1** and **5** were finally reduced to the (di)primary phosphines by LiAlH$_4$ in diethyl ether. The products could be isolated as colourless, distillable liquids [**2**: bp 155 °C, 92% yield; **6**: bp 72 °C/0.9 mbar, mp −39 °C, 89% yield].

DOI: 10.1039/b415326j

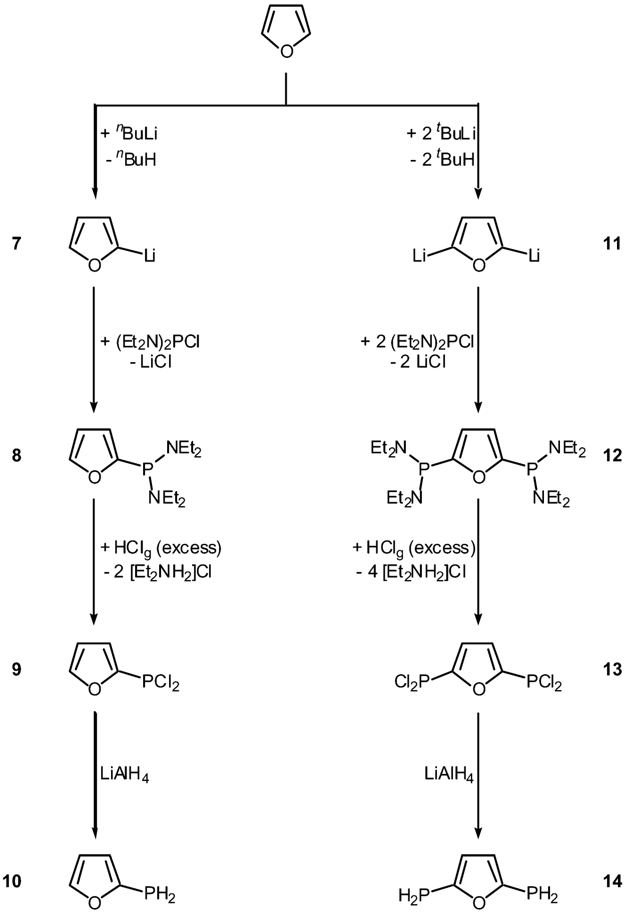


Scheme 1 Preparation of 2-phosphinyl- and 2,5-di(phosphinyl)-thiophenes.

2-Phosphinyl- and 2,5-di(phosphinyl)furan (10, 14)

The two target molecules in the furan series were synthesized starting with furan as illustrated in Scheme 2. Mono- or dilithiation followed by reaction with bis(diethylamino)chlorophosphine in the appropriate molar ratio gave the bis(diethylamino)phosphinyl-substituted furans with the P-atoms regioselectively introduced in the 2- and 2,5-positions, respectively (**8**, **12**). [It should be noted that the same reaction was used to produce the tetraphenylated derivatives with the same substitution pattern: 2,5-$(Ph_2P)_2C_4H_2E$, E = O,[23] E = S.[24]] These primary products could again be readily converted into the corresponding dichlorophosphinyl compounds (**9**, **13**) by passing dry hydrogen chloride into their solutions in hexane. The two compounds were purified by distillation to give **9** as a colourless liquid (mp −40 °C) and **13** as a colourless crystalline solid (mp 28 °C). Reduction of the compounds with $LiAlH_4$ in diethyl ether gave the (di)primary phosphines, of which **10** was difficult to separate from the solvent by distillation. Experiments with high-boiling ethers proved to offer no advantage, and only small amounts of **10** could be isolated by GLC. However, the azeotrope with diethyl ether (5 mol% **10**, bp 35 °C/760 mm Hg) is a good source of **10** for further transformations. Compound **14** was more readily purified and obtained as a colourless liquid of bp 113 °C. Like the two phosphinylthiophenes (**2**, **6**), both phosphinylfurans are extremely malodorous and sensitive to oxygen, igniting on the tip of a syringe or when spread on filter paper.

Compounds **1**, **2**, **4**–**6**, **8**–**10** and **12**–**14** have been characterized by analytical and spectroscopic data (Experimental section), and the crystal structures have been determined for **4**, **9**, **12** and **13** (below).



Scheme 2 Preparation of 2-phosphinyl- and 2,5-di(phosphinyl)furans.

The NMR spectra (in CD_2Cl_2) show extreme high-field ^{31}P signals (*ca.* δ −150 ppm) for the four primary phosphines (**2**, **6**, **10**, **14**) which are split into triplets with large $^1J_{PH}$ coupling constants (*ca.* 200 Hz). By contrast, the ^{31}P resonances of the dichlorophosphinyl compounds (**1**, **5**, **9**, **13**) are shifted into the downfield region around δ +150 ppm, while those of the diaminophosphinyl precursors (**4**, **8**, **12**) appear in an intermediate region (*ca.* δ 80 ppm). The ^1H and ^{13}C spectra show no anomalies. The multiplicities of the signals of the 2-mono- and 2,5-disubstituted compounds indicate that in solution the molecules have virtual C_s and C_{2v} symmetry, respectively, and no further splitting is observed upon lowering the temperature to *ca.* −80 °C. These results suggest that in solution the molecules have symmetrical ground-state conformations or at least free rotation of the functional groups about the P–C bonds.

Relevant spectral and structural data in the literature

The ^1H NMR spectrum of the (dichlorophosphinyl)thiophene **1** (as a neat liquid) was investigated in a very early study,[25] the results of which are in satisfactory agreement with our own data considering the different experimental conditions. (More advanced NMR data are available for the difluorophosphinyl analogue, 2-C_4H_3S–PF_2.)[26]

Compound **1** was further studied (as a solid at 77 K) by ^{35}Cl NQR spectroscopy.[27] The results indicate that two inequivalent chlorine substituents are present in the crystal. In recent work the earlier results have been confirmed and used as a reference for quantum-chemical calculations of the molecular conformation.[28] Two structures with C_s symmetry were considered, which have the sulfur atom in a *cis* or *trans* orientation relative to the lone-pair of electrons at the P-atom. From these calculations, there appears to be a slight preference for the *trans* conformation. This result is in agreement with the crystal structure data of tri(2-furyl)phosphine, in which each of the three furyl groups adopts the *trans* conformation of its oxygen atom relative to the lone-pair of electrons at the phosphorus atom. (The overall geometry approaches point group C_{3v} symmetry.)[13]

From a gas phase electron diffraction[29] and a solution dipole moment study[30] of compound **1** conformations with different dihedral angles between the thiophene plane and the plane containing C1 and bisecting the Cl–P–Cl angle were obtained. Starting from a *trans* arrangement of the sulfur atom and the lone-pair of electrons at the P-atom (taken as 0°), this angle is given as 48 and 32°, respectively.

Furan and thiophene bearing silyl (–SiH_3) and germyl groups (–GeH_3) in the 2- and 2,5-positions have recently been studied by quantum-chemical calculations.[14,15] A ground state conformation with C_s symmetry was found for the *mono*-substituted compounds with one Si- or Ge-bound hydrogen atom in the *Z* configuration (eclipsed) with the hydrogen atom at C3. For the disubstituted compounds the ground state structures are of C_{2v} symmetry with the same conformational pattern. The crystal structure of 2,5-$(H_3Si)_2C_4H_2S$ has been determined and slight distortions relative to the calculated geometry were found, mainly a conrotatory movement of the two silyl groups shifting the two eclipsed hydrogen atoms away from the molecular plane by *ca.* 25° and resulting in a structure with C_2 symmetry. This deviation may be due to crystal packing effects which bring the hydrogen atoms concerned in positions preferred for weak interactions with the heterocyclic π-systems of neighbouring molecules.

Structural results

2-(Dichlorophosphinyl)furan, **9**, crystallizes in the orthorhombic space group *Pbca* with $Z = 8$ molecules in the unit cell (at 143 K). The molecular structure approaches mirror symmetry, with the –PCl_2 group rotated away of the symmetrical position by 9.06° (Fig. 1). The oxygen atom and the lone-pair of electrons at the phosphorus atom are in *trans* positions as proposed for the *sulfur* analogue **1** in the gas and solution phases on the basis of electron diffraction and dipole moment studies,[29,30] respectively, and by theoretical calculations. There is also an analogy with the calculated silyl- and germyl-furan structures.[14,15]

2,5-Bis(dichlorophosphinyl)furan, **13**, crystallizes in the tetragonal space group $P\bar{4}2_1m$ with $Z = 2$ molecules in the unit cell (at 193 K). [Temperature-dependent studies have shown that there appears to be a reversible transition into another phase below *ca.* −86 °C (187 K), but this phenomenon was not investigated any further.] The molecules have crystallographically imposed C_{2v} symmetry with the –PCl_2 groups in the same *trans* conformation as observed (with a slight rotational distortion) for **9** (Fig. 2). This structure is further analogous to those calculated for the 2,5-disilyl/digermyl-furans.[14,15] The geometrical details of **9** and **13** are in excellent agreement as shown for selected data in the captions to Figs. 1 and 2.

2,5-Bis[bis(diethylamino)phosphinyl]-thiophene and -furan (**4** and **12**) form monoclinic crystals (at 143 K), but these have different space groups ($P2_1/n$ and $P2_1$). In the latter there are two independent molecules (I, II) in the asymmetric unit (Fig. 3), while in the former only equivalent molecules are present (Fig. 4). Except for the variations caused by the differences in the parameters for oxygen and sulfur, the structures of molecules **4** and **12** (I/II) are very similar, and therefore no separate discussion is required. None of the molecules has a crystallographically imposed symmetry, but C_2 symmetry is approached quite closely with the twofold axis passing through the heteroatoms (O, S) and bisecting their endocyclic angle. The –$P(NEt_2)_2$ groups are rotated away from the *trans* conformations observed for **9** and **13** into *twist* conformations. This arrangement is probably induced by steric effects: For structures with C_{2v} symmetry (as observed for **13**) severe steric crowding is expected owing to the four bulky –NEt_2 groups (Figs. 3(b), 4(b)). For small substituents X = H,

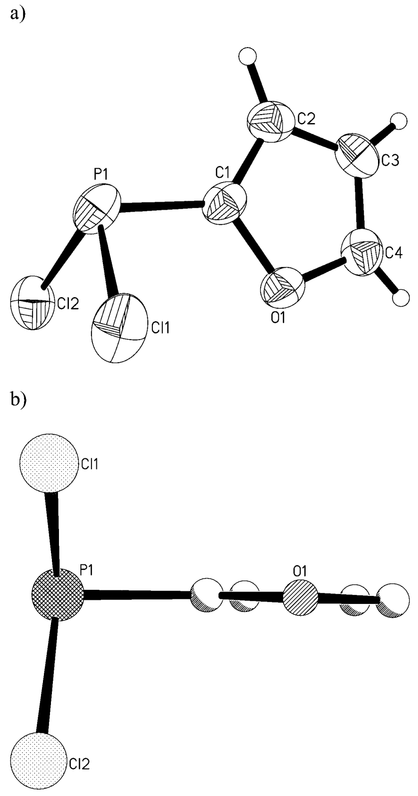


Fig. 1 Two projections of the molecular structure of 2-C_4H_3O–PCl_2 (**9**). (a) ORTEP, 50% probability ellipsoids, with atomic numbering. (b) Arbitrary radii and hydrogen atoms omitted. Selected bond lengths (Å), bond angles and dihedral angles (°): P1–Cl1 2.0643(10), P1–Cl2 2.0680(11), P1–C1 1.776(3); Cl1–P1–Cl2 98.77(4), Cl1–P1–C1 99.80(9), Cl2–P1–C1 100.60(9); O1–C1–P1–Cl1 42.4(2), O1–C1–P1–Cl2 −58.5(2).

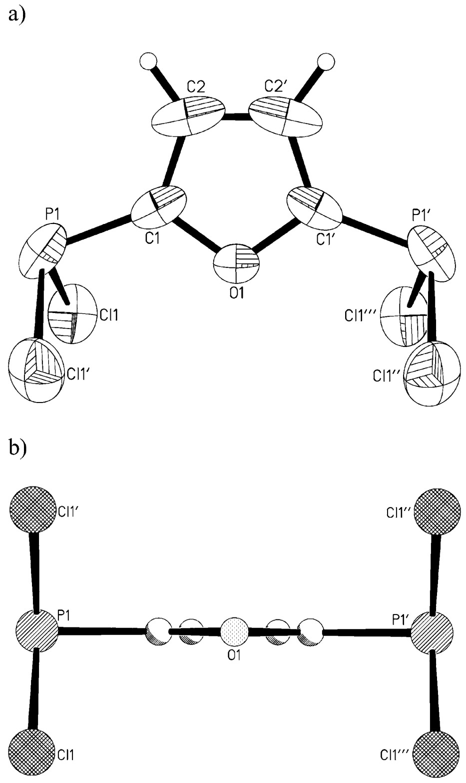


Fig. 2 Two projections of the molecular structure of 2,5-$(Cl_2P)_2C_4H_2O$ (**13**); the molecule has C_{2v} symmetry. (a) ORTEP, 50% probability ellipsoids, with atomic numbering. (b) Arbitrary radii and hydrogen atoms omitted. Selected bond lengths (Å), bond angles and dihedral angles (°): P1–Cl1 2.0464(15), P1–C1 1.788(6); Cl1–P1–Cl1′ 99.86(10), C1–P1–Cl1 98.95(9); O1–C1–P1–Cl1 −50.77(5).

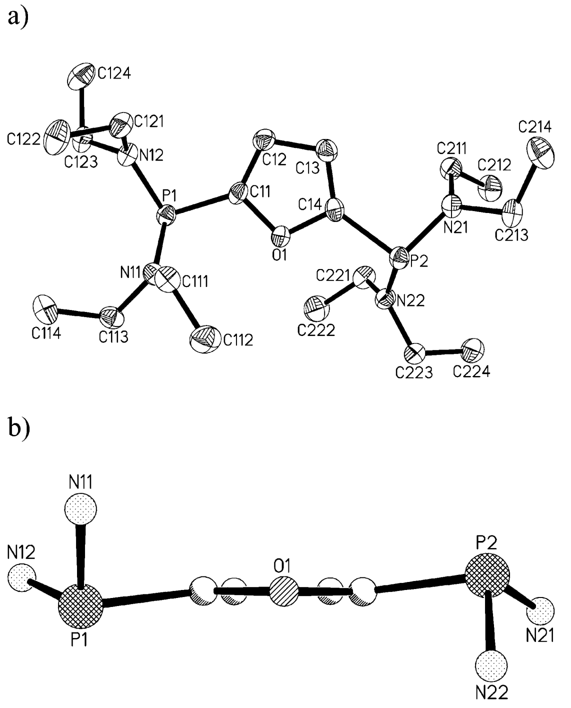


Fig. 3 Molecular structure of 2,5-[$(Et_2N)_2P]_2C_4H_2O$ (**12**). Only one out of two independent molecules is shown in two projections. (a) ORTEP, 50% probability ellipsoids, with atomic numbering; hydrogen atoms omitted. (b) Arbitrary radii and hydrogen atoms omitted. Selected bond lengths (Å), bond angles and dihedral angles (°) for the molecule shown in the figures: P1–N11 1.6857(11), P1–N12 1.6910(12), P1–C11 1.8181(13), P2–N21 1.6919(11), P2–N22 1.6896(11), P2–C14 1.8210(13); N11–P1–N12 113.61(6), N11–P1–C11 98.62(6), N12–P1–C11 98.60(6), N21–P2–N22 113.85(6), N21–P2–C14 97.92(6), N22–P2–C14 99.34(6); O1–C11–P1–N11 53.09(10), O1–C11–P1–N12 168.72(9), O1–C14–P2–N21 165.42(9), O1–C14–P2–N22 49.52(10).

F, Cl in the $-PX_2$ groups the C_{2v} ground state should be valid. Note that the individual molecules with C_2 symmetry (**4**, **12**) are chiral, but that both enantiomers are present in the crystals.

Preparation and structure of gold(I) complexes

In order to provide a few examples for metallation of the new primary heteroaryl-phosphines, the thiophenes **2** and **6** have been converted into a set of four gold(I) complexes **15**–**18** with $^tBu_3P$ and Ph_3P as auxiliary ligands (Scheme 3). The corresponding tri(gold)oxonium tetrafluoroborates[31] were employed as reagents for the phosphines in an equimolar ratio with dichloromethane as the solvent. The products were obtained in nearly quantitative yields, with water as the sole by-product (which, however, was not traced in the reaction mixtures). The compounds are colourless (**15**, **16**) and yellow (**17**, **18**) solids with melting points between 100 and 150 °C, soluble in polar organic solvents without decomposition. Their composition was confirmed by analytical and spectral data (Experimental section), and the crystal structures of the two complexes with the $^tBu_3P$ ligands have been determined.

In the ^{31}P NMR spectra of the two complexes with the $^tBu_3P$ ligands (**15**, **16**) a strong $^2J_{PP}$ coupling is observed (240 Hz, in CD_2Cl_2 at 25 °C) between the central P-atom and the ligand P-atoms indicating that there are no scrambling processes operative in solution under these conditions. By contrast, for the complexes with the PPh_3 ligands (**17**, **18**) this coupling is not resolved owing to ligand exchange phenomena which cause line broadening already at room temperature.

2-Thienyl-tris[(tri-*tert*-butylphosphine)gold(I)]phosphonium tetrafluoroborate, **15**, crystallizes as a 1 : 1 solvate with dichloromethane which is disordered over two sites (triclinic, space group $P\bar{1}$, $Z = 2$). The cations feature a tetrahedrally coordinated central phosphorus atom (P1) surrounded by C1 of the thienyl substituent and three gold atoms. The gold atoms are linearly two-coordinate each bearing a bulky $^tBu_3P$ ligand (Fig. 5). There are no discernible sub-van der Waals contacts between the cations, the anions and the solvent molecules.

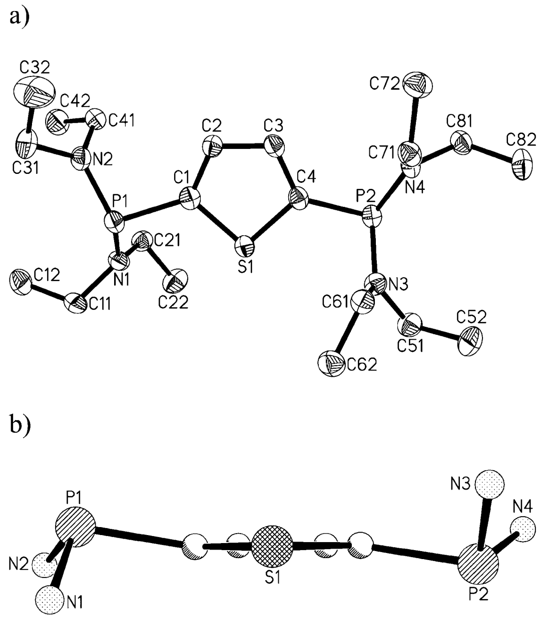
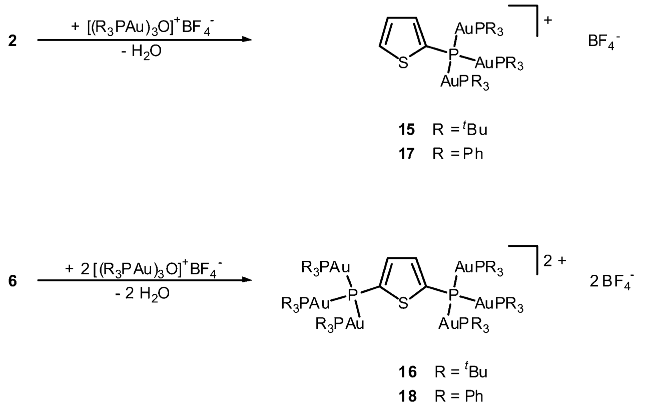


Fig. 4 Two projections of the molecular structure of 2,5-[$(Et_2N)_2P]_2C_4H_2S$ (**4**). (a) ORTEP, 50% probability ellipsoids, with atomic numbering; hydrogen atoms omitted. (b) Arbitrary radii and hydrogen atoms omitted. Selected bond lengths (Å), bond angles and dihedral angles (°): P1–N1 1.692(2), P1–N2 1.686(2), P1–C1 1.825(3), P2–N3 1.694(2), P2–N4 1.692(2), P2–C4 1.823(3); N1–P1–N2 113.42(12), N1–P1–C1 98.62(12), N2–P1–C1 100.38(12), N3–P2–N4 113.73(12), N3–P2–C4 98.34(12), N4–P2–C4 99.78(12); S1–C1–P1–N1 −46.64(18), S1–C1–P1–N2 −162.51(16), S1–C4–P2–N3 −49.25(18), S1–C4–P2–N4 −165.23(15).



Scheme 3 Preparation of tri- and hexanuclear gold complexes.

2,5-Bis{tris[(tri-*tert*-butylphosphine)gold(I)]phosphonio}thiophene bis(tetrafluoroborate), **16**, forms cubic crystals, space group $Im\bar{3}$ with $Z = 12$, in which the anions were found disordered. The dications have crystallographically imposed C_{2v} symmetry (Fig. 6) with dimensions very similar to those of compound **15**.

It is noteworthy that in both cases the tetrahedral angles Au–P1–Au (average for **15** 107.3°) together with large Au–P1 bond lengths (average for **15** 2.313′) preclude any short aurophilic Au–Au contacts. This observation is in agreement with previous findings for the cations of aryl(trigold)phosphonium salts.[32–36] By contrast, there is evidence that *tetra*goldphosphonium cations $\{[(L)Au]_4P\}^+$ have a square-pyramidal structure of the type already confirmed for the arsenic analogues.[37] These cations can be further aurated to give square pyramidal $\{[(L)Au]_5P\}^{2+}$ or $\{[(L)_6Au_5]P\}^{2+}$ dications and even octahedral $\{[(L)Au]_6P\}^{3+}$

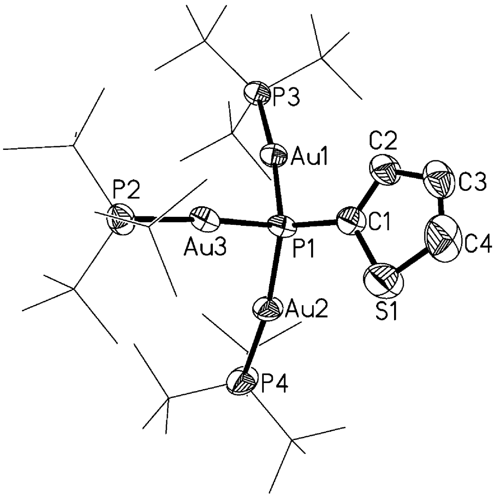


Fig. 5 Structure of the cation $\{2\text{-}C_4H_3S\text{–}P[Au(P^tBu_3)]_3\}^+$ in the tetrafluoroborate salt dichloromethane solvate (**15**). (ORTEP, 50% probability ellipsoids for the core atoms, with atomic numbering.) Selected bond lengths (Å), bond angles and dihedral angles (°): Au1–P1 2.304(2), Au2–P1 2.313(2), Au3–P1 2.321(2), P1–C1 1.803(8), Au1–P3 2.316(2), Au2–P4 2.332(2), Au3–P2 2.318(2); Au1–P1–Au2 104.31(8), Au1–P1–Au3 110.23(9), Au2–P1–Au3 107.48(8); S1–C1–P1–Au1 −159.2(5), S1–C1–P1–Au2 −40.0(7), S1–C1–P1–Au3 80.1(6).

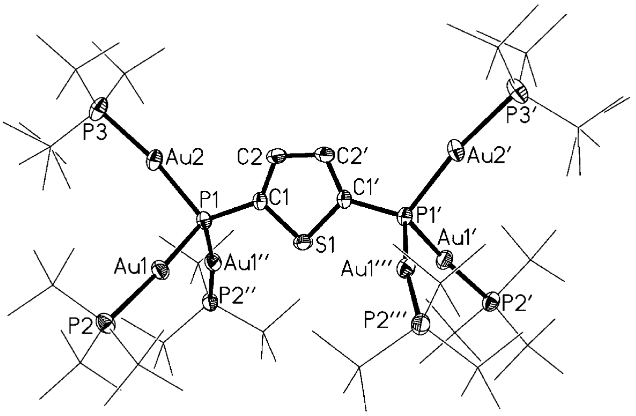


Fig. 6 Structure of the dication $[2,5\text{-}\{[(^tBu_3P)Au]_3P\}_2C_4H_2S]^{2+}$ in the bis(tetrafluoroborate) salt (**16**). (ORTEP, 50% probability ellipsoids for the core atoms, with atomic numbering; the dication has C_{2v} symmetry.) Selected bond lengths (Å), bond angles and dihedral angles (°): Au1–P1 2.316(2), Au2–P1 2.308(4), P1–C1 1.798(13), Au1–P2 2.328(3), Au2–P3 2.314(4); Au1–P1–Au2 105.59(11), Au1–P1–Au1″ 104.99(15); S1–C1–P1–Au1 59.5(2).

trications, where the edges of the PAu_n polyhedra are short enough for aurophilic bonding.[38–40]

Conclusions

Primary phosphines are useful synthons for the generation of organophosphinidenes [RP] (analogues of carbenes) and organophosphide dianions $[RP]^{2-}$. Satisfactory methods of preparation are available for only a very limited number of prototypes. In the present work it has now been shown that primary heteroaryl-phosphines **2** and **10** [R–PH_2 (R = 2-thienyl, 2-furyl)] and the corresponding di-primary phosphines **6** and **14** [H_2P–R′–PH_2 (R′ = 2,5-thiophenediyl, 2,5-furandiyl)] can be readily prepared in convenient high-yield syntheses as stable, distillable compounds (Schemes 1 and 2).

Based on crystal structures of a group of precursor molecules (**9**, **13**, **4**, **12**), and on analogies to reference compounds known in the literature,[10–15,19,27–30] the compounds can be assigned molecular structures with approximate C_s and C_{2v} or (with bulky groups) C_2 symmetry, respectively. In the former two, the –PX_2 groups are in a *trans* conformation regarding the relative positions of the heteroatoms (O, S) and the lone-pair of electrons at the phosphorus atoms, while for the latter a *twist* conformation leads to sterical relaxation.

The new (di)primary phosphines can be used as synthons for the preparation of metal heteroaryl-phosphides in which the PR unit is capping metal triangles. In the first of the two examples presented in this study for which the structure has been determined (**15**), the $[2\text{-}C_4H_3S\text{–}P]^{2-}$ anion is coordinated to three gold atoms to give a tetrahedral 2-thienyl-tri(gold)-phosphonium cation: $\{(2\text{-}C_4H_3S)P[Au(P^tBu_3)]_3\}^+$. This cation can also be viewed as an adduct of the 2-thienylphosphinidene unit (2-C_4H_3S–P) to the trinuclear cation $[Au_3(P^tBu_3)_3]^+$. The latter species is part of the taxonomy of gold clusters and gold cluster cations[41] and *e.g.* appears – capped with a $[Au(P^tBu_3)]^+$ cation – in the tetrahedral, tetranuclear dications $[Au_4(P^tBu_3)_4]^{2+}$.[42] However, the quasi-tetrahedral Au–P–Au angles and the associated large Au–Au distances in **15** (and **16**) indicate that metal–metal bonding present in the $\{[(L)Au]_3\}^+$ cation is quenched upon the capping by the RP unit.

The same structural pattern is valid for the hexanuclear dication of complex **16** derived from the di-primary phosphine **6**, and the –$P[Au(PR_3)]_3$ units in **15** and **16** are virtually superimposible. The NMR data of these units are also almost identical. In **16**, the bulk of the ^{t}Bu$_3$P ligands provides efficient shielding of the thiophene core unit and also retards any intermolecular exchange processes in solution. This lends considerable thermal stability to both compounds. With the smaller Ph_3P ligands (**17**, **18**) the scrambling processes become more rapid (on the NMR time scale) and the thermal stability in solution is markedly reduced. This behaviour parallels the properties of the related arylphosphine complexes, which were also prepared with ^{t}Bu$_3$P and Ph_3P ligands.[32–36]

Experimental

General

All chemicals used as starting materials were commercially available, except bis(diethylamino)chlorophosphine,[43] $[(^tBu_3PAu)_3O]^+BF_4^-$ (**19**)[31a] and $[(Ph_3PAu)_3O]^+BF_4^-$ (**20**)[31b,c] which were prepared according to the literature. All reactions were carried out routinely in an atmosphere of dry and pure nitrogen. All solvents were distilled from an appropriate drying agent and stored over molecular sieves (4 Å) and under nitrogen. Glassware was oven-dried and filled with nitrogen. During reactions with gold compounds exposure to direct sunlight was avoided. Elemental analyses were carried out in the Mikroanalytisches Laboratorium des Anorganisch-chemischen Instituts der Technischen Universität München. The C, H, N percentages were routinely determined using a vario EL elemental analyzer (elementar Analysensysteme GmbH). The P content was determined photometrically (as the molybdate) on an UV-160 spectrophotometer (Shimadzu). Mass spectra were recorded on a HP 5971A (Hewlett-Packard) spectrometer using EI at 70 eV as an ionization method. For the gold compounds a Finnigan MAT 90 spectrometer (positive FAB source; matrix material 4-nitrobenzyl alcohol) was employed. NMR spectra were obtained at room temperature on JEOL JNM-GX-400 or JEOL 400 Eclipse spectrometers. Chemical shifts are reported in δ values relative to the residual solvent resonances of CD_2Cl_2 (^1H,^{13}C). ^{31}P, ^{11}B and ^{19}F NMR spectra are referenced to external aqueous H_3PO_4 (85%), $BF_3\cdot OEt_2$ and $CFCl_3$, respectively. GC-MS analyses of the reaction mixtures were carried out on a HP 5890 Series II (Hewlett-Packard) gas chromatograph with a HP 5971A mass-selective detector. Capillary Column (Agilent Technologies): HP-1 (Crosslinked Methyl Siloxane) 12.5 m × 0.2 mm × 0.33 μm Film Thickness, HP Part No. 19091-60312.

Syntheses

2-(Dichlorophosphinyl)thiophene, 1. The preparation followed a literature procedure;[17] for analytical data see also ref. 25. Complementary data: NMR ($CDCl_3$, 25 °C), $^{31}P\{^1H\}$: 145.5 (s). $^{13}C\{^1H\}$: 142.8 (d, $^1J_{CP} = 72.3$ Hz, *C*2), 135.9 (d, $^3J_{CP} = 2.3$ Hz, *C*5), 135.7 (d, $^2J_{CP} = 43.8$ Hz, *C*3), 127.8 (d, $^3J_{CP} = 8.5$ Hz, *C*4). ^1H: 7.84 (dd, $^3J_{HH} = 4.8$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, *H*5), 7.64 (ddd, $^3J_{HP} = 7.0$ Hz, $^3J_{HH} = 3.7$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, *H*3), 7.13 (ddd, $^3J_{HH} = 4.8$ Hz, $^3J_{HH} = 3.8$ Hz, $^4J_{HP} = 2.0$ Hz, 1H, *H*4). MS (EI) *m/z* 184 $[M]^+$, 149 (100%) $[M - Cl]^+$, 114 $[M - 2Cl]^+$, 101 $[PCl_2]^+$.

2-Phosphinylthiophene, 2. A solution of **1** (23.15 g, 125.1 mmol) in diethyl ether (100 mL) was added slowly to a stirred suspension of $LiAlH_4$ (19.00 g, 500.7 mmol) in diethyl ether (500 mL) at −78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. For workup degassed water (120 mL) was added dropwise at 0 °C and the mixture stirred at room temperature for 1 h. The precipitate was separated and extracted with diethyl ether (2 × 100 mL), and the combined organic phases were dried over $MgSO_4$. Distillation yielded a colourless liquid: 13.32 g, 91.7% yield, bp 155 °C. NMR ($CDCl_3$, 25 °C), $^{31}P\{^1H\}$: −151.3 (s). ^{31}P: −151.3 (tm, $^1J_{PH} = 207.4$ Hz). $^{13}C\{^1H\}$: 137.5 (d, $^2J_{CP} = 27.7$ Hz, *C*3), 131.9 (s, *C*5), 128.0 (d, $^3J_{CP} = 8.5$ Hz, *C*4), 124.1 (d, $^1J_{CP} = 23.1$ Hz, *C*2). ^1H: 7.52 (dd, $^3J_{HH} = 5.1$ Hz, $^4J_{HH} = 0.7$ Hz, 1H, *H*5), 7.32 (ddd, $^3J_{HP} = 5.3$ Hz, $^3J_{HH} = 3.8$ Hz, $^4J_{HH} = 0.8$ Hz, 1H, *H*3), 7.08 (ddd, $^3J_{HH} = 5.1$ Hz, $^3J_{HH} = 3.7$ Hz, $^4J_{HP} = 1.5$ Hz, 1H, *H*4), 4.15 (d, $^1J_{HP} = 207.2$ Hz, 2H, PH_2). MS (EI) *m/z* 116 (100%) $[M]^+$, 115 $[M - H]^+$, 114 $[M - 2H]^+$. Calc. for C_4H_5PS (116.12): C, 41.37; H, 4.34; P, 26.67. Found: C, 41.80; H, 4.45; P, 26.36%.

2,5-Bis[bis(diethylamino)phosphinyl]thiophene, 4. The preparation of 2,5-dilithiothiophene **3** was based on literature procedures.[20–22] A solution of ^nBuLi (128 mL, 205 mmol, 1.6 M in hexane) was added to a solution of TMEDA (23.80 g, 205 mmol) in hexane (180 mL) at room temperature and the solution stirred for 30 min. After addition of thiophene (6.90 g, 82 mmol) the reaction mixture was refluxed for 3 h and allowed to cool to 0 °C before bis(diethylamino)chlorophosphine (43.20 g, 205 mmol) was added slowly and the reaction mixture allowed to warm to room temperature with stirring over a period of 4 h. The precipitate was separated and extracted with hexane (2 × 100 mL), and the solvents were evaporated from the combined organic phases *in vacuo*. The residue was dissolved in the minimum amount of hexane and stored at −30 °C to precipitate colourless crystals: 29.61 g, 83.5% yield, mp 61 °C. Block-shaped single crystals could be obtained by recrystallization from CH_2Cl_2. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: 87.6 (s). $^{13}C\{^1H\}$: 149.7 (d, $^1J_{CP} = 5.4$ Hz, *C*2/5), 132.0 (d, $^2J_{CP} = 15.4$ Hz, *C*3/4), 43.0 (d, $^2J_{CP} = 17.7$ Hz, CH_2), 14.9 (d, $^3J_{CP} = 2.3$ Hz, CH_3). ^1H: 6.97 (m, A-part of an AA‘XX’ spin system, 2H, *H*3/4), 3.14 (m, 16H, CH_2), 1.11 (t, $^3J_{HH} = 7.0$ Hz, 24H, CH_3). MS (EI) *m/z* 432 $[M]^+$, 360 $[M - NEt_2]^+$, 257 $[M - P(NEt_2)_2]^+$, 175 $[P(NEt_2)_2]^+$. Calc. for $C_{20}H_{42}N_4P_2S$ (432.59): C, 55.53; H, 9.79; N, 12.95; P, 14.32. Found: C, 55.49; H, 9.81; N, 12.89; P, 14.20%.

2,5-Bis(dichlorophosphinyl)thiophene, 5. A solution of **4** (29.20 g, 67.5 mmol) in hexane (500 mL) was cooled to 0 °C and saturated with gaseous HCl. The reaction mixture was stirred for 1 h, again saturated with gaseous HCl and stirred for 1 h. This procedure was repeated until the supernatant solution remained clear upon further addition of HCl. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. The diethylammonium chloride precipitate was separated and extracted with hexane (2 × 100 mL). Evaporation of the solvents from the combined organic phases *in vacuo* yielded a colourless oily liquid: 18.33 g, 95.0% yield, mp −1 °C. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: 143.3 (s). $^{13}C\{^1H\}$: 152.6 (d, $^1J_{CP} = 77.6$ Hz, *C*2/5), 135.6 (dd, $^2J_{CP} = 40.0$ Hz, $^3J_{CP} = 6.9$ Hz, *C*3/4). ^1H: 7.66 (m, A-part of an AA‘XX’ spin system, 2H, *H*3/4). MS (EI) *m/z* 286 $[M]^+$, 251 (100%) $[M - Cl]^+$, 214 $[M - 2Cl]^+$, 183 $[M - PCl_2]^+$, 148 $[M - PCl_2 - Cl]^+$, 113 $[M - PCl_2 - 2Cl]^+$, 101 $[PCl_2]^+$. Calc. for $C_4H_2Cl_4P_2S$ (285.88): C, 16.81; H, 0.71; P, 21.67. Found: C, 16.75; H, 0.78; P, 21.38%.

2,5-Di(phosphinyl)thiophene, 6. A solution of **5** (18.05 g, 63.1 mmol) in diethyl ether (100 mL) was added slowly to a stirred suspension of $LiAlH_4$ (19.17 g, 505.1 mmol) in diethyl ether (500 mL) at −78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. For workup degassed water (120 mL) was added dropwise at 0 °C and the mixture stirred at room temperature for 1 h. The precipitate was separated and extracted with diethyl ether (2 × 100 mL), and the combined organic phases were dried over $MgSO_4$. Evaporation of the solvents *in vacuo* yielded a colourless liquid: 8.35 g, 89.3% yield, bp 72 °C (0.9 mbar), mp −39 °C. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: −152.4 (s). ^{31}P: −152.4 (tm, $^1J_{PH} = 207.5$ Hz). $^{13}C\{^1H\}$: 138.8 (dd, $^2J_{CP} = 27.5$ Hz, $^3J_{CP} = 8.3$ Hz, *C*3/4), 132.1 (dd, $^1J_{CP} = 25.4$ Hz, $^3J_{CP} = 2.6$ Hz, *C*2/5). ^1H: 7.17 (m, A-part of an AA‘XX’ spin system, 2H, *H*3/4), 4.08 (d, $^1J_{HP} = 207.3$ Hz, 4H, PH_2). MS (EI) *m/z* 148 $[M]^+$, 147 $[M - H]^+$, 146 $[M - 2H]^+$, 115 (100%) $[M - PH_2]^+$, 114 $[M - PH_2 - H]^+$, 113 $[M - PH_2 - 2H]^+$. Calc. for $C_4H_6P_2S$ (148.10): C, 32.44; H, 4.08; P, 41.83. Found: C, 32.41; H, 4.19; P, 41.82%.

2-[Bis(diethyl-amino)phosphinyl]furan, 8. The preparation of 2-furyllithium **7** was based on a literature procedure.[44] A solution of ^nBuLi (77 mL, 123 mmol, 1.6 M in hexane) was slowly added to THF (77 mL) at 0 °C and subsequently furan (10.85 g, 159 mmol) was added at the same temperature. The reaction mixture was allowed to warm to room temperature and stirring was continued for 20 min.

Bis(diethylamino)chlorophosphine (29.75 g, 141 mmol) was slowly added at −78 °C and the reaction mixture was allowed to warm to room temperature and stirred for 12 h. The residue remaining upon evaporation of the solvent *in vacuo* was extracted with hexane (200, 100 mL). Evaporation of the combined hexane extracts *in vacuo* yielded a brown oily liquid, which contained only small amounts of bis(diethylamino)chlorophosphine, tris(diethylamino)phosphine and (diethylamino)(2-furyl)chlorophosphine. $^{31}P\{^1H\}$ NMR (hexane, 25 °C): 80.7 (s). MS (EI) *m/z* 242 $[M]^+$, 170 (100%) $[M - NEt_2]^+$, 99 $[M - 2NEt_2 + H]^+$, 72 $[NEt_2]^+$.

2-(Dichlorophosphinyl)furan, 9. A solution of the above product (**8**, with impurities) in hexane (500 mL) was cooled to 0 °C and saturated with gaseous HCl. The reaction mixture was stirred for 1 h, again saturated with gaseous HCl and stirred for 1 h. This procedure was repeated until the supernatant solution remained clear upon further addition of HCl. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. The diethylammonium chloride precipitate was separated and extracted with hexane (2 × 100 mL). Distillation of the combined organic phases yielded a colourless liquid: 13.94 g, 67.0% yield (based on ^nBuLi), bp 181 °C, mp −40 °C. Block-shaped single crystals were grown by slow cooling of the melt. NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: 123.7 (s). $^{13}C\{^1H\}$: 152.6 (d, $^1J_{CP} = 68.4$ Hz, *C*2), 150.4 (d, $^3J_{CP} = 3.1$ Hz, *C*5), 122.7 (d, $^2J_{CP} = 36.1$ Hz, *C*3), 111.7 (d, $^3J_{CP} = 6.1$ Hz, *C*4). ^1H: 7.85 (dd, A-part of an ABCX spin system, $^3J_{HH} = 1.8$ Hz, $^4J_{HH} = 0.7$ Hz, 1H, *H*5), 7.19 (m, B-part, 1H, *H*3), 6.56 (m, C-part, 1H, *H*4). MS (EI) *m/z* 168 $[M]^+$, 133 (100%) $[M - Cl]^+$, 101 $[PCl_2]^+$, 98 $[M - 2Cl]^+$. Calc. for $C_4H_3Cl_2OP$ (168.95): C, 28.44; H, 1.79; P, 18.33. Found: C, 28.44; H, 1.72; P, 18.24%.

2-Phosphinylfuran, 10. A solution of **9** (13.40 g, 79.3 mmol) in diethyl ether (60 mL) was added slowly to a stirred suspension of $LiAlH_4$ (12.00 g, 316.2 mmol) in diethyl ether (300 mL) at −78 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. For workup degassed water (70 mL) was added dropwise at 0 °C and the mixture stirred at room temperature for 1 h. The precipitate was separated and extracted with diethyl ether (2 × 50 mL), and the combined organic phases were dried over MgSO$_4$. **10** could not be isolated from the diethyl ether solution by distillation, but formed an azeotrope: Bp 35 °C, *ca.* 5 mol% of **10**. In the GC separation, using columns as specified in the general part above, compound **10** had a retention time of 1.1 min at 37 °C. NMR (CD$_2$Cl$_2$, 25 °C), ^{31}P{^{1}H}: −164.2 (s). ^{31}P: −164.2 (tm, $^{1}J_{\mathrm{PH}} = 209.3$ Hz). ^{13}C{^{1}H}: 147.8 (s, *C*5), 144.5 (d, $^{1}J_{\mathrm{CP}} = 20.8$ Hz, *C*2), 122.6 (d, $^{2}J_{\mathrm{CP}} = 25.4$ Hz, *C*3), 111.5 (d, $^{3}J_{\mathrm{CP}} = 6.1$ Hz, *C*4). ^{1}H: 7.61 (dd, A-part of an ABCX spin system, $^{3}J_{\mathrm{HH}} = 1.8$ Hz, $^{4}J_{\mathrm{HH}} = 0.7$ Hz, 1H, *H*5), 6.70 (m, B-part, 1H, *H*3), 6.37 (dt, C-part, $^{3}J_{\mathrm{HH}} = 3.3$ Hz, $^{3}J_{\mathrm{HH}} = 1.8$ Hz, $^{4}J_{\mathrm{HP}} = 1.8$ Hz, 1H, *H*4), 3.89 (d, $^{1}J_{\mathrm{HP}} = 209.1$ Hz, 2H, P*H*$_2$). MS (EI) *m*/*z* 100 [M]$^+$, 99 (100%) [M − H]$^+$, 98 [M − 2H]$^+$.

2,5-Bis[bis(diethylamino)phosphinyl]furan, 12. The preparation of 2,5-dilithiofuran **11** was based on a modified literature procedure.[15] A solution of ^{t}BuLi (208 mL, 312 mmol, 1.5 M in pentane) was slowly added to diethyl ether (400 mL) at −78 °C and subsequently a solution of furan (10.50 g, 154 mmol) in diethyl ether (80 mL) was added at the same temperature. The reaction mixture was stirred for 1 h at −78 °C and then allowed to warm slowly to room temperature. During this period the yellow solution changed to a white suspension, which was stirred for additional 1.5 h at room temperature. (In a separate experiment, stirring for a longer time at room temperature resulted in a darkening of the white suspension indicating decomposition.) Bis(diethylamino)chlorophosphine (74.00 g, 351 mmol) was slowly added at −78 °C and the reaction mixture was allowed to warm to room temperature and subsequently stirred for 12 h. The residue remaining upon evaporation of the solvent *in vacuo* was extracted with hexane (250 and 100 mL) and the combined hexane extracts were concentrated *in vacuo* and stored at −30 °C to precipitate colourless, block-shaped crystals. The crystals melted when warmed to room temperature to give a colourless oily liquid: 45.81 g, 71.3% yield, mp 4 °C. NMR (CD$_2$Cl$_2$, 25 °C), ^{31}P{^{1}H}: 79.6 (s). ^{13}C{^{1}H}: 160.6 (dd, $^{1}J_{\mathrm{CP}} = 6.9$ Hz, $^{3}J_{\mathrm{CP}} = 3.1$ Hz, *C*2/5), 117.4 (d, $^{2}J_{\mathrm{CP}} = 16.1$ Hz, *C*3/4), 43.4 (d, $^{2}J_{\mathrm{CP}} = 17.7$ Hz, *C*H$_2$), 15.0 (d, $^{3}J_{\mathrm{CP}} = 2.3$ Hz, *C*H$_3$). ^{1}H: 6.49 (m, A-part of an AA'XX' spin system, 2H, *H*3/4), 3.12 (m, 16H, C*H*$_2$), 1.10 (t, $^{3}J_{\mathrm{HH}} = 7.2$ Hz, 24H, C*H*$_3$). MS (EI) *m*/*z* 416 [M]$^+$, 344 [M − NEt$_2$]$^+$, 241 [M − P(NEt$_2$)$_2$]$^+$, 175 [P(NEt$_2$)$_2$]$^+$. Calc. for C$_{20}$H$_{42}$N$_4$OP$_2$ (416.52): C, 57.67; H, 10.16; N, 13.45; P, 14.87. Found: C, 57.58; H, 9.98; N, 13.37; P, 14.84%.

2,5-Bis(dichlorophosphinyl)furan, 13. A solution of **12** (45.37 g, 108.9 mmol) in hexane (500 mL) was cooled to 0 °C and saturated with gaseous HCl. The reaction mixture was stirred for 1 h, again saturated with gaseous HCl and stirred for 1 h. This procedure was repeated until the supernatant solution remained clear upon further addition of HCl. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. The diethylammonium chloride precipitate was separated and extracted with hexane (2 × 100 mL). Evaporation of the solvent from the combined organic phases and distillation of the residue *in vacuo* yielded a colourless oily liquid. On cooling to 0 °C a polycrystalline solid was obtained: 19.06 g, 64.9% yield, bp 95 °C (0.9 mbar), mp 28 °C. Colourless, block-shaped single crystals formed upon melting the solid, leaving only a small amount of the polycrystalline material as seed crystals and storage of the sample at room temperature. NMR (CD$_2$Cl$_2$, 25 °C), ^{31}P{^{1}H}: 124.6 (s). ^{13}C{^{1}H}: 160.1 (dd, $^{1}J_{\mathrm{CP}} = 71.5$ Hz, $^{3}J_{\mathrm{CP}} = 2.3$ Hz, *C*2/5), 121.6 (dd, $^{2}J_{\mathrm{CP}} = 26.9$ Hz, $^{3}J_{\mathrm{CP}} = 3.8$ Hz, *C*3/4). ^{1}H: 7.24 (m, A-part of an AA'XX' spin system, 2H, *H*3/4). MS (EI) *m*/*z* 270 [M]$^+$, 233 (100%) [M − Cl]$^+$, 198 [M − 2Cl]$^+$, 167 [M − PCl$_2$]$^+$, 132 [M − PCl$_2$ − Cl]$^+$, 101 [PCl$_2$]$^+$, 97 [M − PCl$_2$ − 2Cl]$^+$. Calc. for C$_4$H$_2$Cl$_4$OP$_2$ (269.82): C, 17.81; H, 0.75; P, 22.96. Found: C, 17.88; H, 0.83; P, 23.07%.

2,5-Di(phosphinyl)furan, 14. A solution of **13** (17.00 g, 63.0 mmol) in diethyl ether (100 mL) was added slowly to a stirred suspension of LiAlH$_4$ (19.00 g, 500.7 mmol) in diethyl ether (500 mL) at −78 °C. The reaction mixture was then allowed to warm to room temperature and subsequently stirred for 12 h. For workup degassed water (120 mL) was added dropwise at 0 °C and the mixture stirred at room temperature for 1 h. The precipitate was separated and extracted with diethyl ether (2 × 100 mL), and the combined organic phases were dried over MgSO$_4$. **14** was isolated by fractional distillation: bp 113 °C, 3.60 g, 43% yield. NMR (CD$_2$Cl$_2$, 25 °C), ^{31}P{^{1}H}: −161.9 (s). ^{31}P: −161.9 (t, $^{1}J_{\mathrm{PH}} = 210.1$ Hz). ^{13}C{^{1}H}: 149.6 (d, $^{1}J_{\mathrm{CP}} = 21.5$ Hz, *C*2/5), 123.3 (dd, $^{2}J_{\mathrm{CP}} = 23.8$ Hz, $^{3}J_{\mathrm{CP}} = 6.1$ Hz, *C*3/4). ^{1}H: 6.66 (m, A-part of an AA'XX' spin system, 2H, *H*3/4), 3.92 (d, $^{1}J_{\mathrm{HP}} = 210.3$ Hz, 4H, P*H*$_2$). MS (EI) *m*/*z* 132 [M]$^+$, 131 [M − H]$^+$, 130 [M − 2H]$^+$, 99 (100%) [M − PH$_2$]$^+$, 98 [M − PH$_2$ − H]$^+$, 97 [M − PH$_2$ − 2H]$^+$.

{2-C$_4$H$_3$S–P[Au(P^{t}Bu$_3$)]$_3$}$^+$BF$_4^-$, 15. A solution of phosphine **2** (16.3 mg, 0.14 mmol) in CH$_2$Cl$_2$ (10 mL) was slowly added to a stirred solution of oxonium salt **19** (182.1 mg, 0.14 mmol) in the same solvent (20 mL) at −78 °C. The colourless reaction mixture was warmed to ambient temperature after 2 h and concentrated *in vacuo*. Upon addition of pentane (50 mL) a colourless oil separated, which was dried *in vacuo* to yield **15** as a polycrystalline solid: 191.5 mg, 97.8% yield, mp 130 °C (decomposition). Colourless, block-shaped single crystals could be grown by slow diffusion of diethyl ether vapour into a solution of the compound in CH$_2$Cl$_2$ at −30 °C. NMR (CD$_2$Cl$_2$, 25 °C), ^{31}P{^{1}H}: 99.3 (d, $^{2}J_{\mathrm{PP}} = 240.3$ Hz, ^{t}Bu$_3$*P*), −24.4 (q, $^{2}J_{\mathrm{PP}} = 240.3$ Hz, *P*Au$_3$). ^{31}P: 99.3 (d × 28 (2 × 18 lines resolved), $^{2}J_{\mathrm{PP}} = 240.3$ Hz, $^{3}J_{\mathrm{PH}} = 13.4$ Hz, ^{t}Bu$_3$*P*), −24.4 (qd, $^{2}J_{\mathrm{PP}} = 240.3$ Hz, $^{3}J_{\mathrm{PH}} = 7.1$ Hz, *P*Au$_3$). ^{13}C{^{1}H}: 135.5 (m), 128.1 (m), 40.0 (d, $^{1}J_{\mathrm{CP}} = 13.8$ Hz, *C*(CH$_3$)$_3$), 32.7 (d, $^{2}J_{\mathrm{CP}} = 4.6$ Hz, C(*C*H$_3$)$_3$). ^{1}H: 7.12 (ddd, $^{3}J_{\mathrm{HH}} = 5.1$ Hz, $^{4}J_{\mathrm{HP}} = 2.2$ Hz, $^{4}J_{\mathrm{HH}} = 1.1$ Hz, 1H, *H*5), 7.03 (dd, $^{3}J_{\mathrm{HP}} = 7.3$ Hz, $^{3}J_{\mathrm{HH}} = 3.3$ Hz, 1H, *H*3), 6.94 (dd, $^{3}J_{\mathrm{HH}} = 5.1$ Hz, $^{3}J_{\mathrm{HH}} = 3.3$ Hz, 1H, *H*4), 1.53 (d, $^{3}J_{\mathrm{HP}} = 13.6$ Hz, 81H, C(C*H*$_3$)$_3$). ^{11}B{^{1}H}: −2.1 (s). ^{19}F{^{1}H}: −153.4 (s). MS (FAB) *m*/*z* 1312.4 (100%) [M]$^+$, 1255.3 (15.4) [M − ^{t}Bu]$^+$, 1110.1 (10.8) [M − P^{t}Bu$_3$]$^+$, 913.0 (13.9) [M − AuP^{t}Bu$_3$]$^+$. Calc. for C$_{40}$H$_{84}$Au$_3$BF$_4$P$_4$S (1398.76): C, 34.35; H, 6.05; P, 8.86. Found: C, 34.01; H, 6.18; P, 8.83%.

[2,5-C$_4$H$_2$S{P[Au(P^{t}Bu$_3$)]$_3$}$_2$]$^{2+}$(BF$_4^-$)$_2$, 16. As described for complex **15**, compound **16** was prepared from phosphine **6** (9.4 mg, 0.06 mmol) and oxonium salt **19** (165.1 mg, 0.13 mmol); colourless, polycrystalline solid: 165.7 mg, 96.2% yield, mp 130 °C (decomposition). Colourless, block-shaped single crystals could be grown by slow diffusion of diethyl ether vapour into a solution of the compound in acetone at −30 °C. NMR (CD$_2$Cl$_2$, 25 °C), ^{31}P{^{1}H}: 99.1 (d, $^{2}J_{\mathrm{PP}} = 240.9$ Hz, ^{t}Bu$_3$*P*), −23.2 (q, $^{2}J_{\mathrm{PP}} = 240.9$ Hz, *P*Au$_3$). ^{31}P: 99.1 (d × 28 (2 × 18 lines resolved), $^{2}J_{\mathrm{PP}} = 240.9$ Hz, $^{3}J_{\mathrm{PH}} = 13.4$ Hz, ^{t}Bu$_3$*P*), −23.2 (qd, $^{2}J_{\mathrm{PP}} = 240.9$ Hz, $^{3}J_{\mathrm{PH}} = 7.9$ Hz, *P*Au$_3$). ^{13}C{^{1}H}: 143.7 (d, $^{1}J_{\mathrm{CP}} = 11.4$ Hz, *C*P), 136.8 (m, A-part of an AXX' spin system, *C*H), 40.0 (d, $^{1}J_{\mathrm{CP}} = 14.0$ Hz, *C*(CH$_3$)$_3$), 32.7 (s, C(*C*H$_3$)$_3$). ^{1}H: 6.88 (m, A-part of an AA'XX' spin system, 2H, C*H*), 1.52 (d, $^{3}J_{\mathrm{HP}} = 13.4$ Hz, 162H, C(C*H*$_3$)$_3$). ^{11}B{^{1}H}: −2.1 (s). ^{19}F{^{1}H}: −153.2 (s). MS (FAB) *m*/*z* 1270.9 (54.7%) [M]$^{2+}$, 1242.2 (40.6) [M − ^{t}Bu]$^{2+}$, 1169.5 (6.9) [M − P^{t}Bu$_3$]$^{2+}$, 1070.9 (16.1) [M − AuP^{t}Bu$_3$]$^{2+}$, 601.8 (15.1) [Au(P^{t}Bu$_3$)$_2$]$^+$, 399.5 (35.8) [AuP^{t}Bu$_3$]$^+$. Calc. for C$_{76}$H$_{164}$Au$_6$B$_2$F$_8$P$_8$S (2713.38): C, 33.64; H, 6.09; P, 9.13. Found: C, 33.41; H, 6.09; P, 9.02%.

{2-C$_4$H$_3$S–P[Au(PPh$_3$)]$_3$}$^+$BF$_4^-$, 17. As described for complex **15**, compound **17** was prepared from phosphine **2** (17.3 mg, 0.15 mmol) and oxonium salt **20** (220.6 mg, 0.15 mmol); yellow, polycrystalline solid: 231.2 mg, 98.3% yield, mp 108 °C (decomposition). NMR (CD$_2$Cl$_2$, 25 °C), ^{31}P{^{1}H}: 45.6 (br s, Ph$_3$*P*), −34.8 (br s, *P*Au$_3$). ^{13}C{^{1}H}: 138.3 (m), 136.8 (m), 134.6 (d, $^{2}J_{\mathrm{CP}} = 13.1$ Hz, *o*-*C*$_6$H$_5$), 132.4 (s, *p*-*C*$_6$H$_5$), 129.8 (d, $^{3}J_{\mathrm{CP}} = 9.2$ Hz, *m*-*C*$_6$H$_5$), (*ipso*-*C*$_6$H$_5$ covered by *m*-*C*$_6$H$_5$), 128.6 (m). ^{1}H: 7.68 − 7.32 (m, 48H, C$_6$*H*$_5$ + *H*3/4/5). ^{11}B{^{1}H}: −2.1 (s).

Table 1 Crystal data, data collection and structure refinement for compounds **4**, **9**, **12**, **13**, **15** and **16**

	4	**9**	**12**	**13**	**15**	**16**
Empirical formula	$C_{20}H_{42}N_4P_2S$	$C_4H_3Cl_2OP$	$C_{20}H_{42}N_4OP_2$	$C_4H_2Cl_4OP_2$	$C_{40.76}H_{85.51}Au_3BCl_{1.51}F_4P_4S$	$C_{76}H_{164}Au_6B_{1.67}F_{6.67}P_8S$
M	432.58	168.95	416.52	269.80	1463.08	2684.37
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Tetragonal	Triclinic	Cubic
Space group	$P2_1/n$	$Pbca$	$P2_1$	$P\bar{4}2_1m$	$P\bar{1}$	$Im\bar{3}$
a/Å	13.2635(3)	10.4742(3)	10.8376(1)	9.0431(2)	12.7063(6)	31.4590(6)
b/Å	8.0961(2)	18.5825(6)	15.8571(2)	9.0431	14.5754(8)	31.4590
c/Å	23.8229(5)	6.8165(2)	14.3424(2)	6.2387(2)	16.2534(5)	31.4590
α/°					102.894(3)	90
β/°	102.190(2)	90	90.2038(6)	90	106.329(3)	90
γ/°					97.318(3)	90
V/Å^3	2500.5(1)	1326.74(7)	2464.77(5)	510.19(2)	2757.1(2)	31134(1)
D_c/g cm^{-3}	1.149	1.691	1.122	1.756	1.762	1.718
Z	4	8	4	2	2	12
$F(000)$	944	672	912	264	1420	15580
T/K	143(2)	143(2)	143(2)	193(2)	143(2)	143(2)
Refls. measured	92884	55746	55572	13348	46585	324682
Refls. unique	4401	1197	9043	423	9557	5040
Parameters/restraints	252/0	85/0	823/1	32/0	556/6	285/10
$R1\ [I \geq 2\sigma(I)]$	0.052	0.037	0.024	0.036	0.047	0.052
$wR2^a$	0.144	0.098	0.063	0.096	0.112	0.115
Weighting scheme	$a = 0.0626$ $b = 3.9640$	$a = 0.0398$ $b = 1.5227$	$a = 0.0349$ $b = 0.2103$	$a = 0.0419$ $b = 0.2320$	$a = 0.0267$ $b = 17.2384$	$a = 0.0000$ $b = 1600.2937$
σ_{fin}(max./min.)/e Å^{-3}	0.820/−0.404	0.372/−0.355	0.139/−0.198	0.198/−0.293	2.587/−2.924	3.341/−1.369

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

$^{19}F\{^1H\}$: −153.3 (s). MS (FAB) m/z 1490.9 (9.4%) $[M]^+$, 1228.5 (2.7) $[M - PPh_3]^+$, 720.4 (100) $[Au(PPh_3)_2]^+$, 458.4 (89.0) $[AuPPh_3]^+$. Calc. for $C_{58}H_{48}Au_3BF_4P_4S$ (1578.67): C, 44.13; H, 3.06; P, 7.85. Found: C, 43.91; H, 2.95; P, 7.79%.

$[2,5\text{-}C_4H_2S\{P[Au(PPh_3)]_3\}_2]^{2+}(BF_4^-)_2$, 18. As described for complex **15**, compound **18** was prepared from phosphine **6** (11.9 mg, 0.08 mmol) and oxonium salt **20** (237.9 mg, 0.16 mmol); yellow, polycrystalline solid: 237.5 mg, 96.2% yield, mp 108 °C (decomposition). NMR (CD_2Cl_2, 25 °C), $^{31}P\{^1H\}$: 46.4 (br s, Ph_3P), −35.3 (br s, PAu_3). $^{13}C\{^1H\}$: 141.6 (d, $^1J_{CP}$ = 14.5 Hz, CP), 138.4 (m, A-part of an AXX′ spin system, CH), 134.5 (d, $^2J_{CP}$ = 5.2 Hz, $o\text{-}C_6H_5$), 132.4 (s, $p\text{-}C_6H_5$), 129.8 (s, $m\text{-}C_6H_5$), ($ipso\text{-}C_6H_5$ covered by $m\text{-}C_6H_5$). ^1H: 7.68 – 7.32 (m, 90H, C_6H_5), 7.20 (m, A-part of an AA‘XX’ spin system, 2H, CH). $^{11}B\{^1H\}$: −2.1 (s). $^{19}F\{^1H\}$: −153.3 (s). MS (FAB) m/z 720.4 (100%) $[Au(PPh_3)_2]^+$, 458.4 (70.7) $[AuPPh_3]^+$. Calc. for $C_{112}H_{92}Au_6B_2F_8P_8S$ (3073.19): C, 43.77; H, 3.02; P, 8.06. Found: C, 43.28; H, 3.16; P, 8.18%.

Determination of the crystal structures

Specimens of suitable quality and size of **4**, **9**, **12**, **13**, **15** and **16** 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-Kα radiation. Crystals of **13** undergo a reversible phase transition between −84 and −88 °C. Due to loss of lattice symmetry the low temperature phase is then multiple twinned. 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).[45] The thermal motion was treated anisotropically for all non-hydrogen atoms.

The lattice of **15** contains solvent molecules (CH_2Cl_2) which are disordered over two sites. The independent refinement of the site occupation factors results in an occupation of only 0.76 for the sum of both sites.

After the initial refinement of the cationic part of the crystal structure of **16** the highest residual electron densities were found in the vicinity of special positions with a local symmetry not fulfilling the requirements for tetrahedral symmetry. The $[BF_4]^-$-anions were nevertheless assigned to these positions, owing to a lack of other suitable positions, and are therefore disordered. It was not possible to locate a total of 0.5 $[BF_4]^-$ per asymmetric unit required for a charge neutrality. The structure model therefore is to be considered as incomplete regarding the anionic components.

The hydrogen atoms in **9** and **12** were located and refined with isotropic displacement parameters, those in **4**, **13**, **15** and **16** were calculated in ideal positions and refined using a riding model.

In the structure of **15** all C–Cl bond lengths of the solvent molecules and in the structure of **16** all B–F bond lengths of the $[BF_4]^-$ anions were restrained to be equal.

An absorption correction was carried out for **15** using DELABS, as part of the PLATON suite of programs.[46] The Flack parameter is 0.00(3) for **12** and 0.6(3) for **13**. Further information on crystal data, data collection and structure refinement is summarized in Table 1.

CCDC reference numbers 252034-252039.

See http://www.rsc.org/suppdata/dt/b4/b415326j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and Deutscher Akademischer Austauschdienst. The authors are indebted to Degussa AG and Heraeus GmbH for the donation of chemicals.

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