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Full Paper

Heterotopic As,S,P and As,S,As Ligands: Synthesis and Theoretical Studies

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The heterotopic As,S,P ligands 1-AsPh$_2$-2-S^{t}Bu-3-PPh$_2$-C$_6$H$_3$ (**2**) and 1-AsPh$_2$-2-SH-3-PPh$_2$-C$_6$H$_3$ (**4**) and dinucleating As,S,As ligand 1,3-(AsPh$_2$)$_2$-2-S^{t}Bu-C$_6$H$_3$ (**3**) have been synthesized and characterized. The structural motif of these compounds suggests great potential for their use as monodentate, bidentate chelating, bidentate bridging, and tridentate ligands.

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Introduction

Phosphanyl- and arsanylarylthiolates have great potential as heterotopic ligands in transition metal complexes.[1] In the group of phosphanylarylthiols, 1-PPh$_2$-2-SH-C$_6$H$_4$ (PSH)[2] has been extensively studied,[1] whereas the chemistry of the analogous arsanylarylthiol 1-AsPh$_2$-2-SHC$_6$H$_4$ (AsSH) has been less explored.[3] Furthermore, the chemistry of arylthiolates with two P,S chelating pockets is not well developed and, to the best of our knowledge, is unknown for two As,S donor groups. Literature reports fitting this structural motif include 2,6-bis-(diphenylphosphino)benzenethiol[4] and 2,6-bis(diphenylphosphinomethyl)benzenethiol[5], although in the latter case, the diphenylphosphino groups are not directly connected to the thiophenol core. Whereas the chemistry of thiophenol-based heterodonor P,S and As,S ligands has been explored to some extent, the P,SAs ligand 1-Ph$_2$AsS-2-PPh$_2$-C$_6$H$_4$ is the only example of a thiophenol-based derivative incorporating all three donor atoms.[6,7] The design of potentially tridentate heterotopic P,As,S ligands as well dinucleating As,S,As ligands seemed promising, because all three atoms are excellent donors for a wide range of metals and could exhibit variable coordination modes, e.g. monodentate, bidentate chelating, bidentate bridging or tridentate, in metal complexes.

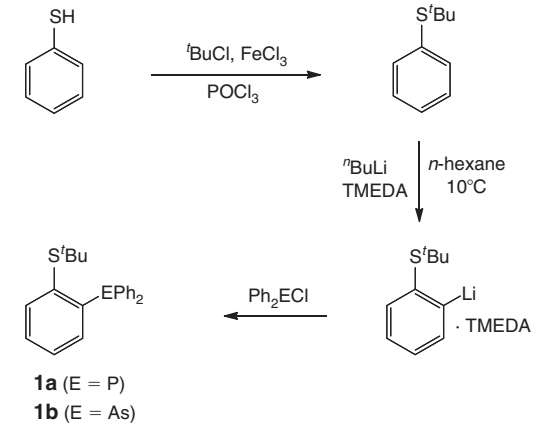
Results and Discussion

In a first approach for the synthesis of the desired P,As,S ligands, 1-PPh$_2$-2-SH-C$_6$H$_4$ (PSH)[2] and 1-AsPh$_2$-2-SH-C$_6$H$_4$ (AsSH)[3] were used as starting materials. To introduce the third donor atom (As or P) in the second *ortho* position of PSH or AsSH, the same conditions were employed as in the dilithiation of thiophenol.[8–10] However, the ^{31}P{^{1}H} NMR spectra of the isolated white solids showed the formation of a mixture of products that could not be separated or characterized. Modification of the reaction conditions (longer or shorter reaction time or lower temperatures (−90°C) to favour substitution in the *ortho* position) did not result in any improvement. Apparently, protection of the sulfur atom is necessary. Whereas anisole is metallated in the *ortho* position giving *o*-methoxyphenyllithium,[11–13] thioanisole is metallated by *n*-butyllithium at the methyl group, resulting in phenylthiomethyllithium.[14–16] Therefore, a methyl group seemed to be less useful as protecting group, whereas protection with a more bulky ^{t}Bu group was expected to direct the lithiation to the *ortho* position.

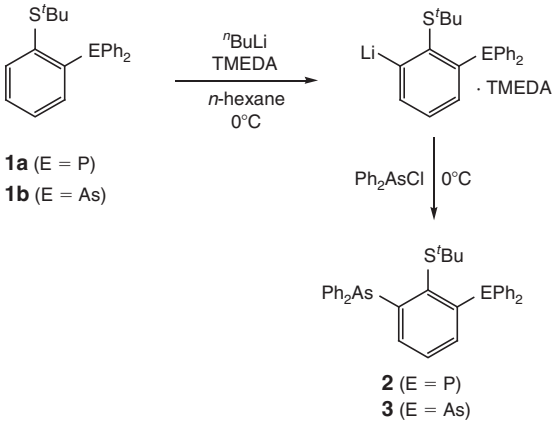
1-PPh$_2$-2-S^{t}Bu-C$_6$H$_4$ (**1a**)[16] was prepared according to the literature from *tert*-butyl phenyl sulfide[17] and *n*-butyllithium in *n*-hexane.[16] 1-AsPh$_2$-2-S^{t}Bu-C$_6$H$_4$ (**1b**) was obtained accordingly by using Ph$_2$AsCl instead of Ph$_2$PCl (Scheme 1). Workup gave **1b** as a white solid in good yield.

Treatment of 1-PPh$_2$-2-S^{t}Bu-C$_6$H$_4$ (**1a**) with ^{n}BuLi and slow addition of TMEDA (Me$_2$NCH$_2$CH$_2$NMe$_2$) followed by very slow addition (over 2–3 h) of Ph$_2$AsCl gave 1-AsPh$_2$-2-S^{t}Bu-3-PPh$_2$-C$_6$H$_3$ (**2**) as a pale yellow solid in moderate yield. Alternatively, compound **2** can be prepared from **1b** and Ph$_2$PCl, albeit in slightly lower yield. 1,3-AsPh$_2$-2-S^{t}Bu-C$_6$H$_3$ (**3**) was obtained in moderate yield as a white solid in a similar way to **2** starting from **1b** (Scheme 2).

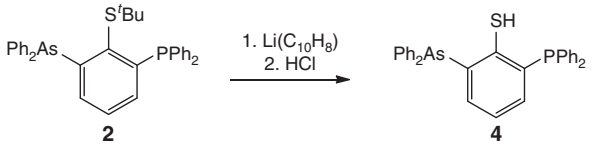
To restore the –SH functionality, **2** was treated with lithium naphthalenide, followed by acidification of the reaction medium (Scheme 3). Even though literature data suggested higher selectivity for S–C bond cleavage when lithium naphthalenide is used instead of sodium naphthalenide,[4,18] small quantities of products containing P–H and As–H bonds were formed besides 1-AsPh$_2$-2-SH-3-PPh$_2$-C$_6$H$_3$ (**4**), which was isolated as a waxy, pale-yellow solid. We have already reported a structural isomer



Scheme 1. Synthetic route to **1a** and **1b**.



Scheme 2. Synthesis of **2** and **3**.



Scheme 3. Synthesis of **4**.

of **4**, namely the P,SAs ligand 1-Ph_2AsS-2-PPh_2-C_6H_4.[6] However, this compound reacts with Group 10 metal dihalides with cleavage of the As–S bond and coordination of the resulting bidentate phosphanylthiolato ligand.[6]

In the ^{1}H NMR spectra, compounds **1b**–**4** show signals in the range of $\delta = 7.4$–6.7 due to the aromatic protons, a singlet at δ 1.65 (**2**), δ 1.35 (**1b**), and δ 1.65 (**3**) assigned to the ^{t}Bu protons, and a doublet at δ 4.75 ($^4J_{PH}$ 4.5 Hz) for the SH proton in **4**. Compound **2** exhibits a singlet in the ^{31}P{^{1}H} NMR spectrum at δ −6.7, whereas replacement of the ^{t}Bu group with a hydrogen atom in **4** results in a high-field shift (δ −11.7). In the electrospray ionization (ESI) and electron ionization (EI) mass spectra of **1b**–**4**, the corresponding molecular ion peaks as well as appropriate fragmentations were observed. Whereas (±)-(2-mercaptoethyl)methylphenylphosphine[19] and its arsenic analogue[20] were reported to be air-sensitive and (±)-(2-mercaptoethyl)methylphenylphosphine is photochemically active even under room lighting,[19] compounds **1b**–**4** can be handled in air for a short period of time and show no photosensitivity even after long-term storage under room lighting. However, for longer storage periods, an inert atmosphere is recommended.

Crystals of **1b** suitable for single-crystal X-ray diffraction analysis were obtained from a two-layer diethyl ether/*n*-hexane system at room temperature. The compound 2-(*tert*-butylthio) phenyl-diphenylarsine crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit (Table 1). The two independent molecules have a very similar conformation, and there are only small deviations in bond lengths and angles; thus, further discussion will focus on only one molecule. Compounds **2**–**4** crystallize in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Table 1). The molecular structures of **2** and **3** are isomorphous. In **2** and **4**, the arsenic and phosphorus atoms were found to be disordered on the same position (0.54 : 0.46 in **2**; 0.61 : 0.39 in **4**).

Compounds **1b** (Fig. 1), **2**, and **3** (Fig. 2) adopt a conformation in which the PPh_2, $AsPh_2$, and ^{t}BuS substituents are rotated around the bonds connecting the heteroatoms to the central phenyl ring to minimize the steric interactions between the ^{t}Bu group and the phenyl rings. Owing to the less sterically demanding (disordered) SH group in **4** (Fig. 3), the PPh_2 and $AsPh_2$ substituents are no longer forced to only one side of the plane of the central phenyl ring as in **2** and **3**. The phosphorus and arsenic atoms in **1b**–**4** are coordinated in a slightly distorted pyramidal fashion by the three carbon atoms of the aromatic rings (Table 2). Bond lengths and angles are in the expected ranges and comparable with those of other phosphanylarylthiols.[21,22]

Computational Results

The optimized geometries of **2** and **4** are in good agreement with the experimentally determined values (Table 2). The HOMO of **2** consists mainly of the lone pairs of electrons at sulfur, phosphorus, and arsenic, with the maximum atomic orbital coefficient at sulfur (0.27), followed by 0.18 on phosphorus and 0.11 at arsenic (Fig. 4). This indicates that the P,S chelating pocket may be favoured over the As,S unit during an electrophilic attack. This is also supported by the electrostatic potential surface, on which the negative regions are concentrated around the lone pairs of electrons at sulfur and phosphorus (Fig. 5). The LUMO of **2** consists mainly of unoccupied orbitals at the carbon atoms of the central aromatic ring, but also shows a slight S–C(8) antibonding character (Fig. 4). Removing the ^{t}Bu group from **2** results in the HOMO being localized only at the P,S chelating pocket, and the lone pair of electrons at arsenic is shifted to HOMO-2. Thus, the HOMO of **4** mainly consists of the lone pairs of electrons at sulfur and phosphorus, with the maximum atomic orbital coefficient at sulfur (0.24), followed by 0.21 on phosphorus (Fig. 4). The negative regions of the electrostatic potential surface are also concentrated around the lone pairs of electrons at sulfur and phosphorus (Fig. 5). These results indicate that the P,S chelating pocket becomes even more favoured over the As,S unit during an electrophilic attack after removing the bulky ^{t}Bu group.

Conclusion

The synthesis and structural characterization of the heterotopic As,S,P ligands 1-$AsPh_2$-2-S^{t}Bu-3-PPh_2-C_6H_3 (**2**) and 1-$AsPh_2$-2-SH-3-PPh_2-C_6H_3 (**4**) and dinucleating As,S,As ligand 1,3-$(AsPh_2)_2$2-2-S^{t}BuC_6H_3 (**3**) are reported, as well as theoretical studies concerning their reactivity. The structural motif of **2**–**4**

Table 1. Crystallographic data for compounds 1b–4

	1b	**2**	**3**	**4**
Formula	$C_{22}H_{23}AsS$	$C_{34}H_{32}AsPS$	$C_{34}H_{32}As_2S$	$C_{30}H_{24}AsPS$
M_r	394.38	578.55	622.50	522.44
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [pm]	2083.19(8)	921.65(6)	921.16(7)	839.05(4)
b [pm]	787.77(3)	1236.3(1)	1238.00(8)	1167.49(5)
c [pm]	2474.1(1)	1278.91(7)	1284.9(1)	1335.16(6)
α [°]	90	92.800(5)	92.984(6)	91.364(4)
β [°]	106.118(4)	98.685(5)	98.332(7)	106.260(4)
γ [°]	90	94.037(6)	94.077(6)	94.377(4)
V [nm^3]	3.9006(3)	1.4343(2)	1.4433(2)	1.2505(1)
Z	8	2	2	2
D_{calcd} [g cm^{-3}]	1.343	1.340	1.432	1.387
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.850	1.335	2.409	1.523
$F(000)$	1632	600	636	536
Crystal size [mm]	0.25 × 0.09 × 0.06	0.2 × 0.2 × 0.1	0.2 × 0.15 × 0.05	0.3 × 0.2 × 0.07
θ range [°]	2.82–30.51	2.89–30.51	2.89–30.51	2.96–30.51
hkl range	$-29 \le h \le 29; -11 \le k \le 11; -35 \le l \le 35$	$-13 \le h \le 12; -17 \le k \le 14; -18 \le l \le 17$	$-12 \le h \le 13; -17 \le k \le 13; -18 \le l \le 18$	$-11 \le h \le 11; -16 \le k \le 16; -19 \le l \le 19$
Reflections collected	52742	14510	16112	23906
Reflections unique	11903 [$R_{int} = 0.0802$]	8743 [$R_{int} = 0.0317$]	8749 [$R_{int} = 0.0457$]	7618 [$R_{int} = 0.0410$]
Parameters refined	439	339	337	308
GoF on F^2	1.030	1.020	1.007	1.026
R_1 [$I > 2\sigma(I)$]	$R1 = 0.0560$	$R1 = 0.0465$	$R1 = 0.0403$	$R1 = 0.0434$
	$wR2 = 0.0772$	$wR2 = 0.0867$	$wR2 = 0.0692$	$wR2 = 0.0880$
R indices (all data)	$R1 = 0.0984$	$R1 = 0.0718$	$R1 = 0.0746$	$R1 = 0.0645$
	$wR2 = 0.0881$	$wR2 = 0.0974$	$wR2 = 0.0940$	$wR2 = 0.0966$
$\Delta\rho_{fin}$ [eÅ^{-3}]	0.462 and −0.509	0.456 and −0.296	0.860 and −0.825	0.414 and −0.300

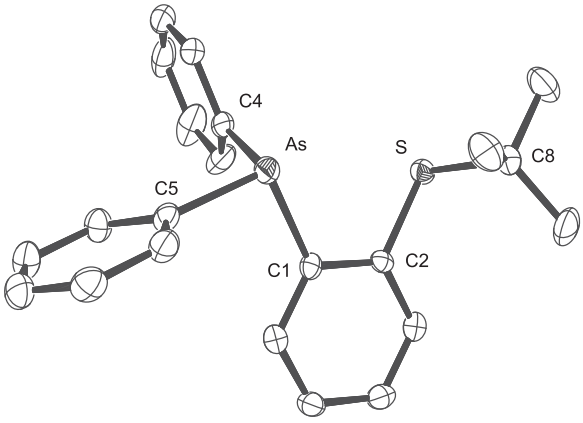


Fig. 1. Molecular structure of **1b**. Only one of the two independent molecules is shown. Hydrogen atoms are omitted for clarity.

suggests variable potential coordination modes. Compounds **2** and **4** in particular promise interesting coordination chemistry due to the presence of three different donor atoms. Density functional theory calculations indicate that the P,S chelating pocket may be favoured over As,S during an electrophilic attack. These studies are now under way.

Experimental and Computational Methods

All reactions were carried out under nitrogen using standard Schlenk techniques. TMEDA and solvents were dried and

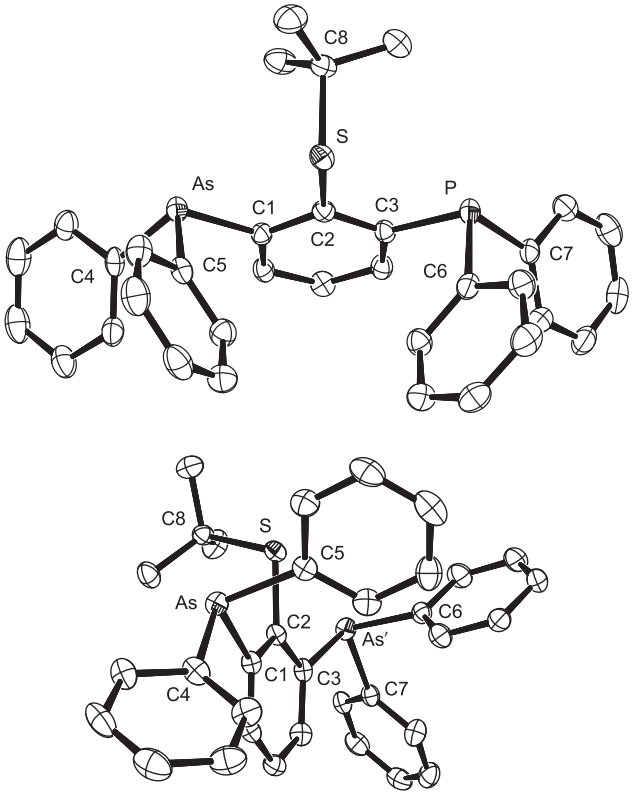


Fig. 2. Molecular structure of **2** (top), and **3** (bottom). Hydrogen atoms are omitted for clarity.

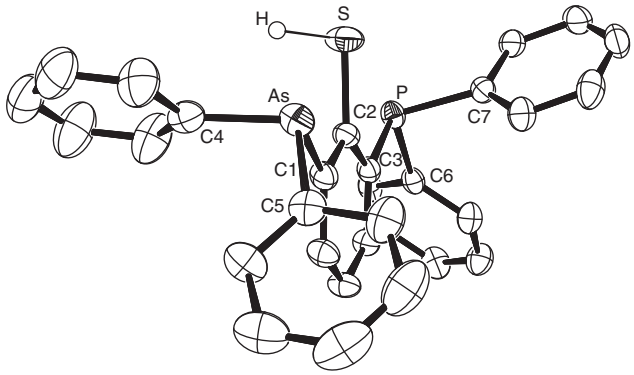


Fig. 3. Molecular structure of **4**. Hydrogen atoms (other than the disordered S–H; only one position is shown) are omitted for clarity.

distilled before use by described procedures or by use of a solvent purification system (MB SPS-800, MBRAUN GmbH). Ph_2AsCl,[23] ^{t}BuSPh,[24] and 1-PPh_2-2-S^{t}Bu-C_6H_4[16] were prepared according to literature procedures; all other chemicals were used as purchased.

Elemental analysis was performed with a Vario EL-Heraeus microanalyser. The melting points were determined in sealed capillaries and are uncorrected. The IR spectra were recorded on a Perkin–Elmer System 2000 Fourier-transform (FT)IR spectrometer scanning between 4000 and 400 cm^{-1} using KBr disks. ^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P NMR (162 MHz) spectra were recorded at 24°C in $CDCl_3$ and C_6D_6 on a Bruker Avance DRX-400 instrument with TMS as internal standard (^1H NMR) and 85 % H_3PO_4 as external standard (^{31}P NMR). The mass spectra were recorded on a VG12–520 mass spectrometer

Table 2. Selected bond lengths [pm] and angles [°] for compounds 1b and 2–4
The appropriate B3LYP/6-31G(d,p) optimized values are shown in brackets

	1b	2	3	4
As–C(5)	195.2(3)	191.2(2) [196.46]	195.8(3)	192.2(2) [195.88]
As–C(4)	196.3(3)	192.3(2) [196.98]	197.2(3)	190.7(2) [195.60]
As–C(1)	196.6(2)	192.4(2) [197.33]	196.3(3)	194.1(2) [196.60]
P(As′)–C(6)	–	190.4(2) [185.34]	195.8(3)	189.6(2) [185.33]
P(As′)–C(7)	–	190.5(2) [185.82]	195.6(3)	189.3(2) [185.22]
P(As′)–C(3)	–	192.3(2) [186.77]	197.0(2)	190.2(2) [186.24]
S–C(2)	178.2(2)	178.6(2) [180.65]	178.7(3)	177.3(2) [179.87]
S–C(8)	185.0(3)	187.3(2) [190.24]	187.1(3)	–
S–H(1S)	–	–	–	130.7(2) [135.48]
S–H(1SF)	–	–	–	134.0(2)
C(5)–As–C(4)	97.8(1)	98.2(9) [101.01]	98.1(1)	100.2(9) [101.08]
C(5)–As–C(1)	97.9(1)	98.7(8) [97.35]	98.6(1)	97.4(8) [100.18]
C(4)–As–C(1)	101.0(1)	101.2(8) [98.61]	101.0(1)	100.3(8) [99.64]
C(6)–P(As′)–C(7)	–	98.5(9) [101.71]	98.3(1)	98.8(8) [102.85]
C(6)–P(As′)–C(3)	–	97.6(9) [102.57]	97.9(1)	101.0(8) [102.12]
C(7)–P(As′)–C(3)	–	100.1(8) [101.92]	100.1(1)	99.5(8) [102.59]
C(2)–S–C(8)	105.5(1)	105.0(9) [105.54]	105.2(1)	–
C(2)–S–H(1S)	–	–	–	102.0(2) [95.49]
C(2)–S–H(1SF)	–	–	–	98.0(5)

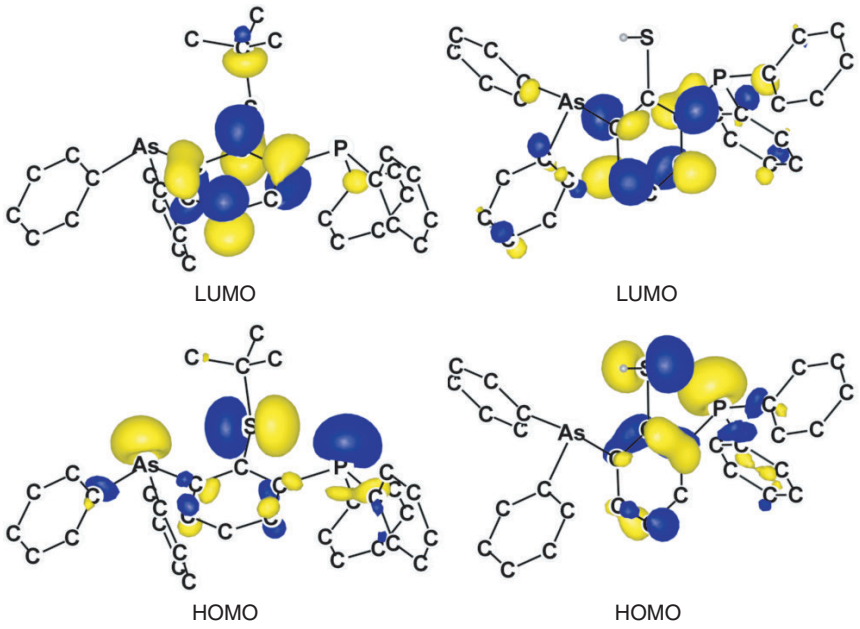


Fig. 4. Frontier molecular orbitals of **2** (left), and **4** (right). Negative orbital contours: blue; positive orbital contours: yellow; isovalue: 0.05 (see the online version for the colour code). Hydrogen atoms are omitted for clarity.

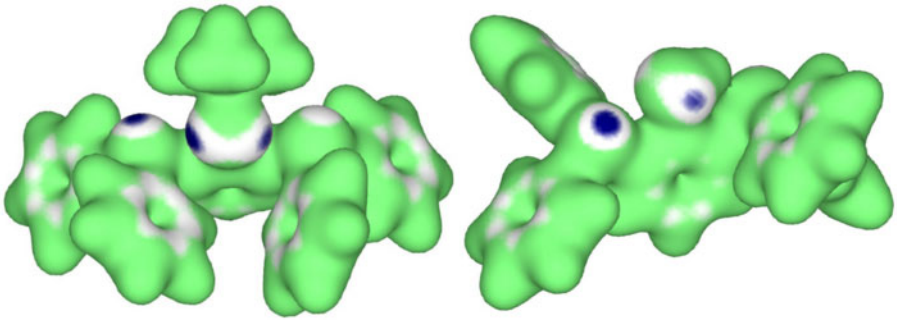


Fig. 5. Electrostatic potential of **2** (left), and **4** (right) mapped onto the electron density surface (isovalue: 0.02). Orientation: PPh_2 moiety on the left, $AsPh_2$ moiety on the right. Negative regions are represented in dark blue and positive regions are in light green (see the online version for the colour code).

(EI-MS, 70 eV, 200°C) and an Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) Bruker Daltonics ESI mass spectrometer (APEXII, 7 T).

The data for the X-ray structures were collected on a Gemini diffractometer (Agilent Technologies) with $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm) and ω-scan rotation. The structures were solved by direct methods (**1b**, **2**, **3**) or Patterson methods (**4**) with the program *SIR92* or *SHELXS-97*.[25] Anisotropic refinement of all non-hydrogen atoms was performed with *SHELXL-97*.[25] Except for SH hydrogen atoms in **4**, all hydrogen atoms were calculated on idealized positions using the riding model. In compounds **2** and **4**, As and P were found to be disordered on the same position (ratio: 0.54(1) : 0.46(1) for **2**, and 0.61(1) : 0.39(1) for **4**). For **4**, interestingly, the disordered hydrogen atoms H(1S) and H(1SF) have the same ratio of 0.61(7) : 0.39(7). Structure figures were generated with *ORTEP*,[26] thermal ellipsoids are drawn at 50 % probability unless otherwise mentioned. CCDC 939321 (**1**), 939322 (**2**), 939323 (**3**), and 939324 (**4**) contain the supplementary crystallographic data for this paper.

All calculations were carried out with the *Gaussian 09* program package[27] using the B3LYP density functional[28,29] and the standard all-electron 6-31G(d,p) basis set.[30]

*Synthesis of 1-$AsPh_2$-2-S^tBu-C_6H_4 (**1b**)*

Freshly distilled TMEDA (3.25 g, 28 mmol) was added dropwise over 1 h to a stirred, cooled (10°C) solution of *tert*-butyl phenyl sulfide (4.07 g, 25 mmol) and *n*-butyllithium (2.1 M in *n*-hexane, 10.87 mL, 23 mmol) in *n*-hexane (120 mL) under a nitrogen atmosphere. The resulting clear, light-yellow solution was stirred at room temperature for 20 h. A white precipitate formed. The yield of the metallation step was assumed to be 85 %. Ph_2AsCl (5.51 g, 21 mmol) was added dropwise in situ to this suspension. The obtained mixture was stirred for 2 h and hydrolysed with degassed 10 % solution of NaOH. The organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$. Filtration and concentration of the diethyl ether solution under vacuum to 2/3 of its volume gave **1b** as a white crystalline precipitate. Crystals of **1b** suitable for X-ray diffraction analysis were obtained from a two-layer diethyl ether/*n*-hexane system at room temperature.

Yield 5.81 g (71 % based on Ph_2AsCl), mp 110–111°C. ν_{max} (KBr)/cm^{-1} 3049 (m), 2959 (m), 1653 (m), 1577 (s), 1480 (m), 1432 (s), 1420 (m), 1364 (m), 1263 (m), 1169 (m), 1074 (m), 1023 (m), 803 (m), 763 (s), 740 (s), 696 (s), 475 (s). δ_H 7.59 (d, $^3J_{H,H}$ 7.5, 1 H, aryl H), 7.30 (m, 7 H, aryl H), 7.24 (m, 5 H, aryl H), 6.94 (d, $^3J_{H,H}$ 7.6, 1 H, aryl H), 1.35 (s, 9 H, ^{t}Bu). δ_C 148.7, 140.7, 138.5, 137.8, 133.9, 133.9, 128.9, 128.6, 128.5, 128.2, 77.2, 47.9, 31.2. *m/z* (EI) 394.1 ($[M]^+$, 23 %), 337 ($[M - {}^tBu]^+$, 100 %), 306.1 ($[M - {}^tBuS]^+$, 16 %), 258.9 ($[SAsPh_2]^+$, 24 %), 226.9 ($[AsPh_2]^+$, 77 %), 183.9 ($[SAsPh]^+$, 58 %), 152 ($[AsPh]^+$, 57 %), 56.9 ($[{}^tBu]^+$, 40 %). Anal. calc. for $C_{22}H_{23}AsS$: C 67.00, H 5.88. Found: C 66.96, H 5.94 %.

*Synthesis of 1-$AsPh_2$-2-S^tBu-3-PPh_2-C_6H_3 (**2**)*

n-Butyllithium (2.68 mL of a 2.1 M solution in *n*-hexane, 5.62 mmol) was added dropwise to an ice-cold solution of 2-(*tert*-butylthio)phenyldiphenylphosphine (**1a**) (1.97 g, 5.62 mmol) in *n*-hexane (60 mL), and then TMEDA (0.89 g, 7.64 mmol) in *n*-hexane (20 mL) was slowly added (over 45 min). The reaction mixture was stirred for 20 h and allowed to attain room temperature, leading to the formation of a pale-yellow suspension. The yield of the metallation step was considered to be 100 %. The suspension was cooled in an ice-bath and a solution of Ph_2AsCl (1.49 g, 5.62 mmol) in *n*-hexane (20 mL) was slowly added (2–3 h) to the stirred suspension. The solution was stirred for 24 h and hydrolysed with degassed 5 % aqueous NaOH. The organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$. After filtration, the solution was concentrated under vacuum to half its volume and kept at 8°C for 2 days, until compound **2** precipitated as a pale-yellow powder. Crystals of **2** suitable for single-crystal X-ray diffraction analysis were obtained from a two-layer diethyl ether/*n*-hexane system at room temperature over 1 week.

Yield 1.51 g (47 %), mp 173–174°C. ν_{max} (KBr)/cm^{-1} 3068 (m), 3049 (m), 2956 (m), 2915 (m), 2889 (m), 2363 (w), 1944 (w), 1869 (w), 1717 (w), 1700 (w), 1653 (m), 1577 (m), 1540 (m), 1480 (m), 1433 (s), 1364 (m), 1262 (w), 1197 (w), 1160 (m), 1093 (m), 1073 (m), 1025 (m), 999 (m), 914 (w), 848 (w), 787 (m), 737 (s), 696 (s), 548 (m), 498 (m), 472 (m), 449 (m), 428 (m). δ_H 7.34 (m, 8 H, aryl H), 7.08 (m, 13 H, aryl H), 6.98 (d, $^3J_{H,H}$ 7.6, 1 H, aryl H), 6.73 (t, $^3J_{H,H}$ 7.6, 1 H, aryl H), 1.63 (s, 9 H, ^{t}Bu). δ_C 152.4, 149.0 (d, $J_{C,P}$ 9.9), 143.6 (d, $J_{C,P}$ 29.3), 134.1 (d, $J_{C,P}$ 23.5), 133.9 (m), 129.4, 128.0 (m), 77.3, 50.6, 32.1 (d, $J_{C,P}$ 5.4). δ_P –6.7 (s). *m/z* (EI) 578 ($[M]^+$, 7 %), 521.6 ($[M - {}^tBu]^+$, 100 %), 293.2 ($[M - {}^tBu - AsPh_2]^+$, 63 %), 229 ($[AsPh_2]^+$, 10 %), 183.1 ($[PPh_2]^+$, 16 %), 57.2 ($[{}^tBu]^+$, 14 %). Anal. calc. for $C_{34}H_{32}AsPS$: C 70.58, H 5.57. Found: C 70.47, H 5.67 %.

*Synthesis of 1,3-($AsPh_2$)$_2$2-2-S^{t}Bu-C_6H_3 (**3**)*

Compound **3** was synthesized similarly to compound **2**. *n*-Butyllithium (2.1 M solution in *n*-hexane, 1.99 mL, 4.18 mmol) was added dropwise to an ice-cold solution of 2-(*tert*-butylthio)phenyldiphenylarsine (**1b**) (1.65 g, 4.18 mmol) in *n*-hexane (75 mL), and then TMEDA (0.66 g, 5.69 mmol) was slowly added (over 45 min). The reaction mixture was stirred for 20 h and allowed to attain room temperature, leading to the formation of a pale-yellow suspension. The yield of the metallation step was considered to be 90 %. The reaction vessel was cooled in an ice bath and a solution of Ph_2AsCl (1.00 g, 3.76 mmol) in *n*-hexane (10 mL) was slowly added (2–3 h) to the stirred suspension. The solution was stirred for 24 h and hydrolysed with degassed 5 % aqueous NaOH. The organic phase was separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were dried over $MgSO_4$. After filtration, the solution was concentrated slowly under vacuum to half its volume to give **3** as a very fine white precipitate. Crystals of **3** suitable for single-crystal X-ray diffraction analysis were obtained from a two-layer diethyl ether/*n*-hexane system at room temperature over 2 days.

Yield 0.63 g (27 %), mp 172–173°C. ν_{max} (KBr)/cm^{-1} 3067 (m), 3051 (m), 2956 (m), 2889 (m), 1950 (w), 1883 (w), 1814 (w), 1580 (m), 1480 (m), 1432 (s), 1363 (m), 1304 (m), 1262 (w), 1159 (m), 1073 (m), 1023 (m), 1000 (m), 913 (w), 848 (w), 785 (s), 734 (s), 696 (s), 527 (m), 480 (m), 471 (m), 418 (w). δ_H 7.41 (m, 8 H, aryl H), 7.19 (m, 14 H, aryl H), 6.84 (t, $^3J_{H,H}$ 7.6, 1 H, aryl H), 1.65 (s, 9 H, ^{t}Bu). δ_C 152.6, 144.0, 134.9, 134.8, 133.9, 130.1, 128.6 (m), 77.7, 50.7, 32.4. *m/z* (EI) 622 ([M]$^+$, 5 %), 564.9 ([M − ^{t}Bu], 20 %), 336.9 ([M − ^{t}Bu−$AsPh_2$]$^+$, 63 %), 258.8 ([M − ^{t}Bu−4Ph]$^+$, 41 %), 226.9 ([$AsPh_2$]$^+$, 92 %), 183.9 ([SPhAs]$^+$, 92 %), 152 ([AsPh]$^+$, 67 %), 107 ([SPh]$^+$, 23 %), 76.9 ([Ph]$^+$, 26 %), 56.9 ([^{t}Bu]$^+$, 100 %). Anal. calc. for $C_{34}H_{32}As_2S$: C 65.60, H 5.18. Found: C 65.03, H 5.17 %.

*Synthesis of 1-$AsPh_2$-2-SH-3-PPh_2-C_6H_3 (**4**)*

A solution of **2** (1.32 g, 2.28 mmol) in THF (20 mL) was added to a cold (0°C) lithium naphthalenide solution, generated from lithium (39.7 mg, 5.73 mmol) and naphthalene (0.62 g, 4.86 mmol) in THF (30 mL). The reaction mixture was stirred for 3 h at 0°C and then anhydrous HCl (3 mL, 2 M solution in diethyl ether) was added. The solution was concentrated under vacuum, and *n*-pentane (30 mL) was added to the remaining oily mass. A white precipitate (LiCl) was separated from the pale yellow solution by filtration. All volatiles were removed under vacuum, including naphthalene by sublimation. Compound **4** was obtained as a waxy pale-yellow solid and was further purified by washing with *n*-pentane. Compound **4** crystallized from a saturated diethyl ether solution at room temperature over 1 week.

Yield 0.79 g (66 %), mp 166–167°C. ν_{max} (KBr)/cm^{-1} 3051 (m), 2964 (w), 2467 (w), 1952 (w), 1882 (w), 1811 (w), 1581 (w), 1479 (m), 1434 (s), 1366 (s), 1305 (w), 1262 (s), 1183 (m), 1095 (s), 1024 (s), 913 (w), 803 (s), 739 (s), 695 (s), 544 (w), 501 (m), 445 (w), 422 (w). δ_H 7.33 (m, 8 H, aryl H), 7.03 (m, 14 H, aryl H), 6.68 (t, $^3J_{H,H}$ 7.5, 1 H, aryl H), 4.75 (d, $^4J_{P,H}$ 4.5, 1 H, SH). δ_C 143.5 (d, $J_{C,P}$ 28.6), 142.3, 139.0, 138.7 (d, $J_{C,P}$ 9.7), 136.0 (d, $J_{C,P}$ 10.6), 134.4 (d, $J_{C,P}$ 25.9), 134.2, 134.0, 128.8, 128.7 (d, $J_{C,P}$ 7.0), 128.5, 127.7 (m), 126.5. δ_P −11.7 (s). *m/z* (ESI) 521.0 ([M − H]$^+$. Anal. calc. for $C_{30}H_{24}AsPS$: C 67.98, H 4.63. Found: C 67.96, H 4.61 %.

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