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Terminally Coordinated AsS and PS Ligands

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Dedicated to Professor Max Herberhold on the occasion of his 70th birthday

Abstract: The terminal AsS and PS complexes [(N_3N)W(ES)] ($N_3N = N(CH_2CH_2NSiMe_3)_3$; E = P (**3**), As (**4**)) were synthesised by reaction of [(N_3N)W≡As] and [(N_3N)W≡P], respectively, with cyclohexene sulfide. Both complexes present very short W−E and E−S bond lengths. The bonding was investigated by density functional theory (DFT) calculations using the fragment calculation method and natural bond orbital (NBO) analysis. According to the fragment analysis, in which the complexes were separated in an ES and a (N_3N)W fragment, the bonding in complexes **3**, **4** and [(N_3N)W(SbS)] (**5**) is realised over a set of two σ (1σ and 2σ) and two degenerate π molecular orbitals (MOs) (1π and 2π). The 1σ MO is a bonding MO extended over the N_{ax}-W-E-S core, whereas the 2σ MO is localised mainly on the E–S fragment. The 1π set is a E–S localised bonding molecular orbital, whereas the 2π set is in phase with respect to W–E but in antiphase with respect to E–S. Both methods indicate bond orders around two for both the E−S and the W−E bonds. The polarity of the complexes was examined by Hirshfeld charge analysis. This shows that complexes **3** and **4** are only slightly polarised, whereas **5** is moderately polarised toward the sulphur. As suggested by the computational results, the π system in complexes **3**–**5** is best described by two three-centre four-electron bonds.

Keywords: As ligands • density functional calculations • P ligands • pnicogen monosulfide ligands • sulfur

Introduction

In contrast to the well-known coordination chemistry of nitric oxide or nitric sulfide, the coordination chemistry of phosphorus monosulfide is less common. The scarcity of PS-containing complexes is a consequence of the poor ligating properties and the need to adopt a sophisticated synthetic approach to generate the PS ligand. However a few complexes with an end-on-coordinated μ_3-PS[1] ligand, such as [{W(CO)$_2$Cp}$_3$(μ_3-PS)],[1d] [{Co($C_5tBu_2H_3$)}$_3$(μ_3-PS)$_2$],[1b] [{Ni(C_5iPr_4H)}$_2$W(CO)$_4$(μ_3-PS)$_2$][1c] and [{FeCp(CO)$_2$}{Fe$_2$(CO)$_3$Cp$_2$}(μ_3-PS)$_2$][1e] have been reported. Complexes of arsenic monosulfide, in which only the arsenic atom is coordinated to a transition metal, have not yet been reported. However, some complexes that contain side-on-coordinated AsS ligands have been characterised.[2]

The general route for the synthesis of μ_3-PS complexes is the oxidation of the corresponding phosphorus complexes with elemental sulphur or a different sulphur source. This method was successfully used by Cummins et al. for the preparation of the so far only known terminally coordinated PS complex [(Ph′RN)$_3$Mo(PS)],[3,4] by oxidation of the phosphido complex [(Ph′RN)$_3$Mo≡P] (Ph′ = 3,5-$Me_2C_6H_3$, R = C(CD_3)$_2$Me)[3] with sulphur. However, access to the heavier analogues of the PS complexes was not possible due to the lack of the heavier pnictido complexes of the type [(Ph′RN)$_3$Mo≡E]. The synthesis of the terminal phosphido and arsenido compounds and our recent success in the synthesis of the stibido complex of the type [(N_3N)W≡E] ($N_3N = N(CH_2CH_2NSiMe_3)_3$; E = P,[5,6] As,[6] Sb[7]) make the synthesis of complexes containing the heavier Group 15 elements as terminally coordinated ES ligands possible. Herein we report the synthesis and the spectroscopic characterisation of the terminal PS complex [(N_3N)W(PS)] ($N_3N = N(CH_2CH_2NSiMe_3)_3$) and the first terminal AsS ligand complex [(N_3N)W(AsS)]. Comprehensive DFT studies of the unusual bonding modes in these complexes shed light on the

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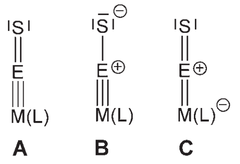
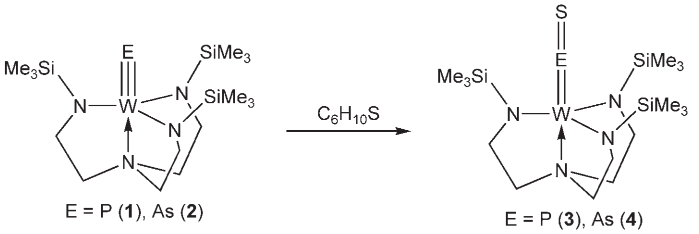
bonding situation and contribute to our basic knowledge by a possible representation of a Lewis-type structure of such a system (e.g. **A**–**C**).



Results and Discussion

Synthesis and characterisation: Oxidation of the phosphido and arsenido complexes [$(N_3N)W{\equiv}E$] (E = P (**1**), As (**2**)) with cyclohexane sulfide leads to the isolation of the terminal ES complexes [$(N_3N)W(PS)$] (**3**) and [$(N_3N)W(AsS)$] (**4**) in good yields [Eq. (1)]. Compounds **3** and **4** are yellow crystalline solids that are stable at room temperature under an inert atmosphere.



(1)

The ^1H NMR spectra of **3** and **4** indicated that the resonances associated with the CH_2 groups of the ligand are shifted slightly to lower field than those in **1** and **2**. A more drastic change is observed in the ^{31}P NMR spectra of **3** when compared with those of **1**. The characteristic signal for the terminal phosphide in **1** occurs at $\delta = 1080.0$ ppm, whereas in **3** the chemical shift of the ^{31}P nucleus is at $\delta = 342.3$ ppm, with ^{183}W satellites showing a large phosphorus–tungsten coupling of 772 Hz. The ^{31}P NMR chemical shift for **3** is comparable with that found in [$(Ph'RN)_3Mo(PS)$] (Ph' = 3,5-$Me_2C_6H_3$, R = $C(CD_3)_2Me$) ($\delta = 383$ ppm)[3] and is shifted 82.2 ppm to lower field compared with that for [$(Ph'RN)_3Mo(PO)$][8] ($\delta = 259.8$ ppm). In the Raman spectrum of **3** a relatively strong emission band at 345 cm^{-1} was attributed to the symmetric stretching vibration of the WPS unit. Unfortunately, no Raman spectrum (of acceptable quality) could be recorded for **4** due to fluorescence phenomena.

Single crystals of **4** were obtained from a solution of the compound in THF at −28 °C, whereas single crystals of **3** were obtained from a saturated solution of the compound in C_6D_6 at room temperature. Compound **4**·THF crystallises in the monoclinic space group $P2_1/c$, whereas **3** crystallises in the orthorhombic $Pna2_1$ space group. Compounds **3** and **4** are monomeric in the solid state and show pseudo-threefold symmetry around the nearly linear N1-W-E-S moiety (W-E-S angles are 177.4(3)° and 177.6(1)° and the torsion angles are 14° and 12.6° for **3** and **4**, respectively; Table 1). The molecular structures of **3** and **4** are isostructural and the general structure is depicted in Figure 1.

The As–S distance in **4** is very short (2.048(2) Å) and is indicative of an As–S double bond. As–S bond lengths in uncoordinated Ph_3AsS are 2.086, 2.095 Å[9] and 2.076(2), 2.082(2) Å[10] and a typical As–S single bond length, as in β-As_4S_4, is 2.243 Å.[11] The only shorter As–S distance (2.01(1) Å) reported is for the co-crystallised species [$WS_4Ag_3I(AsPh_3)_3$]·($SAsPh_3$),[12] which was synthesised by using standard solid-state techniques. In **3** the P–S distance (1.941(2) Å) is slightly longer than the corresponding distance found in [$(Ph'RN)_3Mo(PS)$][4] (Ph' = 3,5-$Me_2C_6H_3$, R = $C(CD_3)_2Me$) (1.921(3) Å) and is comparable with the P–S distance in the μ_3-coordinated PS complexes.[1] The As–W distance in **4**

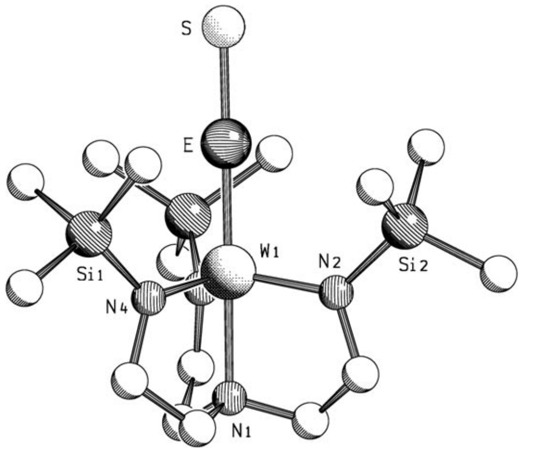


Figure 1. Molecular structure of [$(N_3N)W(ES)$] (E = P (**3**), As (**4**)). Hydrogen atoms are omitted for clarity.

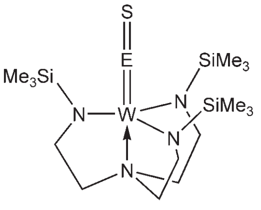
Table 1. Comparison of selected experimental and calculated geometrical parameters [Å,°] of complexes **3**, **4** and **5**.[a]

		E–S	W–E	N_{ax}–W	N_{eq}–W	S-E-W	E-W-N_{ax}
3	exptl	1.941(2)	2.158(1)	2.217(3)	1.981(11)–2.004(9)	177.4(3)	178.52(16)
3	calcd	1.94	2.15	2.22	1.98	180	180
4	exptl	2.048(2)	2.255(1)	2.214(6)	1.993(5)–1.998(6)	177.59(8)	178.77(16)
4	calcd	2.05	2.25	2.21	1.98	180	180
5	calcd	2.25	2.45	2.20	1.98	180	180

[a] **3**: E = P, **4**: E = As, **5**: E = Sb.

(2.256(1) Å) is slightly shorter than that in the parent arsenido complex **2** (2.290(1) Å).[6] The W–P distance (2.158(1) Å) in **3** is almost equal to the W–P distance in **1** (2.162(4) Å)[5] but longer than in the triply bound compounds [(*t*BuO)$_3$W≡P→W(CO)$_5$] (2.132(4) Å)[13] or [thf(Ph″O)$_3$W≡P→W(CO)$_5$] (Ph″ = 2,6-Me$_2$C$_6$H$_3$) (2.127(2) Å).[14] These comparisons show that upon oxidation of the pnictido complexes the W–E distance becomes slightly shorter, a phenomenon that is more accentuated for the heavier congeners. The N$_{eq}$–W and the N$_{ax}$–W distances in **3** and **4** are similar within experimental error.

Analysis of the bonding pattern by DFT calculations: To gain insight into the nature of the W–E and E–S bonds, density functional theory (DFT) calculations were carried out on the complexes [(N$_3$N)W(PS)] (**3**), [(N$_3$N)W(AsS)] (**4**) and on the hypothetical complex [(N$_3$N)W(SbS)] (**5**).



E = P (**3**), As (**4**), Sb (**5**)

The geometries of **3**–**5** were optimised with no symmetry constraints; the resultant structures were very close to three-fold symmetry. The calculated geometrical parameters for the optimised structures of **3** and **4** are in excellent agreement with the experimental data (Table 1). Also the calculated WPS symmetric stretching frequency for **3** at 350 cm^{-1} is in good agreement with the experimental value (345 cm^{-1}). Similar W–P and P–S distances were reported for the model complex [NH$_3$(NH$_2$)$_3$W(PS)] (**6**) calculated with the B3LYP functional, whereas HF and MP2 methods give longer and shorter distances, respectively.[15] Also the N$_{ax}$–W distances in **3** (2.22 Å) and **4** (2.21 Å) compare very well with the experimental data (2.217(3) Å and 2.214(6) Å for **3** and **4**, respectively). The earlier calculations gave longer N$_{ax}$–W bond lengths for [(N$_3$N)WE] (E = P, As, Sb)[6,7] than the reported experimental values for [(N$_3$N)WE] (E = P,[5] As,[6] Sb[7]), and also predicted a longer W–N$_{ax}$ distance for **6** than found for **3**.[15] The difference between the calculated and experimental N$_{ax}$–W distances was attributed to solid-state effects but our results suggest that the discrepancies may be due to the simpler ligand set.[15]

Two approaches were used to characterise the W-E-S bonding, that is, fragment analysis and natural bond order (NBO) calculations. The bonding in the complexes **3**, **4** and **5** was examined by fragment analysis, in which the molecular orbitals (MOs) of the molecule are expressed as a linear combination of the fragment orbitals. The fragments retain the geometry that they have in the whole molecule and are in a singlet state. Initial restricted calculations yield the basis orbitals. Thus, both the interaction of an S atom with the (N$_3$N)WE fragment (E = P, As and Sb) and the interaction of the ES fragment with the (N$_3$N)W fragment were analysed. Orbital interaction schemes for **4** are depicted in Figure 2.

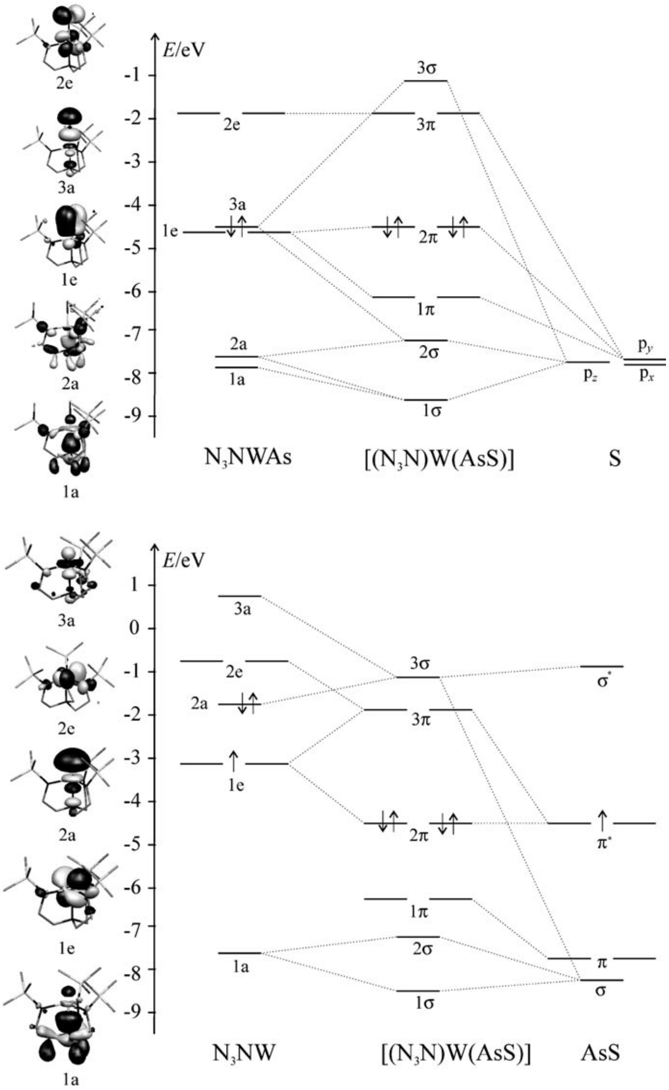


Figure 2. Molecular orbital interaction scheme for [(N$_3$N)W(AsS)] (**4**). The (N$_3$N)W and (N$_3$N)WAs fragment levels are labelled in C$_3$ symmetry and those of **4** with σ and π symmetry with respect to the NWAs axis. The relevant molecular orbitals of the (N$_3$N)W and (N$_3$N)WAs fragment are given on the left-hand side of the diagram.

The results of a fragment analysis, in which **4** was separated into an S and an (N$_3$N)WAs fragment, show that the p$_z$ orbital of S mixes with the a orbitals of the (N$_3$N)WE fragment, containing contributions from N$_{ax}$ (p$_z$), As (p$_z$) and from W (d$_{z^2}$ and s) to form two occupied molecular orbitals of σ symmetry (1σ and 2σ, Figure 2 and Figure 3). Molecular orbital 1σ is an all in-phase combination, whereas 2σ is As–S bonding, and has minimal W contribution and thus is N$_{ax}$ nonbonding. Furthermore, the p$_x$ and p$_y$ orbitals of the S in-

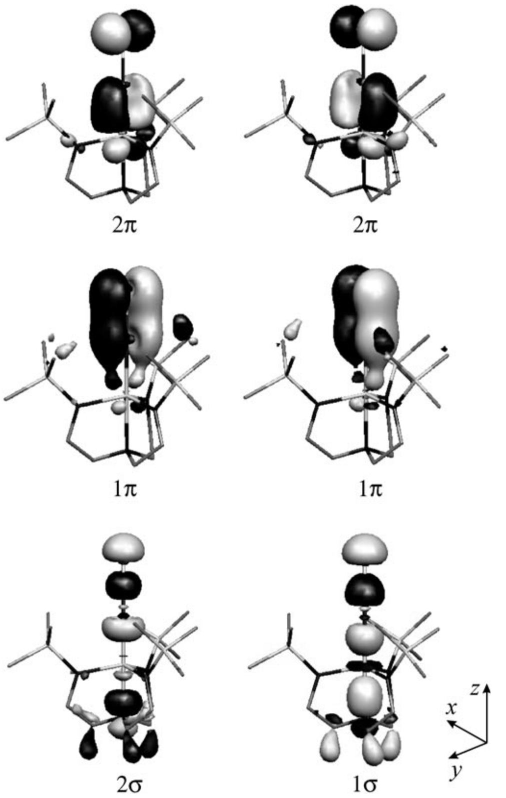


Figure 3. Isosurfaces of 2π, 1π, 1σ and 2σ MOs of $[(N_3N)W(AsS)]$ (**4**).

teract with the two degenerate π orbitals of the WE unit (1e) to give two sets of π orbitals (1π and 2π) from which the 1π set is bonding over all three atoms (W, As and S) but with only a minor contribution from W and the 2π set is anti-bonding with respect to the ES and bonding with respect of the WE unit (Figure 3).

An analysis of the interaction of the AsS fragment with the $(N_3N)W$ fragment shows that the π orbitals of the AsS fragment increase slightly in energy, but do not mix much with the orbitals of the $(N_3N)W$ fragment, remaining localised as As−S π bonds (forming 1π). In contrast, the π* orbitals of the AsS fragment interact with the orbitals 1e of the $(N_3N)W$ fragment, containing mainly the tungsten d_{yz} and d_{xz} orbitals respectively, to give a strong W−As π bonding interaction (2π). The out-of-phase combination is unoccupied and forms the LUMO (3π). Overall the WES π system is best described by two three-centre four-electron (3c–4e) bonds.

The bonding in the complexes **3** and **5** is very similar to that described above for **4**; however, some differences emerge when quantifying the orbital interactions. The most significant change on going from P to Sb appears in the σ bonding. The mixing between the σ orbitals is strongest when E = P, either with the sulphur p_z orbital with the $(N_3N)WE$ σ MOs or the σ orbital of the ES fragment with $(N_3N)W$ fragment orbitals, respectively. Changes also occur in the π sets of MOs. Whereas in **3** and **4** the mixing of the fragment orbitals to form the 1π set of MOs is similar, in **5** the mixing is lower, leading to a more localised 1π set. It has to be emphasised that the 1π set of MOs is based mainly on the π orbitals of the ES fragment (74 %, 73 % and 90 % for **3**, **4** and **5**, respectively). The mixing of the ES fragment π* orbital into the 2π set MOs of the complex presents a maximum for **4** (48 %) and decreases slightly for **3** (43 %) and **5** (40 %), respectively.

The triple bond character of the W−E and the 2.5 bond order of the E−S bonds of the fragments are reflected in the fractional bond orders obtained from the fragment calculations. By considering the $(N_3N)WE$ fragment 1e orbitals as W−P bonding, the 2e as W−E antibonding and the 3a orbital as bonding and considering the fragment occupation in the molecule, an overall W−E fractional bond order was calculated of 2.22, 2.24 and 2.20 for **3**, **4** and **5**, respectively. Similarly, by considering the occupation of π, π*, σ and σ* orbitals of the ES fragment in the complex, a fractional E−S bond order of 2.03, 1.83 and 2.12 is estimated for **3**, **4** and **5**, respectively. Thus, both the W−E and E−S bonds may be regarded as double bonds.

Wiberg bond index (WBI) calculations give lower estimates for the W−E and E−S bonds, but this is compensated by the addition of a bond index for WS (Table 2).

Table 2. Wiberg bond indices for $[(N_3N)W(ES)]$ (E = P, As and Sb).

	P	As	Sb
W−E	1.79	1.75	1.70
E−S	1.54	1.48	1.43
W−S	0.41	0.41	0.36

The WBIs are similar to those reported by Frenking and Wagener for the model complex $[NH_3(NH_2)_3W(PS)]$ (**6**) (1.89 for the W−P and 1.59 for the P−S bond)[15] and significantly lower than the WBI in $[(MeO)_3W{\equiv}E]$ (W−E 2.56, 2.55 and 2.54 for E = P, As and Sb, respectively)[16] or in $[(N_3N)W{\equiv}E]$ (W−E 2.38, 2.35 and 2.28 for E = P, As and Sb, respectively).[7]

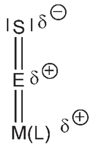
To model the effect of the *trans* N donor group on the MES bonding we extended our studies by optimising the geometry of $[(MePhN)_3Mo(PS)]$ (**7**), as a model for the known complex $[(Ph'RN)_3Mo(PS)]$ ($Ph' = 3{,}5\text{-}Me_2C_6H_3$, $R = C(CD_3)_2Me$).[3,4] The absence of the donor nitrogen atom *trans* to the PS unit in **7** compared with the situation in **3**, stabilises the P−S 3σ orbital. Its energy falls below the energy of the 3π orbitals and it becomes the LUMO. This leads to a much lower HOMO–LUMO gap (1.89 and 2.30 eV in **7** and **3**, respectively) and to a weaker P−S σ bond in **7** compared to that in **3**. Similar energy schemes to that found for **7** were reported for $[(NH_2)_3Mo(PO)]$,[17] whereas in $[NH_3(NH_2)_3M(PS)]$ (M = Mo, W) a stronger P−S bonding than in $[(NH_2)_3M(PS)]$ (M = Mo, W) was predicted by means of DFT calculations.[15]

Analysis of the Hirshfeld[18] charge distribution shows that the complexes **3** and **4** are slightly and **5** moderately polarised towards the sulphur atom. The tungsten atom is positively charged (0.38 for **3** and **4** and 0.35 for **5**), the pnicogen atom is slightly positive (0.05, 0.10 and 0.22 for **3**, **4** and **5**, respectively), whereas the sulphur is negatively charged (−0.18, −0.22 and −0.30 for **3**, **4** and **5**, respectively). On descending the group, the sulphur atom gains in negative charge, whereas the pnicogen atom increases its positive charge. Concurrently, the positive charge of the tungsten atom decreases, but to a lower extent than the positive charge on the pnicogen increases.

The high HOMO–LUMO gap (2.85, 2.56 and 2.20 eV for **3**, **4** and **5** respectively) and the calculated E−S bond dissociation energies (BDE) (349, 302 and 209 kJ mol^{-1} for **3**, **4** and **5**, respectively) in **3**, **4** and **5** are consistent with the stability observed experimentally for **3** and **4**. The BDE for **5** is indeed lower than in **3** and **4** but its absolute value is high enough to make the isolation of **5** possible.

Conclusion

The results presented show that the terminally coordinated ES complexes **3** and **4** can be readily obtained by oxidation of the pnictido complexes **1** and **2** with cyclohexene sulfide. The analysis of the bonding in complexes **3**–**5** has shown that the linear arrangement of the N$_{ax}$-W-E-S core results in an unusual bonding situation with a delocalised π-electron system on the W=E=S unit. The fragment calculations in which the complexes **3**–**5** were split in a (N$_3$N)WE and an ES fragment have shown that the mixing of the σ-type orbitals of the fragments is stronger for E = P and decreases slightly for E = As and Sb. This leads to a slight decrease in the strength of the W−E σ bonding. Furthermore, as the atomic number of E increases, the 1π set becomes more localised as an E−S π bonding MO. The presence of the axial nitrogen in the complexes [(N$_3$N)W(ES)] (E = P (**3**), As (**4**) and Sb (**5**)) destabilises the 3σ MO giving rise to a higher HOMO–LUMO gap than in the complex [(MePh-N)$_3$Mo(PS)] (**7**). This also yields a stronger P−S bond in **3** compared to that in **7**.



D

The complexes **3**–**5** have relatively weak ionic character as was shown by the Hirshfeld charge analysis. Overall the π-electron system in complexes **3**–**5** can be described by two three-centred four-electron bonds. In general, the bonds between W and E and E and S are best described as double bonds with a polarisation as shown in the Lewis-type formula **D**.

Experimental Section

General remarks: All manipulations were performed under an atmosphere of dry nitrogen using glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures.

Synthesis of 3: A slight excess of cyclohexene sulfide (0.01 mL, 0.075 mmol) was added to a solution of [(N$_3$N)WP] (**1**) (18 mg, 0.031 mmol) in C$_6$H$_6$ (1 mL) at room temperature. The mixture was stirred for 10 min and left standing overnight at room temperature. Yellow crystals of **3** precipitated quantitatively and were isolated. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS) $\delta = 0.62$ (s, ^2J(Si,H) = 6.4 Hz, 27 H; CH$_3$), 1.84 (t, ^3J(H,H) 5.6 Hz, 6 H; CH$_2$), 3.38 ppm (t, ^3J(H,H) 5.6 Hz, 6 H; CH$_2$); ^{31}P NMR (162.07 MHz, C$_6$D$_6$, 25 °C, H$_3$PO$_4$) $\delta = 342.26$ ppm (s, ^1J-(W,P) = 771.5 Hz); Raman (solid): $\tilde{\nu} = 345.2$ cm^{-1} (WPS).

Synthesis of 4: Cyclohexene sulfide (0.01 mL, 0.075 mmol) was added to a solution of [(N$_3$N)WAs] (**2**) (21 mg, 0.034 mmol) in THF (10 mL) at 0 °C. The mixture was stirred for 3 h at room temperature, filtered and concentrated. After two weeks at 5 °C yellow crystals of **4**·THF (19 mg, 78 %) were formed. ^{1}H NMR (250 MHz, CD$_2$Cl$_2$, 25 °C, TMS) $\delta = 0.33$ (s, ^2J(Si,H) = 6.3 Hz, 27 H; CH$_3$), 2.80 (t, ^3J(H,H) 5.9 Hz, 6 H; CH$_2$), 3.91 ppm (t, ^3J(H,H) 5.9 Hz, 6 H; CH$_2$).

Computational details: DFT calculations were carried out using the Amsterdam Density Functional program version 2004.01 and 2005.01.[19] Scalar relativistic corrections were included by using the ZORA method.[20] The generalised gradient approximation was employed, using the local density approximation of Vosko, Wilk, and Nusair[21] together with the nonlocal exchange correction by Becke[22] and non-local correlation corrections by Perdew.[23] TZP basis sets were used with triple-zeta accuracy and two polarisation functions added. The cores of the atoms were frozen up to 1s for C and N, 2p for Si, P and S, 3p for As, 4p for Sb and 4d for W. All quoted electronic structure data from optimised structures use an integration grid of 4.0, except for the frequency calculation of **3**, where an integration grid of 6.0 was used and have gradient corrections applied after the SCF cycles. No symmetry restraints were used. The NBO analysis was performed with the Gaussian03 program[24] using the BP86[22,23] functional and the 6–31 G** basis sets[25] with one diffuse function added, for C, H, N, Si, P and S and the Stuttgart-Dresden SDDALL basis set[26] with an additional d function added, for As, Sb and W.

Crystal structure analysis: Crystal structure analyses for **3** and **4** were performed on a STOE IPDS diffractometer with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) for **3** and Ag$_{K\alpha}$ radiation ($\lambda = 0.56087$ Å) for **4**. The structures were solved by direct methods with the program SHELXS-97,[27a] and full-matrix least-squares refinement on F^2 in SHELXL-97[27b] was performed, with anisotropic displacements for non-hydrogen atoms. Hydrogen atoms were located in idealised positions and refined isotropically according to the riding model. **3**: C$_{15}$H$_{39}$N$_4$PSSi$_3$W, $T = 173(1)$ K, orthorhombic $Pna2_1$, $a = 17.296(4)$, $b = 9.5205(19)$, $c = 15.784(3)$ Å, $V = 2599.1(9)$ Å^3, $Z = 4$, $\mu = 4.732$ mm^{-1}, $F(000) = 1216$, 17807 reflections collected, 4966 unique [$R_{int} = 0.0302$], 4966 data, 235 parameters, GOF on $F^2 = 0.983$, $R_1 = 0.0240$, $wR_2 = 0.0553$ for $I > 2\sigma(I)$, $R_1 = 0.0302$, $wR_2 = 0.0569$ for all data, Flack parameter 0.46(2). **4**: C$_{19}$H$_{47}$AsN$_4$OSSi$_3$W, $T = 200(2)$ K, monoclinic $P2_1/c$, $a = 9.865(2)$, $b = 16.842(3)$, $c = 18.394(4)$ Å, $\beta = 95.82(3)°$, $V = 3040.3(11)$ Å^3, $Z = 4$, $\mu = 2.723$ mm^{-1}, $F(000) = 1448$, 18920 reflections collected, 7383 unique [$R_{int} = 0.0952$], 7383 data, 280 parameters, GOF on $F^2 = 1.019$, $R_1 = 0.0482$, $wR_2 = 0.1007$ for [$I > 2\sigma(I)$], $R_1 = 0.0833$, $wR_2 = 0.1139$ for all data.

CCDC-609362 (**3**) and CCDC-609361 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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