

Coordination isomerism in N-heterocyclic phosphonium thiocyanates

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Dedicated to Professor Dr. Neil Burford.

Abstract: Two N-heterocyclic phosphines with exocyclic SCN-substituents were synthesised via metathesis of chlorophosphine precursors with KSCN and fully characterised. The crystallographic studies reveal that the products exhibit pronounced structural differences. The thiocyanato-unit binds in one case via the nitrogen atom to yield a molecular structure with a slightly elongated P–N single bond, and in the other case via the sulfur atom to form a structure that is best described as an ion pair and forms a one-dimensional coordination polymer in the crystal. DFT calculations suggest that the P–N and P⋯S interactions can be described as covalent and dative bonds, respectively, and that the structural differences correlate with the different cation stabilities of the individual phosphonium cation fragments.

Introduction

The reaction between a Lewis acid (electron pair acceptor) and a Lewis base (electron pair donor) to form a complex (or Lewis pair) is one of the most fundamental chemical processes. Neutral molecules and anions containing a phosphorus atom in a low valence state like phosphines R_3P or phosphides R_2P^- exhibit normally Lewis base behaviour due to the presence of one or more lone-pairs of electrons on the P-atom. However, in cationic species of composition R_2P^+ ("phosphenium ions"), the lone-pair influence is offset by the effects of the positive charge and a formally vacant p-orbital, which render these species powerful Lewis acceptors.¹ Isolable salts containing well-defined phosphenium cations result if the intrinsically high electrophilicity is to some extent toned down by attachment of one or – even better – two amino substituents which permit to delocalise the positive charge through π -conjugation effects.^{1,2} In N-heterocyclic phosphenium ions (Scheme 1), the geometrical constraints imposed by a cyclic structure are further used to establish a rigid conformation which ensures optimum p-orbital overlap in the NPN unit and thereby maximises the electronic stabilisation achievable from the π -delocalisation.^{2,3}

- Scheme 1, here -

Scheme 1: Representation of the molecular structures of two types of N-heterocyclic phosphenium ions. The canonical structures given illustrate the π -conjugation in the NPN-unit.

Extensive chemical studies have established the existence of adducts between aminophosphenium cations and various neutral Lewis bases including tertiary amines and pyridines,⁴ phosphines,⁵ or carbenes,⁶ respectively. The structural diversity of these species stems not only from the different element combinations in the donor-acceptor bond but also from the large discrepancies in the interaction strength, which spans a wide range from cases featuring strong bonding with similar atomic distances as in genuine covalent bonds to weak adducts which partially dissociate in solution. In contrast to the adducts with neutral donors, interaction of phosphenium ions with anionic Lewis

bases X^- yields neutral species which are normally addressed as molecular entities with covalent rather than dative P–X bonds. Exemptions from this scheme have become known in the case of certain diazaphosphenes $III[X]$ (Scheme 2) which exhibit unusually long and easily polarisable P–X distances and were described as Lewis pairs consisting of a phosphonium cation and an anionic donor connected by a "dative" (coordinative) P–X bond.⁷

- Scheme 2, here -

Scheme 2: Representation of the polarisation of the exocyclic P–X bonds in diazaphosphenes III (X = Cl, Br, I, phospholyl, triphospholyl)

The donor fragments in these molecular complexes are, apart from (poly)phospholide anions which give rise to interesting cases of homonuclear dative bonds, mainly the heavier halide ions Cl^- , Br^- , I^- . The finding that a similar bond polarisation as in diazaphosphenium halides^{7a,b} prevails also in azido-substituted derivatives⁸ drew our attention to pseudohalide anions as viable candidates for the realisation of further examples of phosphonium-based Lewis pairs. A particular interesting case along this line is thiocyanate which can interact with Lewis acids via the S- and N-terminus, respectively. This ambident behaviour is well established for metal complexes where a sizable number of species featuring S- and N-bound thiocyanato ligands bound to the same metal centre is known.⁹ Analogous examples featuring a non-metal as central atom seem to be limited to a single Te(II) compound.¹⁰ Thiocyanato-substituted phosphines have likewise been reported¹¹ but structural information is scarce^{11g,h} and the few species where data is available exhibit exclusively N-bound ligands. We report here the synthesis and characterisation of two thiocyanato-substituted N-heterocyclic phosphines representing examples of coordination isomers with different anion bonding modes. The molecule featuring the S-bound anion can be described as a phosphonium-thiocyanate Lewis pair and represents the first structurally confirmed case of S-coordination of a thiocyanate to phosphorus.

Experimental Section

All experiments were carried out under dry Nitrogen or Argon atmosphere in flame-dried glassware or Gloveboxes. Solvents were dried using standard procedures. NMR-spectra were recorded on Bruker AV 250 or AV 400 spectrometers at 303 K if not stated otherwise. Chemical Shifts were referenced to ext. TMS (^1H , ^{13}C , ^{29}Si), MeNO₂ ($\Xi = 7.226317$ MHz, ^{14}N ; $\Xi = 10.136767$ MHz, ^{15}N), or 85% H₃PO₄ ($\Xi = 40.480747$ MHz, ^{31}P). ^{13}C NMR signals of the SCN carbon atoms were not detected, presumably due to extensive line broadening. Elemental analyses were carried out using an Elementar Micro Cube elemental analyser. IR-spectra were recorded on a Thermo Scientific iS5 FT-IR-spectrometer equipped with an iD5 diamond ATR unit.

1,3-Di-tert-butyl-2-thiocyanato-1,3diazaphospholene 3. A solution of **1**^{7a} (3.00 g, 10.7 mmol) and KSCN (1.60 g, 16.1 mmol) in THF (50 mL) was stirred at 50 °C for 12 h. The formed yellow solid was filtered off, washed three times with Et₂O (15 mL) and then dissolved in CH₂Cl₂ (30 mL). The solution was filtered and the filtrate evaporated to dryness to yield the product as colourless solid (yield 2.17 g, 79%). Crystals suitable for XRD were obtained from THF/CH₂Cl₂. ^1H NMR (CDCl₃): $\delta = 1.74$ (d, 18 H, $^4J_{\text{PH}} = 1.9$ Hz, CCH₃), 7.87 (s, 2 H, NCH). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 198.2$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 31.0$ (d, $^3J_{\text{PC}} = 9.6$ Hz, CCH₃), 61.4 (d, $^2J_{\text{PC}} = 7.7$ Hz, CCH₃), 129.6 (d, $^2J_{\text{PC}} = 4.9$ Hz, NCH). ^{14}N NMR (CDCl₃): $\delta = -146.8$ (br, *Nt*Bu), -160.4 (br, SCN). IR (THF): $\bar{\nu} = 2030$ cm⁻¹ (νCN). C₁₁H₂₀N₃PS (257.33): calcd. C 51.34 H 7.83 N 16.33, found C 51.00 H 7.73 N 15.89.

1,3-di-tert-butyl-2-isothiocyanato-4,4,5,5-tetramethyl-1,3,2,4,5-diazaphosphadisolidine 4. A solution of KSCN (0.22 g, 2.3 mmol) in THF (20 mL) was cooled to -78 °C. A solution of 2-chloro-diazaphosphasilolidine **2**¹² (0.75 g, 2.3 mmol) in THF (20 mL) was added dropwise. The mixture was stirred at -78 °C for 1 h, allowed to warm to room temperature, and filtered through a pad of silica. The remaining solid washed twice with THF (2 mL). The filtrate was evaporated to dryness and the residue dissolved in a small amount of acetonitrile. Storage at -24 °C overnight gave colourless crystals (0.80 g, 99%). ^1H NMR (THF-d₈): $\delta = 0.38$ (br, 6 H, SiCH₃), 0.45 (br, 6 H, SiCH₃), 1.41 (s, 18 H,

CCH₃). ¹³C{¹H} NMR (THF-d₈): δ = 0.3 (br s, SiCH₃), 2.5 (br s, SiCH₃), 32.2 (d, ³J_{CP} = 13.9 Hz, CCH₃), 56.8 (d, ²J_{CP} = 29.6 Hz, CCH₃). ¹⁴N NMR (THF-d₈): δ = -234.3 (d, ¹J_{NP} = 71 Hz, P-NCS). ¹H,¹⁵N-gsHMQC (THF-d₈): δ = -291.0 (d, ¹J_{NP} = 112 Hz, NCCH₃). ²⁹Si{¹H}-DEPT NMR (THF-d₈): δ = -2.6 (d, ²J_{SIP} = 9.8 Hz, SiCH₃). ³¹P{¹H} NMR (THF-d₈): δ = 144.2 (t, ¹J_{14N,P} = 71 Hz). IR (solid): $\bar{\nu}$ = 2021 cm⁻¹ (νCN). IR (THF): $\bar{\nu}$ = 2013 cm⁻¹ (νCN). C₁₃H₃₀N₃PSSi₂ (347.61): calcd. C 44.92 H 8.70 N 12.09 S 9.22, found C 44.22 H 8.54 N 11.85 S 9.16.

Single-crystal X-ray Diffraction studies were carried out on a Bruker Kappa APEXII Duo

diffractometer at $T = 100(2)$ K (**3**) or $T = 130(2)$ K (**4**) using Mo- K_{α} radiation ($\lambda = 0.71073$ Å). The structures were solved by using Direct Methods (SHELXS-97) and refined with a full-matrix least-squares scheme on F^2 (SHELXL-97). Semi-empirical absorption corrections were applied. Non-hydrogen atoms were refined anisotropically, and H atoms in CH bonds with a riding model on F^2 . CCDC-1577610 (**3**) and CCDC-1577611 (**4**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3: colourless blocks, C₁₁H₂₀N₃PS, $M = 257.33$ g mol⁻¹, crystal size 0.56 × 0.43 × 0.10 mm, monoclinic, space group $P2_1/c$, $a = 10.5888(18)$ Å, $b = 12.5801(17)$ Å, $c = 10.8359(17)$ Å, $\beta = 94.046(5)^\circ$, $V = 1439.8(4)$ Å³, $Z = 4$, $\rho(\text{calcd}) = 1.187$ Mg m³, $F(000) = 552$, $\theta_{\text{max}} = 28.46^\circ$, $\mu = 0.317$ mm⁻¹, max. / min. transmission 0.7457 / 0.7068, 12871 reflections measured, 3566 unique reflections [$R_{\text{int}} = 0.034$] for structure solution and refinement with 151 parameters, $R1$ ($I > 2\sigma(I)$) = 0.035, $wR2 = 0.079$, GoF = 1.017, largest diff. peak and hole: 0.322 and -0.249 e Å⁻³.

4: colourless prisms, C₁₃H₃₀N₃PSSi₂, $M = 347.61$ g mol⁻¹, crystal size 0.46 × 0.18 × 0.13 mm, orthorhombic, space group $P2_12_12_1$, $a = 8.3531(7)$ Å, $b = 14.1312(8)$ Å, $c = 17.0639(12)$ Å, $V = 2014.2(2)$ Å³, $Z = 4$, $\rho(\text{calcd}) = 1.146$ Mg m³, $F(000) = 752$, $\theta_{\text{max}} = 27.5^\circ$, $\mu = 0.355$ mm⁻¹, max. / min. transmission 0.7454 / 0.7056, 14878 reflections measured, 4129 unique reflections [$R_{\text{int}} = 0.037$] for

structure solution and refinement with 181 parameters, $R1 (I > 2\sigma(I)) = 0.034$, $wR2 = 0.083$, $GoF = 1.029$, Flack x parameter = $0.02(4)$, largest diff. peak and hole: 0.269 and $-0.207 \text{ e } \text{\AA}^{-3}$.

Computational studies. RI-DFT calculations were carried out on the bwUniCluster with the TURBOMOLE¹⁴ program suite. Initial energy optimisation of the molecular structures of **3S** and **4N** were carried out using different functionals (BP86, B3LYP, PBE0) with a def2-tzvp basis set,¹⁵ Grimme's D3BJ formalism¹⁶ to include dispersion effects, and the conductor-like screening model¹⁷ with the solvent parameters for THF and acetonitrile to simulate solvation effects (COSMO-RS). The B3LYP functional gave the best match between measured and calculated geometrical parameters and was therefore used for all further calculations. Molecular structures were identified as local minima on the energy hypersurface by harmonic vibrational frequency calculations. Natural population analysis¹⁸ was performed with the module as implemented in the software.

Results and Discussion

The thiocyanato-substituted N-heterocyclic phosphines **3**, **4** were readily prepared by metathesis of the precursors **1**,^{7a} **2**¹² with KSCN (Scheme 3) and isolated in crystalline form after work-up.

- Scheme 3, here -

Scheme 3: Synthesis of **3**, **4** (R = *t*Bu)

Both products were characterised by analytical and spectroscopic (NMR, IR) data and single-crystal X-ray diffraction studies. The molecular structures are depicted in Figures 1, 2, and important bond distances and angles are compiled in Table 1.

- Figure 1, here -

Figure 1: Representation of the molecular structure of **3** in the crystal. Thermal ellipsoids were drawn at the 50% probability level and hydrogen atoms were omitted for clarity. Neighbouring ion pairs were drawn using a wire model and intermolecular interactions between phosphorus and sulfur atoms in different molecular subunits are drawn as dotted lines. Selected distances and angles are listed in Table 1.

– Table 1, here –

Crystalline **3** contains pairs of diazaphospholenium cations and thiocyanate anions that are stacked to form one-dimensional zig-zag chains along the direction of the crystallographic *c*-axis. The cations contain planar five-membered rings and exhibit bond distances (Table 1) which match the expectation values¹⁹ for ionic diazaphospholenium salts. The shortest anion-cation contact (P1⁺⋯S1 3.1758(3) Å) occurs between the sulfur atom of the thiocyanate and the phosphorus atom in the cation and lies more than halfway between a P–S single bond (2.12 Å²⁰) and the sum of the van-der-Waals radii (3.60 Å²¹). The sulfur atom exhibits a further van-der-Waals contact to the cation of a neighbouring ion pair (P1#1 –P1 3.5706(5) Å). The N-terminus of the thiocyanate features no specific intermolecular contacts apart from weak H-bridging interactions to ring-hydrogen atoms in neighbouring cations.

The one-dimensional ion stacks in crystalline **3** resemble at first glance the packing motifs which had been found for the iodo-diazaphospholene **III**[I]^{7b} and a homologous 2-chloro-diazastibolene²² featuring Sb–Cl in the place of the P–I units; both compounds were described as consisting of arrays of ion pairs which engage in intermolecular Lewis-acid/base interactions to form one-dimensional coordination polymers. However, a closer look reveals that **3** exhibits a more significant asymmetry in the intermolecular interactions between an individual anion or cation and its two neighbouring ions of opposite charge. As a consequence, crystalline **3** still contains clearly distinguishable molecular subunits and must be considered to be closer to a molecular crystal.

- Figure 2, here -

Figure 2: Representation of the molecular structure of **4** in the crystal. Thermal ellipsoids were drawn at the 50% probability level and hydrogen atoms were omitted for clarity. Selected distances and angles are listed in Table 1.

In contrast to **3**, the solid phase of **4** contains isolated molecules without any specific intermolecular interactions. The five-membered heterocycle exhibits an envelope conformation with eclipsed SiMe₂-units and the phosphorus atom as flap. The thiocyanate unit resides in a flagpole position and binds via the N-terminus as is common for phosphorus compounds. The endocyclic P–N distances match those in other N-heterocyclic phosphines¹⁹ while the exocyclic bond to the NCS-nitrogen atom is perceptibly longer (P1–N1 1.814(3) Å) and exceeds also the bond lengths in the only two other P(III)-isothiocyanato-derivatives known (P–N 1.6508(15),^{11h} 1.7073(72) Å^{11g}). These features can be regarded as a first hint towards a description of the P–NCS interaction as a dative bond. The shortening of the C–S and lengthening of the C–N bond in the SCN-unit of **4** compared to **3** (see Table 1) suggest that the switch from S- (in **3**) to N-coordination (in **4**) of the SCN-unit shifts the balance of the two dominant resonance structures (S–C≡N ↔ S=C=N) to the side of the cumulene structure.

The access to structural information in solution is less clear-cut than in the solid state. Michalski et al. claimed that the position of the IR absorption band attributable to the νCN-vibrational mode allows a distinction between (thio)phosphoryl thiocyanates (S-bound) and isothiocyanates (N-bound),²³ but it is also known that for isomeric transition metal complexes the ranges of νCN overlap.²⁴ Considering that solid **3** and **4** exhibit, regardless of their different bonding modes, quite similar νCN frequencies, IR data were in the present case not considered a reliable probe for structural assignment.

Gratifyingly, it was possible to derive further information from NMR data. The ¹H and ³¹P NMR chemical shifts of **3** are much larger than expected for molecular diazaphospholenes with covalent exocyclic bonds and come close to the values of diazaphospholenium salts.¹⁹ Even if this trend does not necessarily imply an ionic structure, it was nonetheless identified^{7a,b} as a specific sign of

increased ionic bond polarisation. Considering that the actually observed chemical shifts of **3** exceed those of $\text{III}[I]$,^{7b} we assume that **3** exists likewise as ion pair with a high electrostatic contribution to the bonding between phosphonium and thiocyanate units. This view is further corroborated by the finding that the ^{14}N NMR chemical shift of the thiocyanato-nitrogen atom ($\delta^{14}\text{N}$ -160.4) is close to that of ionic thiocyanates²⁵ ($\delta^{14}\text{N} \approx -169$) while at the same time the deshielding of the signal of the endocyclic nitrogen atoms ($\delta^{14}\text{N}$ -146.8) with respect to neutral diazaphospholenes ($\delta^{14}\text{N} \approx -245$) is a typical indication of the PN multiple bonding in a phosphonium ion.¹⁹

The ^{31}P and $^{14/15}\text{N}$ NMR chemical shifts of **4** are, in contrast to those of **3**, well compatible with the persistence of the covalent structure found in the solid state. In addition, the presence of an intact P–NCS unit is immediately evident from the characteristic splitting of the ^{31}P and ^{14}N NMR signals by ^{14}N , ^{31}P spin coupling. It should be noted that the N-binding mode of the SCN-unit is also associated with a substantial shielding of the ^{14}N nucleus ($\delta^{14}\text{N}$ -234.3) by some 74 ppm with respect to **3** and approximately 64 ppm relative to SCN^- . A similar, albeit even more pronounced, effect had previously been reported for compounds $\alpha\text{-P}_4\text{S}_3(\text{NCS})\text{X}$ ($\text{X} = \text{Cl}, \text{I}, \text{NCS}$).²⁶

In order to cast further light on the nature of the bonding in aminophosphonium thiocyanates and try to understand the factors which control the switch between N- and S-binding modes, we sought to validate our phenomenologically derived explanation by a DFT study on **3**, **4**, and the 1,3,2-diazaphospholidine **5** (cf. Figure 3) featuring a saturated $-\text{CH}_2\text{CH}_2-$ backbone in the heterocycle. To this end, we calculated energy-optimised molecular structures for isomers with both N- and S-bound thiocyanato units (denoted as **3N-5N** and **3S-5S**, respectively) in the gas phase and in two solvents with different dielectric properties (THF, MeCN). All final molecular structures (see Figure 3 and supporting information) were identified as local minima on the energy hypersurface by harmonic vibrational frequency calculations. Important structural parameters, bond indexes and fragment charges as well as relative electronic energies and Gibbs free energies are given in Tables 2,3.

- Figure 3, here -

Figure 3: Representation of the molecular structures of the κN -isomers (top row) and κS -isomers (bottom row) of **3**, **5**, and **4** (from left to right) calculated at the RI-B3LYP-D3BJ/def2-tzvp-level in the gas phase. Selected distances and angles are listed in Table 2.

– Table 2, here –

Inspection of the calculated geometries reveals that all molecules adopt quite similar phosphine-type structures with pyramidal coordination at the phosphorus atom, but differ considerably in their resilience to undergo structural relaxation upon embedding in a dielectric medium. The effects of this relaxation show up in a substantial lengthening of the exocyclic P–N/S distances and concurrent smaller variations of CN/CS and PN distances in the thiocyanato and phosphonium units, respectively (Table 2). Evaluation of Wiberg Bond Indexes (WBI, Table 2) and fragment charges (Table 3) obtained from Natural Population Analyses¹⁸ suggests interpreting these structural distortions in terms of a solvent induced ionic polarisation of the exocyclic P–N/S bonds, which is accompanied by a redistribution of π -electron density in the thiocyanato and a strengthening of the N–P hyperconjugation in the phosphonium fragment, respectively. The extent of the structural flexibility depends on the cation stability of the respective phosphonium ion (which is readily assessed from the energies of suitable isodesmic anion transfer reactions, see supporting information) and the SCN bonding mode. The least structural response to an external dielectric medium is found for **4N** which displays also the highest WBI for the exocyclic P–N bond and is best described as a rigid molecule in which the SCN and phosphonium units are connected by a polar bond with high covalent character. The ionic polarisation increases somewhat in **4S** and the diazaphospholidines **5N**, **5S** but these species may still be considered molecular systems with polar covalent P–N or P–S bonds. The other extreme is marked by **3N** and **3S** where the charge separation increases and the covalent P–E (E = N, S) bonding contribution, which is already in the gas phase smaller than for **4**, **5**, drops sharply when the molecules are immersed in dielectric solvents of increasing polarity. Such behaviour has been

identified as a trait of donor-acceptor bonding,²⁷ and we address both isomers of **3** thus as intimate contact ion pairs which are held together by dative bonds with dominant electrostatic character.

A comparison of the structural parameters of **3**, **4** with those calculated for **3S** and **4N**, respectively, reveals that the best match between theory and experiment results when the calculated structures in the most polar solvent (CH₃CN) are considered. Similar findings had previously also been reported for diazaphospholene halides and imply that the crystal itself is – in the same way as a polar solvent – a polarising medium.^{7b}

– Table 3, here –

The observed switch from N- (in **4**) to S-binding of the thiocyanato-unit (in **3**) is in accord with the computed energetics (Table 3). In the gas phase, the N-bound isomer is for all heterocycles studied more stable than the S-bound isomer. This energy difference is largest for **4** and shrinks eventually in **5** and **3**, as well as upon embedding the molecules into a polar solvent. The solvent influence is sufficient to enforce a change in the energetic order of the isomers of **3** upon moving from the gas phase to solution, where **3S** now is the more stable isomer. The reason for this preference of an S- over an N-bound structure may be explained in simple terms by assuming that a dielectric medium enforces some separation of the phosphonium and thiocyanate units in **3**, and that at long distances the contact between the phosphorus and the soft and polarisable sulfur atom allows to maintain a higher degree of covalency in the bonding interaction between cation and anion than a P⁺–N contact, and can thus provide some extra stabilisation.

Conclusions

Thiocyanato-substituted N-heterocyclic phosphines are accessible from the corresponding chloro-substituted precursors through metathesis reactions with KSCN. Crystal structural studies reveal that the nature of the heterocyclic framework has a strong influence on the P⁺–SCN interaction and may either stabilise a structure with an N-bound ligand and a P–N distance that is still in the range of a

single bond, or a structure with an S-bound ligand forming a much weaker interaction that is halfway between a bond and a mere van-der-Waals contact. DFT-studies suggest that these differences can be traced back to the different cation stabilities of the individual phosphonium fragments and imply a structural change from a molecule with a polar covalent P–N bond to an ion pair that is held together by a dative bond and engages in further intermolecular interactions in the crystalline state.

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Supplementary Data

Packing diagram for crystalline **4**, representations of NMR spectra of **3**, **4**, calculated isodesmic reaction energies, computed atomic coordinates for **3N/3S** – **5N/5S**.

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