

A general synthesis of phosphorus- and arsenic-containing analogues of the thio- and seleno-cyanate anions

Frank Tambornino,^[a] Alexander Hinz,^[b] Ralf Köppe,^[b] and Jose M. Goicoechea^{*[a]}

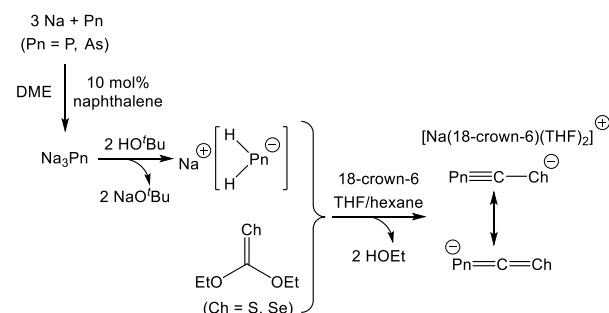
Abstract: A general synthetic protocol for the synthesis of phosphorus- and arsenic-containing analogues of the thio- and seleno-cyanate anions is reported. This procedure allows for the isolation of three unprecedented species: the phosphoethynselenolate, PCSe^- (**1**), the arsaethynthiolate, AsCS^- (**2**), and the arsaethynselenolate, AsCSe^- (**3**), anions. The structures, electronic properties, and spectroscopic signatures of these species are reported.

The chemistry of the cyanate anion (NCO^-), and of its heavier chalcogen-containing congeners, the thio- and seleno-cyanate ions (NCS^- and NCSe^- , respectively), is well-established and features prominently in general chemistry textbooks.^[1] These archetypal pseudohalogen ions have been extensively employed in coordination chemistry and organic synthesis.^[1–3] By contrast, the heavier tellurium-containing analogue of these ions (NCTe^-), first synthesised in 1968, is less well studied.^[2b,4–6] Related anions in which the nitrogen atom is replaced by a heavier pnictogen element are also relatively rare. The lithium salt of the 2-phosphoethynolate anion (PCO^-) was first reported by Becker and co-workers in 1992,^[7] however due to difficulties associated with its manipulation, its chemistry remained dormant for decades. The report of several novel syntheses of the ion as the more stable sodium and potassium salts has rekindled interest in this reagent.^[8] Over the course of the last four years it has received significant attention as a viable precursor to rare (often unprecedented) phosphorus-containing compounds.^[9–11] The heavier arsenic-containing ion, AsCO^- , was first isolated in 2016 by our research group,^[12] and promises to be a similarly versatile reagent in chemical synthesis, having already been employed for the synthesis of several novel molecules.^[13]

To date, cyanate analogues containing both heavier group 15 and group 16 elements are limited to the 2-phosphoethynthiolate anion (PCS^-) which can be synthesised by reaction of PCO^- with CS_2 . As with PCO^- , this species was first isolated by Becker,^[14] and its chemistry has largely been limited to fundamental coordination chemistry studies and some gas phase measurements.^[15,16] Clearly, there are still a number of valence isoelectronic ions related to such species that have yet

to be experimentally realised. Ions such as PnCO^- ($\text{Pn} = \text{Sb}$ and Bi) have been the subject of theoretical studies and postulated to be isolable (although they remain elusive).^[17] Similarly, with the exception of PCS^- , heavier analogues of the thio-, seleno- and tellurocyanate anions are unknown, and somewhat surprisingly, unexplored in theoretical or gas phase studies. This vacancy in chemical space prompted us to explore the synthesis of such novel anions. Herein we report our first attempts in the field, and describe the isolation of the phosphoethynselenolate, PCSe^- (**1**), the arsaethynthiolate, AsCS^- (**2**), and the arsaethynselenolate, AsCSe^- (**3**), anions, three rare and remarkably stable species that can be isolated and manipulated with ease under anaerobic and anhydrous conditions.

Reactions of dimethoxyethane (DME) solutions of sodium phosphanide or arsanide (NaPnH_2 , where $\text{Pn} = \text{P}, \text{As}$) with either diethylthionocarbonate or diethylselenonocarbonate afford dark orange solutions after the course of 24 hours (Scheme 1). These crude reaction mixtures were found to contain the target anions (PCS^- , PCSe^- (**1**), AsCS^- (**2**) and AsCSe^- (**3**)) by *in situ* infrared and ^{13}C NMR spectroscopy. ^{31}P NMR spectroscopy was also used to probe the formation of the phosphorus-containing anions. The products can be purified by reducing the reaction mixtures to dryness under a dynamic vacuum. Extraction of the products with THF in the presence of 18-crown-6, followed by filtration and precipitation with hexane affords $[\text{Na}(18\text{-crown-6})(\text{THF})_2][\text{PnCCh}]$ ($\text{Pn} = \text{P}, \text{As}$; $\text{Ch} = \text{S}, \text{Se}$). This synthetic procedure allows for the isolation of compositionally pure salts of PCS^- , PCSe^- , AsCS^- and AsCSe^- in moderate yields (typically around 30–40%). Variation of these conditions allows for the synthesis of several additional salts and solvates such as $[\text{Na}(18\text{-crown-6})(\text{dioxane})][\text{AsCS}]$ -dioxane or $[\text{Na}(\text{dioxane})_3][\text{AsCS}]$ (see SI for details).



Scheme 1. Synthesis of $[\text{Na}(18\text{-crown-6})(\text{THF})_2][\text{PnCCh}]$ (where $\text{Pn} = \text{P}, \text{As}$; $\text{Ch} = \text{S}, \text{Se}$).

Off-white to pale yellow crystals of the $[\text{Na}(18\text{-crown-6})(\text{THF})_2]^+$ salts of all four anions were obtained by slow diffusion of hexane into THF solutions of the reaction products (Figure 1 shows the structure of $[\text{Na}(18\text{-crown-6})(\text{THF})_2][\text{AsCS}]$). The samples are isotopic and crystallise in the asymmetric

[a] Dr. F. Tambornino, Prof. Dr. J. M. Goicoechea
Department of Chemistry, University of Oxford,
Chemistry Research Laboratory
12 Mansfield Road, Oxford, OX1 3TA (UK)
E-mail: jose.goicoechea@chem.ox.ac.uk

[b] Dr. A. Hinz, Dr. R. Köppe
Karlsruhe Institute of Technology
Institute of Inorganic Chemistry, Engesserstr. 15
76131 Karlsruhe, Germany

Supporting information for this article is given via a link at the end of the document.

monoclinic space group type $P2_1$. All but one of the anions, PCSe^- , are well defined and do not exhibit notable positional crystallographic disorder in the lattice, which allows of a comparison of their bond metric properties. Admittedly, accurately distinguishing between phosphorus and sulphur (or arsenic and selenium), is not viable using single crystal X-ray diffraction, however, using the structure of the AsCS^- ion as a benchmark, assignment of the positions of the arsenic and selenium atoms in the structure of AsCSe^- is possible based on bond metric data. The same is also true for the structure of the PCS^- salt using previously reported structural values and DFT data. The crystal structures reveal essentially linear anions with Pn-C-Ch angles close to 180° as shown in Table 1.

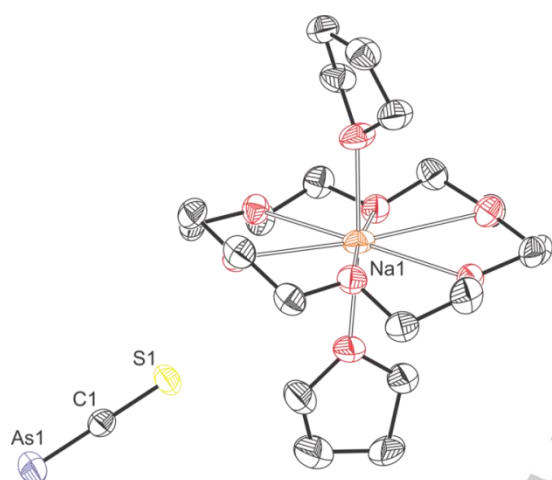


Figure 1. Molecular structure of $[\text{Na}(\text{18-crown-6})(\text{THF})_2][\text{AsCS}]$. Anisotropic displacement ellipsoids pictured at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): As1-C1 , 1.691(5); C1-S1 , 1.605(5); As1-C1-S1 , 179.6(3).

Table 1. Experimentally determined bond metric data and calculated values (in parentheses)^[a] for the thio- and seleno-cyanate ions and their heavier phosphorus- and arsenic-containing analogues.

Anion	Pn-C (Å)	C-Ch (Å)	Pn-C-Ch ($^\circ$)
NCS^- ^[18]	1.053(6) (1.165)	1.655(5) (1.654)	176.2(4)
PCS^-	1.579(4) (1.578)	1.613(4) (1.627)	179.3(3)
AsCS^-	1.691(5) (1.700)	1.605(5) (1.619)	179.6(3)
NCSe^- ^[19]	1.162(4) (1.161)	1.801(3) (1.815)	178.9(3)
PCSe^- ^[b]	1.46(3)/1.53(7) (1.569)	1.78(3)/1.85(7) (1.787)	179(3)/180(6)
AsCSe^-	1.699(4) (1.690)	1.745(4) (1.780)	179.5(3)

^[a] Calculated at the wB97XD/Def2QZVP level of theory with a Polarizable Continuum Model (PCM) to model solvation (pyridine was used as a solvent).

^[b] Anion exhibits positional disorder in the lattice (values for both components given).

The structure of the PCS^- anion was previously reported by Becker as the $[\text{Li}(\text{DME})_3][\text{PCS}]$ salt (P-C , 1.555(11) Å; C-S , 1.620(11) Å; P-C-S , 178.9(7) $^\circ$),^[14] and our data for $[\text{Na}(\text{18-crown-6})(\text{THF})_2][\text{PCS}]$ compare well with reported values (P-C ,

1.579(4) Å; C-S , 1.613(4) Å; P-C-S , 179.3(3) $^\circ$). The P-C bond length is identical to that previously determined for the PCO^- ion in $[\text{K}(\text{18-crown-6})][\text{PCO}]$, 1.579(3), which approximates the value predicted for a $\text{P}\equiv\text{C}$ triple bond (1.54 Å).^[20] Given the disorder in the structure of the PCSe^- anion, no meaningful information can be extracted from the structure, however, computational studies suggest that, from a bond metric standpoint, there should be no significant change to the length of the P-C bond, and that this is largely consistent with a triple bond as the $\text{P}\equiv\text{C-Ch}^-$ resonance form is the greatest contributor to the overall structure according to a Natural Resonance Theory (NRT) analysis ($\text{P}\equiv\text{C-S}^-$: 52.2%; $\text{P}\equiv\text{C-Se}^-$: 55.2%). This is also in line with computed Wiberg bond indices (WBI) which predict value of 2.38 and 2.47 for the P-C bonds in PCS^- and PCSe^- , respectively (Table 2).

The arsenic-containing anions allow for a much more detailed comparison of bond lengths. As1-C1 interatomic distances (**2**: 1.691(5) Å; **3**: 1.699(4) Å) are slightly longer than that expected for an As-C triple bond (1.66 Å) and consistent with the value previously reported for AsCO^- (1.707(3) Å). These bonds are notably shorter than the predicted double bond length (1.81 Å).^[20] The C-Ch bond lengths (C-S : 1.605(5) Å; C-Se : 1.745(4) Å) approximate values predicted for C=Ch double bonds (C-S : 1.61 Å; C-Se : 1.74). Theoretical NRT analyses of the anions support these values and predict that the $\text{As}\equiv\text{C-Ch}^-$ resonance forms of the anions have the greatest contribution to the overall structure 49.5 and 54.2% for AsCS^- and AsCSe^- , respectively, (whereas the $^-\text{As}=\text{C=Ch}$ resonance forms contributes to a lesser degree: 20.3 and 17.5% for AsCS^- and AsCSe^- , respectively). It should be noted that the contribution of the $\text{Pn}\equiv\text{C-Ch}^-$ resonance form is greatest for the thio- and seleno-cyanate ions, and that on descending the group 15 elements the C-S and C-Se bonds lengths decrease in a monotonic sequence for $\text{Pn}\equiv\text{C-S}^-$ and $\text{Pn}\equiv\text{C-Se}^-$, respectively.

Table 2. Natural Bond Orbital (NBO) atomic charges (e) and Wiberg Bond Indices (WBI) of the known valence isoelectronic cyanate ions predicted with the wB97XD/Def2QZVP level of theory.

Anion	q_{Pn}	q_{C}	q_{Ch}	$\text{WBI}(\text{Pn-C})$	$\text{WBI}(\text{C-Ch})$
NCO^-	-0.85	0.60	-0.75	2.4250	1.5203
NCS^-	-0.59	0.06	-0.47	2.6267	1.3839
NCSe^-	-0.57	0.03	-0.47	2.6937	1.2803
PCO^-	-0.48	0.13	-0.65	2.2031	1.6673
PCS^-	0.03	-0.74	-0.28	2.3798	1.5210
PCSe^-	0.13	-0.83	-0.30	2.4683	1.3397
AsCO^-	-0.53	0.16	-0.63	2.1162	1.7120
AsCS^-	0.01	-0.76	-0.25	2.3082	1.5753
AsCSe^-	0.13	-0.87	-0.26	2.3986	1.4467

An unprecedented feature is the remarkable stability of these ions. We rationalised this by analysing the contributions of the

$2^-Pn-C\equiv Ch^+$ resonance to the overall structure. For PCO^- and $AsCO^-$ our calculations show 5.2% and 13.5%, respectively, allowing for a facile decarbonylation pathway which has been explored synthetically to generate " Pn ". This decomposition pathway is hampered for all heavier homologues, as the respective contribution of the aforementioned resonance is less pronounced. It is highest for $AsCS^-$ (2.9%) and lowest for $PCSe^-$ (1.9%). Calculated bond dissociation energies (BDE) corroborate hindrance of " CCh " formation as the required energies (from $AsCS^-$: 126 kJ/mol to $PCSe^-$: 156 kJ/mol) approach double the value reported for $AsCO$ (70 kJ/mol; see SI for details).

Bond metric data suggest that the preferred binding mode of $AsCCh^-$ anions should be through the chalcogen atom, however attempts to synthesize adducts of these anions via salt metathesis reactions have thus far been unsuccessful. One reason for this may be the fact that for all four of the heavier $PnCCh^-$ ions, the greatest degree of negative charge accumulates on the central carbon atom (in contrast to the thio- and seleno-cyanate anions, PCO^- , and $AsCO^-$). This implies that while such species are formally pseudo-halide ions, their reactivity differs from such species due to a lack of significant negative charge build up on the terminal atoms, and that such ions are in fact susceptible to attack at the carbon centre by electrophiles.

All anions were characterized by multi-element NMR spectroscopy. The $PCSe^-$ ion exhibits a singlet in its ^{31}P NMR spectrum at -46.9 ppm which is at a considerably higher frequency than the PCO^- and PCS^- anions, -392.0 and -120.9 ppm, respectively. The observed deshielding is consistent with the decreased contribution of the $^-P=C=Ch$ resonance form on descending the group 16 elements (33.1, 19.0 and 17.2% for PCO^- , PCS^- and $PCSe^-$, respectively). ^{13}C NMR spectroscopy reveals a doublet at 189.3 ppm with a $^1J_{P-C}$ of 22.8 Hz. This resonance is only slightly shifted relative to that of the PCS^- ion (194.6 ppm) consistent with a high degree of similarity of the electronic structures of PCS^- and $PCSe^-$. The ^{77}Se NMR spectrum of $PCSe^-$ exhibits a doublet at 84.3 ppm due to coupling with the phosphorus nucleus ($^2J_{P-Se} = 39.3$ Hz).

Table 3. Selected nuclear magnetic resonance data for all of the $PnCCh^-$ ions ($Pn = P, As$; $Ch = S, Se$). All NMR data recorded in ds -pyridine. Chemical shifts give in ppm, coupling constants in Hz.

	^{31}P	^{13}C	^{77}Se	$^1J_{P-C}$	$^2J_{P-Se}$	$^1J_{C-Se}$
PCS^-	-120.9	193.6	N.A.	19.3	N.A.	N.A.
$PCSe^-$	-46.9	189.3	84.3	22.8	39.3	N.A.
$AsCS^-$	N.A.	210.0	N.A.	N.A.	N.A.	N.A.
$AsCSe^-$	N.A.	206.4	248.4	N.A.	N.A.	264

The ^{13}C NMR spectra of $AsCS^-$ and $AsCSe^-$ revealed singlets at 210.03 and 206.36 ppm, both at higher frequency than the corresponding phosphorus-containing analogues. The latter reveals ^{77}Se satellites with a ^{13}C - ^{77}Se coupling constant of 264 Hz. This value corresponds with previously reported $^1J_{C-Se}$ coupling constants in which the C-S bond exhibits double bond

character (226–286 Hz, the latter for $SeCO$), and differ significantly from values expected for C-Se single bonds (90–100 Hz).^[21] The ^{77}Se NMR shift of the $AsCSe^-$ ion, 248.35 ppm, differs greatly from that of $PCSe^-$ (39.3 ppm), which we attribute to the greater π -acidity of the central carbon atom in $AsCSe^-$ relative to $PCSe^-$.^[22]

The infrared spectra of the phosphorus-containing anions $PCCh^-$ ($Ch = S, Se$) reveal bands at 1374 and 1311 cm^{-1} , respectively, for their ν_1 ("antisymmetric") stretching modes. The latter is partially encumbered by bands from the 18-crown-6 sequestering agent. The arsenic-containing anions reveal bands at 1270 and 1171 cm^{-1} for the ν_1 modes of $AsCS^-$ and $AsCSe^-$, respectively. The values are shifted with respect to their phosphorus-containing homologues owing to the heavier atomic weight of arsenic. The ν_3 (or "symmetric") stretching vibrations for all ions in question are computed below 600 cm^{-1} and thus unobservable in the IR spectra.

Table 4. Vibrational data for the $PnCCh^-$ ions ($Pn = P, As$; $Ch = O, S, Se$; $C_{\infty v}$ symmetry each). Frequencies given in cm^{-1} , potential energy distribution (PED) upon the internal coordinates given in percentages.

	ν_1 (IR)	ν_1 (R)	ν_1 (DFT)	PED ₁	ν_3 (R)	ν_3 DFT	PED ₃
PCO^-	1780 ^[a]	1786	1798	CO:92 PC:22	802	790	CO:11 PC:80
PCS^-	1374	1370	1374	CS:43 PC:72	595	593	CS:59 PC:30
$PCSe^-$	1311	1305	1309	CSe:27 PC:85	447	446	CSe:74 PC:17
$AsCO^-$	1755 ^[b]	1755	1775	CO:97 AsC:14	618	601	CO:5 AsC:88
$AsCS^-$	1270	1270	1334	CS:58 AsC:58	474	469	CS:44 AsC:44
$AsCSe^-$	1171	1176	1176	CSe:40 AsC:74	339	336	CSe:62 AsC:28

[a] Data from reference 8a. [b] Data from reference 12.

To facilitate a better understanding of basic vibration patterns, Raman spectra for all compounds, and for the parent ions PCO^- and $AsCO^-$, were collected. Spectra in the series $PCCh^-$ ($Ch = O, S, Se$) show ν_1 stretching modes at 1786, 1370, and 1305 cm^{-1} , respectively, corresponding nicely to the values from infrared spectra. The ν_3 stretching modes in the Raman spectra and found at 802, 595 and 447 cm^{-1} , respectively (see Table 4). As with the ν_1 modes determined by IR spectroscopy, the frequencies in this series decrease monotonically owing to the increase in atomic weight from O-Se. The arsenic-containing anions $AsCCh^-$ ($Ch = O, S, Se$) reveal ν_1 stretching modes at 1755, 1270, and 1176 cm^{-1} , respectively, which is in accordance with IR and computational data. The ν_3 stretching vibrations were observed at 618, 474 and 339 cm^{-1} , respectively. Analogously to the phosphorus-containing anions, the vibration energies decrease with increasing atomic weight of the comprising elements.

Table 5. Valence force constants $f(\text{C}-\text{Ch})$ and $f(\text{C}-\text{Pn})$ for the PnCCCh^- ions ($\text{Pn} = \text{P}, \text{As}$; $\text{Ch} = \text{O}, \text{S}, \text{Se}$) as well as for typical examples of $\text{C}-\text{Ch}$ and $\text{C}-\text{Pn}$ single and multiple bonds, given in $\text{mdyn } \text{\AA}^{-1}$.

	$f(\text{C}-\text{Ch})$	$f(\text{C}-\text{Pn})$	$f(\text{C}-\text{Ch}/\text{Pn})$
PCO^-	12.94	6.73	$\text{CH}_3\text{C}\equiv\text{P}, \text{H}_3\text{C}-\text{PF}_2$ 8.89 ^[23] , 2.97 ^[24]
PCS^-	5.44	7.71	$\text{CH}_3\text{C}\equiv\text{As}, \text{AsPh}_3$ 7.29 ^[25] , 2.46 ^[26]
PCSe^-	4.01	8.10	$\text{Cl}_2\text{C}=\text{O}, (\text{CH}_3)_2\text{O}$ 14.0 ^[27] , 5.38 ^[28]
AsCO^-	13.36	5.14	$\text{Cl}_2\text{C}=\text{S}, (\text{CH}_3)_2\text{S}$ 6.42 ^[27] , 3.40 ^[28]
AsCS^-	5.49	6.53	$\text{Cl}_2\text{C}=\text{Se}, (\text{CH}_3)_2\text{Se}$ 5.0 ^[27] , 2.68 ^[28]
AsCSe^-	4.02	6.80	

The calculated potential energy distributions (PED) quantify the coupling between the stretching vibrations in these molecules of $C_{\infty v}$ symmetry (Table 4).^[29] One finds strong coupling of the bonds especially within the sulfur compounds: in PCS^- and AsCS^- the attribution of a band to a certain motion is not possible. Furthermore, it means that the $\text{P}\equiv\text{C}$ vibration might be attributed to the range from 802 to 1370 cm^{-1} , the signal of the $\text{As}\equiv\text{C}$ vibration within 608 and 1270 cm^{-1} .

The vibrational force constants serve as a highly reliable measure for the experimental characterization of a bond and especially of multiple bonding as they directly reflect the situation of the bonding electrons between two nuclei.^[30] More accurately, the force constant f represents the restoring force which resists to a small elongation of the atoms from the equilibrium distances. By a normal coordinate analysis the force constant values (Table 5) were determined for the molecules under discussion; they confirm in a rather sensitive manner the findings of the X-ray structure determinations as well as of the quantum chemical calculations.

In summary, we have developed a modular synthetic protocol towards the combined heavier group 15/16 homologues of cyanate PnCCCh^- ($\text{Pn} = \text{P}, \text{As}$; $\text{Ch} = \text{S}, \text{Se}$). Crystallographic data reveals essentially linear anions with triple bond character for the $\text{Pn}\equiv\text{C}$ bonds. NMR, IR and Raman spectroscopy show distinct trends with permutation of the pnictogen and chalcogen atoms. We propose that the negative charge is largely localized at the central carbon atom as indicated by NBO analysis. Studies exploiting this unique charge distribution are currently under way including redox chemistry, coordination modes, and reactivity towards a library of organic compounds.

Acknowledgements

We gratefully acknowledge the EPSRC (EP/M027732/1) and the DFG (TA 1357/1-1) for financial support. The University of Oxford is acknowledged for access to Advanced Research Computing and Chemical Crystallography facilities, and we thank Elemental Microanalysis Ltd. (Devon) for determination of the elemental analyses.

Keywords: Cyanates • Main-Group Chemistry • Fundamental Ions • Phosphorus • Arsenic

- [1] N. N. Greenwood, A. Earnshaw in *Chemistry of the Elements* 2nd Ed., Elsevier Butterworth-Heinemann, Oxford, **1997**.
- [2] (a) A. H. Norbury, *Adv. Inorg. Chem. Radiochem.* **1975**, 17, 231–402; (b) J. L. Burmeister, *Coord. Chem. Rev.* **1990**, 105, 77–133.
- [3] For a recent review on organic thiocyanates see: T. Castanheiro, J. Suffert, M. Donnard, M. Gulea, *Chem. Soc. Rev.* **2016**, 45, 494–505.
- [4] A. W. Downs, *Chem. Commun.* **1968**, 1290.
- [5] A. S. Foust, *J. Chem. Soc., Chem. Commun.* **1979**, 414–415.
- [6] A. H. Norbury, M. Thompson, and J. Songstad, *Inorg. Nuclear Chem. Letters* **1973**, 9, 347.
- [7] G. Becker, W. Schwarz, N. Seidler, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1992**, 612, 72–82.
- [8] (a) F. F. Puschmann, D. Stein, D. Heift, C. Hendriksen, Z. A. Gal, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2011**, 50, 8420–8423; (b) I. Krummenacher, C. C. Cummins, *Polyhedron* **2012**, 32, 10–13; (c) A. R. Jupp, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2013**, 52, 10064–10067; (d) D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.* **2014**, 43, 831–840.
- [9] (a) A. R. Jupp, J. M. Goicoechea, *J. Am. Chem. Soc.* **2013**, 135, 19131–19134; (b) A. M. Tondreau, Z. Benkő, J. R. Harmer, H. Grützmacher, *Chem. Sci.* **2014**, 5, 1545–1554; (c) X. Chen, S. Alidori, F. F. Puschmann, G. Santiso-Quinones, Z. Benkő, Z. Li, G. Becker, H.-F. Grützmacher, H. Grützmacher, *Angew. Chem. Int. Ed.* **2014**, 53, 1641–1645; (d) D. Heift, Z. Benkő, H. Grützmacher, *Angew. Chem. Int. Ed.* **2014**, 53, 6757–6761; (e) M. B. Geeson, A. R. Jupp, J. E. McGrady, J. M. Goicoechea, *Chem. Commun.* **2014**, 50, 12281–12284; (f) D. Heift, Z. Benkő, H. Grützmacher, *Chem. Eur. J.* **2014**, 20, 11326–11330; (g) T. P. Robinson, M. J. Cowley, D. Scheschke, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2015**, 54, 683–686; (h) T. P. Robinson, J. M. Goicoechea, *Chem. Eur. J.* **2015**, 21, 5727–5731; (i) A. R. Jupp, G. Trott, É. Payen de la Garanderie, J. D. G. Holl, D. Carmichael, J. M. Goicoechea, *Chem. Eur. J.* **2015**, 21, 8015–8018; (j) Z. Li, X. Chen, M. Bergeler, M. Reiher, C. Su, H. Grützmacher, *Dalton Trans.* **2015**, 44, 6431–6438; (k) D. Heift, Z. Benkő, H. Grützmacher, A. R. Jupp, J. M. Goicoechea, *Chem. Sci.* **2015**, 6, 4017–4024; (l) R. Suter, Z. Benkő, H. Grützmacher, *Chem. Eur. J.* **2016**, 22, 14979–14987; (m) Z. Li, X. Chen, Z. Benkő, L. Liu, D. A. Ruiz, J. L. Peltier, G. Bertrand, C.-Y. Su, H. Grützmacher, *Angew. Chem. Int. Ed.* **2016**, 55, 6018–6022; (n) R. Suter, Y. Mei, M. Baker, Z. Benkő, Z. Li, H. Grützmacher, *Angew. Chem. Int. Ed.* **2017**, 56, 1356–1360; (o) Z. Li, X. Chen, D. M. Andrada, G. Frenking, Z. Benkő, Y. Li, J. R. Harmer, C.-Y. Su, H. Grützmacher, *Angew. Chem. Int. Ed.* **2017**, 56, 5744–5749; (p) E. N. Faria, A. R. Jupp, J. M. Goicoechea, *Chem. Commun.* **2017**, 53, 7092–7095; (q) D. W. N. Wilson, A. Hinz, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2018**, 57, 2188–2193.
- [10] (a) S. Alidori, D. Heift, G. Santiso-Quinones, Z. Benkő, H. Grützmacher, M. Caporali, L. Gonsalvi, A. Rossini, M. Peruzzini, *Chem. Eur. J.* **2012**, 18, 14805–14811; (b) D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.* **2014**, 43, 5920–5928; (c) C. Camp, N. Settineri, J. Lefèvre, A. R. Jupp, J. M. Goicoechea, L. Maron, J. Arnold, *Chem. Sci.* **2015**, 2, 6379–6384.
- [11] (a) L. Liu, D. A. Ruiz, F. Dahcheh, G. Bertrand, R. Suter, A. M. Tondreau, H. Grützmacher, *Chem. Sci.* **2016**, 7, 2335–2341; (b) S. Yao, Y. Xiong, T. Szilvási, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2016**, 55, 4781–4785; (c) Y. Wu, L. Liu, J. Su, J. Zhu, Z. Ji, Y. Zhao, *Organometallics* **2016**, 35, 1593–1596; (d) N. Del Rio, A. Baceiredo, N. Saffon-Merceron, D. Hashizume, D. Lutters, T. Müller, T. Kato, *Angew. Chem. Int. Ed.* **2016**, 55, 4753–4758; (e) Y. Xiong, S. Yao, T. Szilvási, E. Ballester-Martínez, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2017**, 56, 4333–4336; (f) L. N. Grant, B. Pinter, B. C. Manor, R. Suter, H. Grützmacher, D. J. Mindiola, *Chem. Eur. J.* **2017**, 23, 6272–6276; (h) L. Liu, D. A. Ruiz, D. Munz, G. Bertrand, *Chem* **2016**, 1, 147–

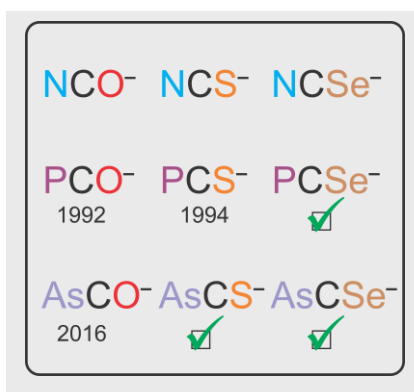
- 153; (b) M. M. Hansmann, R. Jazzar, G. Bertrand, *J. Am. Chem. Soc.* **2016**, *138*, 8356–8359.
- [12] A. Hinz, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2016**, *55*, 8536–8541.
- [13] (a) A. Hinz, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2016**, *55*, 15515–15519; (b) S. Yao, Y. Grossheim, A. Kostenko, E. Ballester-Martínez, S. Schutte, M. Bispinghoff, H. Grützmacher, M. Driess, *Angew. Chem. Int. Ed.* **2017**, *56*, 7465–7469; (c) E. Ballester-Martínez, T. J. Hadlington, T. Szilvási, S. Yao, M. Driess, *Chem. Commun.* DOI: 10.1039/c8cc01928b.
- [14] G. Becker, K. Hübler, *Z. Anorg. Allg. Chem.* **1994**, *620*, 405–417.
- [15] A. R. Jupp, M. B. Geeson, J. E. McGrady, J. M. Goicoechea, *Eur. J. Inorg. Chem.* **2016**, 639–648.
- [16] G.-L. Hou, B. Chen, W. J. Transue, Z. Yang, H. Grützmacher, M. Driess, C. C. Cummins, W. T. Borden, X.-B. Wang, *J. Am. Chem. Soc.* **2017**, *139*, 8922–8930.
- [17] Y. Lu, H. Wang, Y. Xie, H. Liu, H. F. Schaefer, *Inorg. Chem.* **2014**, *53*, 6252–6256.
- [18] Data from structure for [Na(2,2,1-crypt)][INCS] reported in: F. Mathieu, B. Metz, D. Moras, R. Weiss, *J. Am. Chem. Soc.* **1978**, *100*, 4412–4416.
- [19] Data from structure for [(CH₃)₃Se][SeCN] reported in: T. M. Klapötke, B. Krumm, P. Mayer, H. Piotrowski, K. Polborn, I. Schwab, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1831–1834.
- [20] (a) P. Pykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186–197; (b) P. Pykkö, M. Atsumi, *J. Chem. Eur. J.* **2009**, *15*, 12770–12779; (c) P. Pykkö, S. Riedel, M. Patzschke, *Chem. Eur. J.* **2005**, *11*, 3511–3520.
- [21] (a) W. Gombler, *Z. Naturforsch. B* **1981**, *12*, 1561–1565; (b) A. Sørensen, B. Rasmussen, M. Pittelkow, *J. Org. Chem.* **2015**, *80*, 3852–3857.
- [22] A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269–5272.
- [23] K. Ohno, H. Matsuura, *J. Mol. Struct.* **1991**, *242*, 303–314.
- [24] J. D. Odom, A. E. Stanley, Mei-Shiow Cheng, J. R. Durig, *J. Raman Spectr.* **1987**, *18*, 25–35.
- [25] H. M. Schmidt, H. Stoll, H. Preuss, G. Becker, O. Mundt, *J. Mol. Struct. (Theochem)* **1992**, *262*, 171–185.
- [26] C. Ludwig, M. Dolny, H.-J. Götze, *Spectrochim. Acta A* **1997**, *53*, 2363–2372.
- [27] A. Darmadi, A. Haas, H. Willner, H. Schnöckel, *Z. Naturforsch.* **1981**, *36b*, 1261–1264.
- [28] Y. Imai, K. Aida, K. Itaya, *Spectrochim. Acta A* **1988**, *44*, 179–183.
- [29] H. J. Becher, *Fortschr. Chem. Forsch.* **1967**, *10*, 156–205.
- [30] (a) S. Brownridge, T. S. Cameron, H. Du, C. Knapp, R. Köppe, J. Passmore, J. M. Rautiainen, H. Schnöckel, *Inorg. Chem.* **2005**, *44*, 1660–1671; (b) R. Köppe, H. Schnöckel, *Chem. Sci.* **2015**, *6*, 1199–1205.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Heavyweight anions. We report on the isolation of the heavier homologues of cyanate $PnCCh^-$ ($Pn = P, As$; $Ch = S, Se$). The isostructural and isoelectronic anions show unprecedented stability and intriguing charge distribution as shown by a combination of spectroscopic and density functional theory methods.



Frank Tambornino, Alexander Hinz, Ralf Köppe and Jose M. Goicoechea*

Page No. – Page No.

A general synthesis of phosphorus- and arsenic-containing analogues of the thio- and seleno-cyanate anions