

## Main-Group Chemistry

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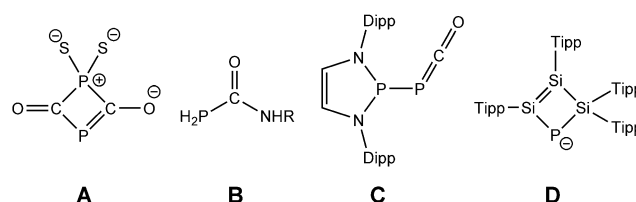
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## A Monoanionic Arsenide Source: Decarbonylation of the 2-Arsaethynolate Anion upon Reaction with Bulky Stannylenes

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**Abstract:** We report fundamental studies on the reactivity of the 2-arsaethynolate anion ( $\text{AsCO}^-$ ), a species that has only recently become synthetically accessible. The reaction of  $\text{AsCO}^-$  with the bulky stannylenes  $\text{Ter}_2\text{Sn}$  ( $\text{Ter} = 2,6\text{-bis}[2,4,6\text{-trimethylphenyl}]$ phenyl) is described, which leads to the unexpected formation of a  $[\text{Ter}_3\text{Sn}_2\text{As}_2]^-$  cluster compound. On the reaction pathway to this cluster, several intermediates were identified and characterized. After the initial association of  $\text{AsCO}^-$  to  $\text{Ter}_2\text{Sn}$ , decarbonylation occurs to give an anion featuring monocoordinate arsenic,  $[\text{Ter}_2\text{SnAs}]^-$ . Both species are not stable under ambient conditions, and  $[\text{Ter}_2\text{SnAs}]^-$  rearranges to form  $[\text{TerSnAsTer}]^-$ , an unprecedented mixed Group 14/15 alkene analogue.

The chemistry of the known heavier Group 15 analogues of the cyanate ion,  $\text{PCO}^-$  and  $\text{AsCO}^-$ , has been shown to often differ dramatically from that of their lighter congener. These species are of interest as the controlled handling of monoanionic pnictides can be useful for bottom-up approaches towards clusters and materials. Both of the heavier Group 15 analogues of the cyanate ion ( $\text{PCO}^-$  and  $\text{AsCO}^-$ ) can be envisaged as useful starting materials for this purpose. The controlled transfer of  $\text{P}^-$  or  $\text{As}^-$  to molecular substrates is a feasible stepping stone for the atom-by-atom assembly of quantum dots and semiconducting materials. Whereas  $\text{AsCO}^-$  was synthesized only recently, the 2-phosphaethynolate anion ( $\text{PCO}^-$ ) was first isolated as its  $\text{Li}^+$  salt in 1992,<sup>[1]</sup> and its relative instability towards oxidation was established in early reactivity studies. For example, reactions with elemental sulfur were found to form cyclic systems such as **A** (Figure 1), and oxidation with iodine or sulfur dioxide afforded  $\text{Li}_2[(\text{PCO})_4]$ .<sup>[2,3]</sup> The synthesis of stable salts of  $\text{PCO}^-$ , such as  $[\text{Na}(\text{dioxane})_x]\text{PCO}^-$  ( $x = 2.5\text{--}2.8$ ), has enabled more comprehensive studies on this remarkable species in recent years (Figure 1).<sup>[4,5]</sup> Protonation of  $\text{PCO}^-$  in the presence of amine nucleophiles yielded phosphinecarboxamides (**B**) in a reaction analogous to Wöhler's historic

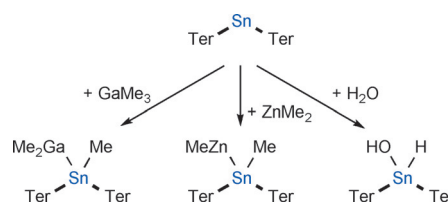


**Figure 1.** Examples for the reactivity of  $\text{PCO}^-$ . R = H, cyclohexyl, prop-2-yn-1-yl, for example. Dipp = 2,6-diisopropylphenyl, Tipp = 2,4,6-triisopropylphenyl.

synthesis of urea.<sup>[6–9]</sup> Metathesis reactions provide access to various coordination complexes of main-group elements,<sup>[10]</sup> actinides,<sup>[11]</sup> and transition metals<sup>[12–14]</sup> as well as phosphaketene compounds of the Group 14 and 15 elements (silyl to plumbyl,<sup>[15,16]</sup> germlylenyl,<sup>[17–19]</sup> and phosphanyl,<sup>[20–23]</sup> **C**). Furthermore, cycloaddition reactions towards alkynes,<sup>[24]</sup> ketenes, and carbodiimides have also been reported.<sup>[25,26]</sup> Amongst these many studies, thus far, there are only three examples of  $\text{PCO}^-$  acting as source of phosphide ( $\text{P}^-$ ): towards cyclo-trisilene (resulting in the formation of **D**, Figure 1),<sup>[27]</sup> imidazolium salts,<sup>[28]</sup> and isocyanate.<sup>[29]</sup>

The chemistry of the heavier homologue  $\text{AsCO}^-$  (the 2-arsaethynolate ion) is less well developed as this compound was not isolated until early 2016 as  $[\text{Na}(18\text{-crown-6})][\text{AsCO}]$ .<sup>[30]</sup> It was shown to react with heteroallenes and act as a source of  $\text{As}^-$  as well as to engage in [2+2] cycloaddition reactions.

A gap that has yet to be investigated with regard to the reactivity of the heavy homologues of cyanate is their reactivity towards coordinatively unsaturated metal centers. We set out to explore this reactivity by studying the interaction of  $\text{PCO}^-$  and  $\text{AsCO}^-$  towards Power's bis(terphenyl)stannylenes  $\text{Ter}_2\text{Sn}$  ( $\text{Ter} = 2,6\text{-bis}[2,4,6\text{-trimethylphenyl}]$ phenyl), which is monomeric owing to the presence of the bulky terphenyl substituents.<sup>[31,32]</sup> Surprisingly, there are only a handful of studies on the reactivity of this stannylenes (Scheme 1), which has been shown to react with water and alcohols,<sup>[33]</sup> as well as alkyl aluminum, gallium,<sup>[34]</sup> and zinc compounds,<sup>[35]</sup> but not, for example, with white phosphorus.<sup>[36]</sup>



**Scheme 1.** Known reactivity of bis(terphenyl)stannylenes.

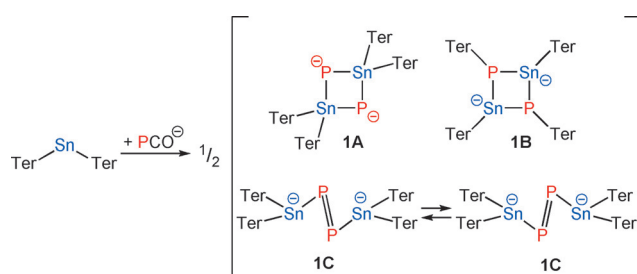
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Herein, we report on the reactivity of  $\text{PCO}^-$  and  $\text{AsCO}^-$  towards  $\text{Ter}_2\text{Sn}$  and demonstrate the thermally or photolytically induced decarbonylation of  $\text{AsCO}^-$ , which thereby acts as a source of  $\text{As}^-$  towards a molecular species.

The addition of one equivalent of  $[\text{Na}(\text{dioxane})_x]\text{PCO}$  ( $x = 2.5\text{--}2.8$ ) to  $\text{Ter}_2\text{Sn}$  afforded a purple solution, which is not visibly distinguishable from solutions of  $\text{Ter}_2\text{Sn}$ . Similarly, the  $^{31}\text{P}$  and  $^{119}\text{Sn}$  NMR spectra of such reaction mixtures revealed only the presence of the starting materials ( $\text{PCO}^-$ ,  $\text{Ter}_2\text{Sn}$ ).<sup>[37]</sup> Heating the sample for 3 days at  $80^\circ\text{C}$  or photolysis of the reaction mixture for several hours induced a very slow reaction, giving rise to a new species, which could be identified by its  $^{31}\text{P}$  ( $-320.5$  ppm,  $^1J_{\text{P-Sn}} = 857$  Hz,<sup>[38]</sup> integral ratio 1:4:1; see the Supporting Information, Figure S1) and  $^{119}\text{Sn}$  NMR resonances ( $+124$  ppm, t,  $^1J_{\text{P-Sn}} = 855$  Hz; Figure S2). This NMR pattern is consistent with the formation of a  $\text{Sn}_2\text{P}_2$  heterocycle (**1**, Scheme 2). However, repeated

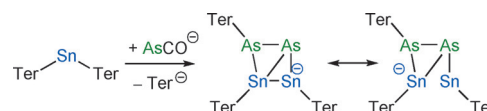


**Scheme 2.** Reaction of  $\text{PCO}^-$  with  $\text{Ter}_2\text{Sn}$ .

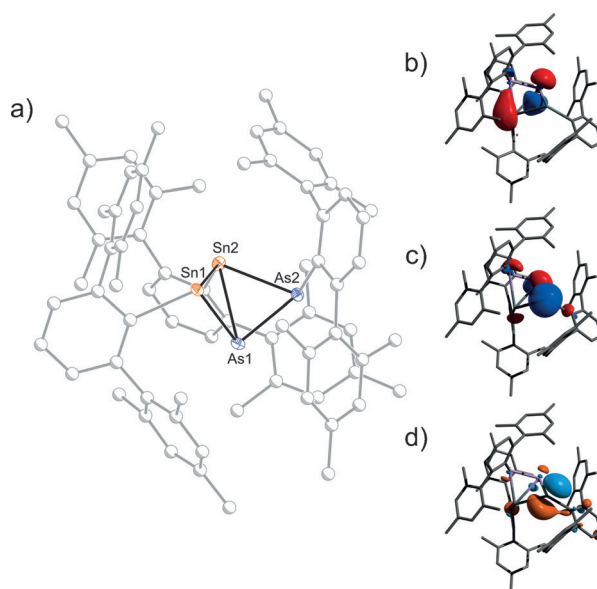
attempts to isolate this compound failed as it could never be enriched to more than 10% according to the integral ratio in the  $^{31}\text{P}$  NMR spectra. The computed  $^{31}\text{P}$  and  $^{119}\text{Sn}$  NMR shifts are in good agreement with the formation of **1**.<sup>[39]</sup> These computations indicated that **1C** is favored over **1A** by  $47\text{ kJ mol}^{-1}$  while **1B** is not a minimum on the energy hypersurface owing to the steric clash of the terphenyl groups.<sup>[40]</sup>

In contrast to the reaction with  $\text{PCO}^-$ , the reaction of  $\text{Ter}_2\text{Sn}$  with  $\text{AsCO}^-$  proceeds more readily, albeit still very slowly. A solution of  $\text{Ter}_2\text{Sn}$  in THF was treated with an equimolar amount of  $[\text{Na}(\text{18-crown-6})]\text{AsCO}$ . After 2 weeks of stirring at room temperature, the initially purple solution turned dark yellow–green. This solution was filtered, and *n*-hexane was allowed to slowly diffuse into it, causing a black oil to deposit. The supernatant was discarded, and extraction of the oil with toluene (tol) afforded a dark green solution, from which black crystals were obtained after standing overnight. Single-crystal X-ray diffraction studies revealed the constitution of the product,  $[\text{Na}(\text{18-crown-6})][\text{Ter}_3\text{Sn}_2\text{As}_2] \cdot 1.5\text{ tol}$  ( $[\text{Na}(\text{18-crown-6})]\mathbf{2} \cdot 1.5\text{ tol}$ , Scheme 3) which was isolated in 31% yield.

The molecular structure of **2** (Figure 2) features a Sn–Sn contact of  $3.0396(2)$  Å, which is well within the range of known Sn–Sn single bonds ( $\Sigma r_{\text{cov}} = 2.80$ ;<sup>[41]</sup> found bond lengths from  $2.7685(2)$  to  $3.5496(9)$  Å),<sup>[42–46]</sup> but an NBO analysis indicated the absence of a covalent Sn–Sn bond.<sup>[47]</sup> The short Sn–Sn distance nevertheless indicates that there is



**Scheme 3.** Formation of  $[\text{Na}(\text{18-crown-6})][\text{Ter}_3\text{Sn}_2\text{As}_2]$  ( $[\text{Na}(\text{18-crown-6})]\mathbf{2}$ ).

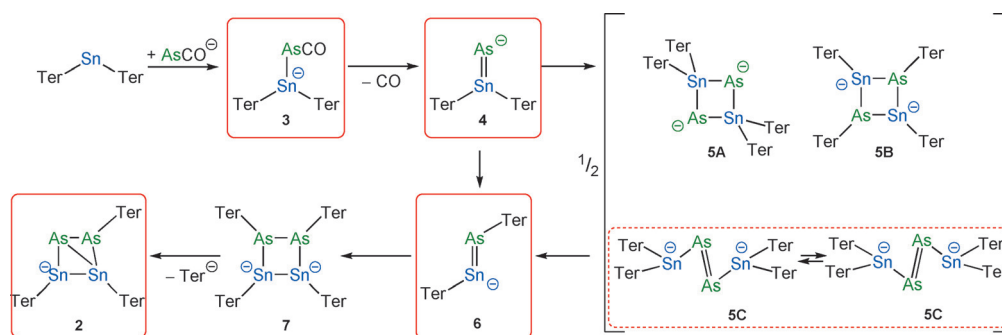


**Figure 2.** a) Molecular structure of **2**. b–d) Selected molecular orbitals of **2**: HOMO–1 (b), HOMO (c), LUMO (d).  $[\text{Na}(\text{18-crown-6})]^+$  and the solvent of crystallization omitted for clarity. Thermal ellipsoids set at 50% probability.

clearly an interaction between Sn1 and Sn2. According to NBO computations, there is donation from both the transannular Sn–As bond and the lone pair of Sn2 into an empty p-type orbital on Sn1 (Figure 2b–d). The overall charge on the  $\text{Sn}_2\text{As}_2$  fragment is positive (Sn1  $+0.607$ , Sn2  $+0.516$ , As1  $-0.545$ , As2  $-0.04$  e), even though **2** is an anionic species.

The bent  $\text{Sn}_2\text{As}_2$  heterocycle also features an elongated Sn2–As1 bond ( $2.8070(2)$ , cf.  $\Sigma r_{\text{cov}} = 2.61$  Å). In contrast, the other Sn–As and As–As bond lengths compare well with the expected values for covalent single bonds (Sn1–As1  $2.6204(2)$ , Sn2–As2  $2.6755(2)$ , As1–As2  $2.4140(2)$  Å). The green color of  $[\text{Na}(\text{18-crown-6})]\mathbf{2}$  can be rationalized by two transitions with maxima at 435 and 630 nm from Sn–As  $\sigma$ -bonding orbitals into an empty orbital of predominantly  $\pi$  character at Sn1 (Figure 2, computed HOMO–1  $\rightarrow$  LUMO 476; HOMO  $\rightarrow$  LUMO 625 nm). Two distinct resonances are observed in the  $^{119}\text{Sn}$  NMR spectrum of  $[\text{Na}(\text{18-crown-6})]\mathbf{2}$  at  $+1380$  for Sn1 and  $-1048$  ppm for Sn2, respectively, which are in good agreement with the computed values ( $+1287$ ,  $-1151$  ppm). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra show three distinct sets of signals for the Ter substituents, for example, three downfield-shifted singlet resonances for the *ipso*-carbon atoms (167.87, 177.67, 183.29 ppm).

The unexpected formation of  $[\text{Na}(\text{18-crown-6})]\mathbf{2}$  inspired a thorough computational analysis of the reaction of  $\text{AsCO}^-$  with  $\text{Ter}_2\text{Sn}$ . We postulate that the initial step in these reactions is the association of  $\text{AsCO}^-$  with  $\text{Ter}_2\text{Sn}$  to form an anionic Lewis acid–base adduct  $[\text{Ter}_2\text{SnAsCO}]^-$  (**3**). The



**Scheme 4.** Full reaction scheme (formally, all of the reactions can be equilibria). Experimental evidence available for the highlighted species.

decarbonylation reaction of **3** to give **4** (Scheme 4) was computed to be endothermic by  $124 \text{ kJ mol}^{-1}$ , indicating that the driving force for this first step must be due to the entropy gain associated with the loss of carbon monoxide. Two possible pathways were considered for the subsequent reaction of **4**; it could either dimerize to give **5** or rearrange to form **6**. In case of the dimerization, the four-membered heterocycle **5A** is formed initially, which can then undergo two successive substituent shifts to afford **5B**. If a formal monomer–dimer equilibrium exists, dimer **5B** is in equilibrium with its monomer **6**, which could also be formed directly from **4**. However, species **5B** is not a minimum on the potential energy hypersurface owing to steric clashes between the terphenyl substituents. The isomeric species **5C** is more favorable than **5A** by  $101 \text{ kJ mol}^{-1}$ . The formation of **5C** was also corroborated by the predicted  $^{119}\text{Sn}$  NMR shift of  $-54 \text{ ppm}$ , which is in much better agreement with the observed value of  $+127 \text{ ppm}$  than the value of  $-399 \text{ ppm}$  calculated for **5A**. The activation barrier for the substituent shift of **4** to **6** is  $70 \text{ kJ mol}^{-1}$ , and the reaction is exothermic by  $168 \text{ kJ mol}^{-1}$ . This means that the reverse reaction requires an activation energy of  $238 \text{ kJ mol}^{-1}$  and is thus not expected to take place. Head-to-head dimerization of **6** affords **7**, which can then formally eliminate a  $\text{Ter}^-$  substituent to afford the observed monoanionic product **2**.

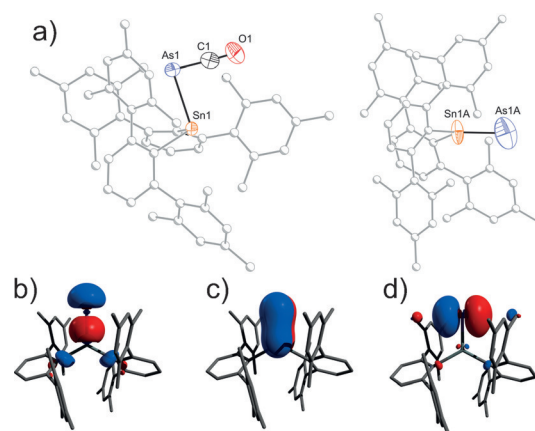
With these computational data in mind, we envisaged the synthesis of intermediates, namely the association product of  $\text{Ter}_2\text{Sn}$  and  $\text{AsCO}^-$  (**3**) and the double-bonded species **4** (as pictured in Scheme 5) as well as its isomer **6**.



**Scheme 5.** Synthesis of  $[\text{Na}(18\text{-crown-6})][\text{Ter}_2\text{SnAsCO}]$  ( $[\text{Na}(18\text{-crown-6})(\text{THF})_2]\mathbf{3}$ ) and  $[\text{Na}(18\text{-crown-6})][\text{Ter}_2\text{SnAs}]$  ( $[\text{Na}(18\text{-crown-6})]\mathbf{4}$ ).

Upon combination of equimolar amounts of  $\text{Ter}_2\text{Sn}$  and  $[\text{Na}(18\text{-crown-6})]\text{AsCO}$  in THF, the solution retained its purple color, still indicating the presence of  $\text{Ter}_2\text{Sn}$ . In contrast, with a stoichiometric excess of  $\text{AsCO}^-$ , the solution turned pale yellow. At ambient temperature, repeated

attempts of crystallizing the yellow species failed, and only crystals of  $\text{Ter}_2\text{Sn}$  and  $[\text{Na}(18\text{-crown-6})]\text{AsCO}$  could be obtained; however, from a THF solution at  $-40^\circ\text{C}$ , yellow crystals of a novel product mixture could be obtained. These crystals were found to be unstable at ambient temperature and decomposed to give



**Figure 3.** a) Molecular structures of **3** (left) and **4** (right). b–d) Selected molecular orbitals of **4**: HOMO–2 (b), HOMO–1 (c), and HOMO (d).  $[\text{Na}(18\text{-crown-6})(\text{THF})_2]^+$  omitted for clarity. Thermal ellipsoids set at 50% probability.

a purple powder (presumably  $\text{Ter}_2\text{Sn}$ ). The crystals contained two co-crystallized compounds (Figure 3), the anionic components of which occupy the same site in the asymmetric unit. They were identified as the association product  $[\text{Na}(18\text{-crown-6})(\text{THF})_2][\text{Ter}_2\text{SnAsCO}]$  ( $[\text{Na}(18\text{-crown-6})(\text{THF})_2]\mathbf{3}$ ) and the anionic arsinidene  $[\text{Na}(18\text{-crown-6})(\text{THF})_2][\text{Ter}_2\text{SnAs}]$  ( $[\text{Na}(18\text{-crown-6})(\text{THF})_2]\mathbf{4}$ ). The molecular structure of **3** shows a  $\text{Sn}-\text{As}$  bond length of  $2.7863(5) \text{ \AA}$  (calc.  $2.811 \text{ \AA}$ ). The  $\text{Sn}-\text{AsCO}$  moiety features the expected bent structure for an arsanone ( $\text{Sn}-\text{As}-\text{C}$   $86.55(15)^\circ$ ,  $\text{As}-\text{C}-\text{O}$   $177.8(4)^\circ$ ) and bond lengths consistent with double bonds ( $\text{As}=\text{C}$   $1.724(5)$ ,  $\text{C}=\text{O}$   $1.170(6) \text{ \AA}$ ). The molecular structure of the minor component **4** shows a  $\text{Sn}-\text{As}$  distance of  $2.425(17) \text{ \AA}$ , which is in reasonable agreement with the value computed for an isolated anion of  $2.375 \text{ \AA}$ . Compound **4** is isoelectronic with a family of  $\text{R}_2\text{Sn}=\text{X}$  ( $\text{X}=\text{S}, \text{Se}, \text{Te}$ ) compounds previously reported in the literature.<sup>[48–50]</sup> The ratio of both compounds was found to vary with subsequent data collections on the same crystal so that we assume that photolytic decarbonylation is caused by X-ray irradiation; however, because of the crystal decomposition, no complete decarbonylation could be achieved in the X-ray beam. Photolysis of the association product  $[\text{Na}(18\text{-crown-6})(\text{THF})_2]\mathbf{3}$  by UV irradiation of the mounted crystal on the goniometer for one hour led to an increase in the relative

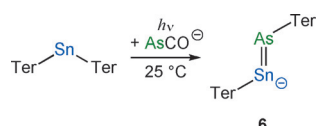


amount of the arsinidene component (39%), but crystal decomposition caused the data sets to become of increasingly poor quality.

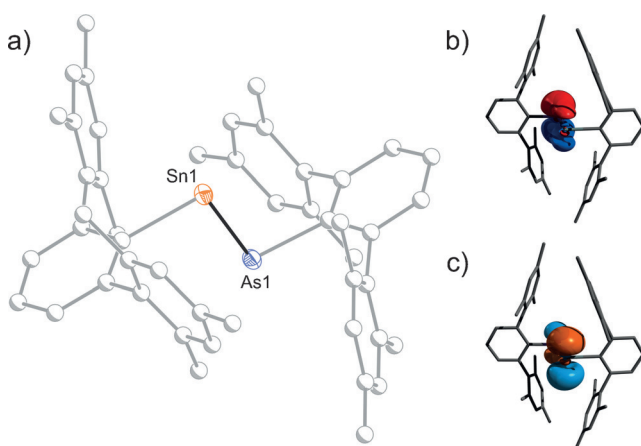
The association of  $\text{AsCO}^-$  to  $\text{Ter}_2\text{Sn}$ , which results in the formation of **3**, could also be observed in the  $^{119}\text{Sn}$  (243 K,  $[\text{D}_8]\text{THF}$ : +55 ppm ( $\nu_{1/2}$  = 70 Hz); 193 K,  $[\text{D}_8]\text{THF}$ : +38 ppm ( $\nu_{1/2}$  = 56 Hz); calc. +114 ppm) and  $^{13}\text{C}$  NMR spectra (see Figure S10; 193 K,  $[\text{D}_8]\text{THF}$ : 170.46, 179.09, 192.13 ppm; calc. coplanar Ter *ipso*-C 181.7, orthogonal Ter *ipso*-C 174.6, AsCO 205.0 ppm) recorded at low temperature. After photolysis of the reaction mixture at  $-78^\circ\text{C}$  (Scheme 5), the formation of a new species was observed, giving rise to a singlet at +254 ppm in the  $^{119}\text{Sn}$  NMR spectrum (243 K,  $[\text{D}_8]\text{THF}$ ), which is in good agreement with the computed value for a contact ion pair of  $[\text{Na}(18\text{-crown-6})]\mathbf{4}$  of +300 ppm (vs. +84 ppm for the isolated anion). Upon warming to  $0^\circ\text{C}$ , this resonance disappeared, and two new signals were observed at +127 and +1510 ppm (+122 and +1499 ppm at 193 K, see Figure S14). The resonance at +127 ppm is in the same range as the resonance for the putative compound **1** in the reaction of  $\text{Ter}_2\text{Sn}$  with  $\text{PCO}^-$  (Scheme 2), hence it was assumed that this is the heavier homologue intermediate (**5C**).

In a second series of experiments targeting the intermediate  $[\text{Na}(18\text{-crown-6})][\text{TerSnAsTer}]$  ( $[\text{Na}(18\text{-crown-6})]\mathbf{6}$ ), equimolar amounts of  $\text{Ter}_2\text{Sn}$  and  $[\text{Na}(18\text{-crown-6})]\text{AsCO}$  were dissolved in THF and photolyzed at ambient temperature for one hour (Scheme 6). This afforded red solutions from which a dark oil was obtained after layering with hexane. Crystallization from toluene or THF/hexane afforded dark orange crystals of  $[\text{Na}(18\text{-crown-6})]\mathbf{6}$  (Figure 4) in 7% yield.

Structural analysis of the  $[\text{Na}(18\text{-crown-6})]\mathbf{6}$  crystals grown from THF/hexane revealed a Sn–As bond length of



**Scheme 6.** Synthesis of  $[\text{Na}(18\text{-crown-6})][\text{TerSnAsTer}]$  ( $[\text{Na}(18\text{-crown-6})]\mathbf{6}$ ).



**Figure 4.** a) Molecular structure of **6**. b, c) Frontier orbitals of **6**: HOMO (b), LUMO (c).  $[\text{Na}(18\text{-crown-6})]^+$  omitted for clarity. Thermal ellipsoids set at 50% probability.

2.535(5) Å. In crystals grown from toluene, disorder occurred in two crystallographically independent molecules. The Sn–As distances were determined to be 2.510(3) and 2.535(2) Å, respectively. These values are in good agreement with the computed double bond length of 2.516 Å, which is considerably longer than the formal double bond in **4**.

The red color of  $[\text{Na}(18\text{-crown-6})]\mathbf{6}$  was attributed to a  $\pi \rightarrow \pi^*$  transition on the Sn–As double bond with a maximum at 540 nm (calc. 486 nm). The  $^{119}\text{Sn}$  NMR resonance of  $[\text{Na}(18\text{-crown-6})]\mathbf{6}$  was found at +1510 ppm (calc. +1416 ppm). The molecular structure of **6** shows slightly different Sn–As–C and As–Sn–C angles, ranging from  $95.2(2)^\circ$  to  $96.8(2)^\circ$  for the former and from  $93.58(12)^\circ$  to  $99.10(9)^\circ$  for the latter. These values are in accord with angles found in bulky diarsenes ( $92.10(14)^\circ$ – $101.02(16)^\circ$ )<sup>[51–55]</sup> and distannynes ( $93.6(4)^\circ$ – $125.24(7)^\circ$ ).<sup>[55–60]</sup>

In conclusion, we have demonstrated the reactivity of a bulky stannylene towards the heavy isocyanate analogues  $\text{PCO}^-$  and  $\text{AsCO}^-$ . Owing to the softness of the tin center, this is a rare instance of a reaction where  $\text{AsCO}^-$  reacts faster than  $\text{PCO}^-$  even though it is less polar. Several intermediates on the path towards the final product  $[\text{Na}(18\text{-crown-6})][\text{Ter}_2\text{Sn}_2\text{As}_2]$  ( $[\text{Na}(18\text{-crown-6})]\mathbf{2}$ ) could be characterized. The initial association product  $[\text{Na}(18\text{-crown-6})][\text{Ter}_2\text{SnAsCO}]$  ( $[\text{Na}(18\text{-crown-6})]\mathbf{3}$ ) could be isolated and is not stable under ambient conditions. As a transient species, the anionic arsinidene  $[\text{Na}(18\text{-crown-6})][\text{Ter}_2\text{SnAs}]$  ( $[\text{Na}(18\text{-crown-6})]\mathbf{4}$ ) could be observed in solution and in the solid state. Finally, the metastable compound  $[\text{Na}(18\text{-crown-6})][\text{TerSnAsTer}]$  could be isolated, as an unprecedented example of a compound featuring mixed multiple bonds between heavy main-group elements.

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Dr. Christian P. Sindlinger is acknowledged for valuable discussions on  $^{119}\text{Sn}$  NMR shifts and their prediction. We thank the EPSRC (EP/M027732/1) for financial support, the University of Oxford for access to Advanced Research Computing and Chemical Crystallography facilities, and Elemental Microanalysis Ltd. (Devon) for elemental analyses.

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