

Synthesis and Redox Behaviour of the Chalcogenocarbonyl Dianions $[(E)C(PPh_2S)_2]^{2-}$: Formation and Structures of Chalcogen–Chalcogen Bonded Dimers and a Novel Selone**

Jari Konu,^[a] Tristram Chivers,*^[a] and Heikki M. Tuononen^[b]

Abstract: The lithium salts of the chalcogenocarbonyl dianions $[(E)C(PPh_2S)_2]^{2-}$ ($E=S$ (**4b**), Se (**4c**)) were produced through the reactions between $Li_2[C(PPh_2S)_2]$ and elemental chalcogens in the presence of tetramethylethylenediamine (TMEDA). The solid-state structure of $\{[Li(TMEDA)]_2[(Se)C(PPh_2S)_2]\}—\{[Li(TMEDA)]_2[4c]\}$ —was shown to be bicyclic with the Li^+ cations bis-S,Se-chelated by the dianionic ligand. One-electron oxidation of the dianions **4b** and **4c** with iodine afforded the diamagnetic complexes $\{[Li(TMEDA)]_2-[(SPh_2P)_2CEEC(PPh_2S)_2]\}$ ($[Li-$

$(TMEDA)]_2[7b]$ ($E=S$), $[Li(TMEDA)]_2[7c]$ ($E=Se$)), which are formally dimers of the radical anions $[(E)C(PPh_2S)_2]^{\cdot-}$ ($E=S$ (**5b**), Se (**5c**)) with elongated central E–E bonds. Two-electron oxidation of the selenium-containing dianion **4c** with I_2 yielded the LiI adduct of a neutral selone $\{[Li(TMEDA)]_2[I(Se)C(PPh_2S)_2]\}—\{[LiI(TMEDA)]_2[6c]\}$ —whereas the analogous reaction with **4b** resulted in the

formation of **7b** followed by protonation to give $\{[Li(TMEDA)]_2-[(SPh_2P)_2CSS(H)C(PPh_2S)_2]\}—[Li(TMEDA)]_2[8b]$. Attempts to identify the transient radicals **5b** and **5c** by EPR spectroscopy in conjunction with DFT calculations of the electronic structures of these paramagnetic species and their dimers are also described. The crystal structures of $\{[Li(TMEDA)]_2[4c]\}$, $\{[Li(TMEDA)]_2[6c] \cdot C_7H_8\}$, $[Li(TMEDA)]_2[7b] \cdot (CH_2Cl_2)_{0.33}$, $[Li(THF)]_2[7b]$, $[Li(TMEDA)]_2[7c]$, $[Li(TMEDA)]_2[8b] \cdot (CH_2Cl_2)_2$ and $[Li([12]-crown-4)_2][8b]$ were determined and salient structural features are discussed.

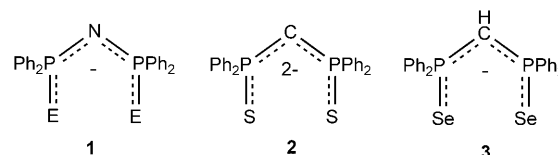
Keywords: chalcogens • electronic structure • oxidation • radicals • tridentate ligands

Introduction

In contrast to the extensively studied N-bridged, monoanionic ligands $[N(PPh_2E)_2]^-$ (**1**, $E=S, Se$), which predominantly form E,E-chelated metal complexes without the participation of the N atom,^[1,2] the isoelectronic C-bridged dianion $[C(PPh_2S)_2]^{2-}$ (**2**) exhibits strong metal–carbon interactions in a variety of coordination complexes. The first example, a binuclear Pt^{II} complex of **2**, involved bis-C,S-chelation and a quaternary carbon bridging the two metal centres.^[3] The recent development of a synthesis of the dilithium de-

rivative of **2** by Le Floch and co-workers opened the way for wide-ranging investigations of this intriguing dithio PCP-bridged ligand.^[4,5] A variety of complexes with main group^[6] and with early^[7] and late transition metals,^[4,8] as well as lanthanides^[9] and actinides,^[10] were subsequently prepared by metathesis of $Li_2\mathbf{2}$ with metal halides and structurally characterised. The recurring theme in these complexes is the prevalence of strong interactions of the metal with the carbene centre of the ligand **2** (S,C,S-chelation).

Unusual carbon-centred reactivity is also observed in the



redox behaviour of compounds **2**. In contrast with the formation of chalcogen–chalcogen bonds upon oxidation of N-bridged ligands of type **1**,^[11] treatment of $Li_2\mathbf{2}$ with the mild oxidising agents C_2Cl_6 or I_2 produces remarkably stable monomeric or dimeric carbenoids, respectively.^[12,13] The nu-

[a] Dr. J. Konu, Prof. T. Chivers
Department of Chemistry, University of Calgary
Calgary, AB T2N 1N4 (Canada)
Fax: (+1) 403-289-9488
E-mail: chivers@ucalgary.ca

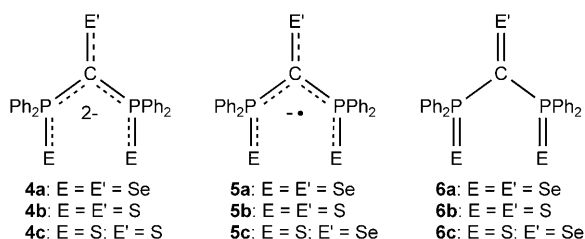
[b] Dr. H. M. Tuononen
Department of Chemistry, University of Jyväskylä
P.O. Box 35, Jyväskylä, 40014 (Finland)

[**] $E=S, Se$

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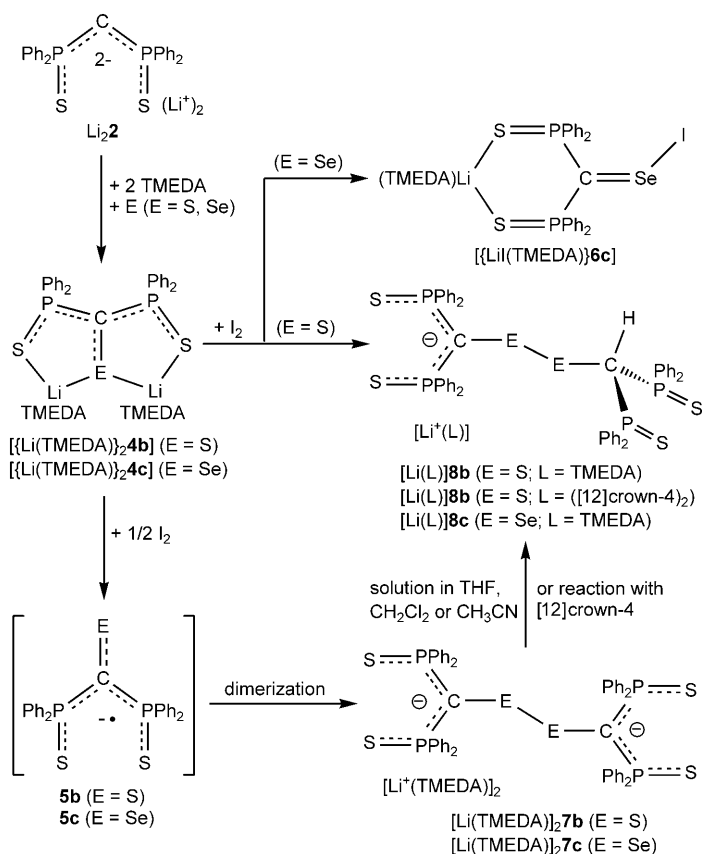
cleophilic reactivity of **2** is also illustrated by the reaction with CS₂ to give the 1,1-ethylenedithiolate [S₂C=C(PPh₂S)₂]²⁻.^[4b]

The diseleno C-bridged monoanion [HC(PPh₂Se)₂]⁻ (**3**), isoelectronic with **1** (E=Se), was first prepared from the neutral ligand [H₂C(PPh₂Se)₂] and *n*BuLi and used as an in situ metathetical reagent for the preparation of homoleptic M^{II} (M=Fe, Co, Ni) complexes.^[14] Competition between the deprotonation process and cleavage of P=Se bonds by RLi reagents makes this synthesis of **3** inefficient, and also preempts the production of the Se analogue of the dianion **2**.^[15] Consequently, we developed an alternative, high-yielding synthesis of Li³ in which the P–Se bonds are installed after the deprotonation step and we showed that this reagent can be used to prepare homoleptic Zn^{II} and Hg^{II} complexes of **3**.^[16] Interestingly, the reactions of MCl₂ (M=Sn, Te) with Li³ in a 1:2 molar ratio produce homoleptic M(IV) complexes of the triseleno dianion [(Se)C(PPh₂Se)₂]²⁻ (**4a**) through a redox process that formally involves selenium–proton exchange.^[17] A dinuclear Hg^{II} complex of **4a** is formed on mild heating of Hg(**3**)₂.^[17] Very recently, homoleptic Pb^{II} complexes of the related trichalcogeno dianions **4b** and **4c** were obtained by chalcogen insertion into the Pb–C bonds of dimeric, homoleptic Pb^{II} complexes of **2**.^[6a]



The first examples of metal complexes of ligands of type **4** exhibit notably different structural features, suggesting a rich coordination chemistry.^[6a,17,18] With this in mind, we sought to develop an efficient synthesis of alkali metal derivatives of these novel tridentate ligands that could be used as metathetical reagents. Concomitantly, we considered that investigations of the redox behaviour of these dianions would represent a worthwhile endeavour in view of the possible generation of chalcogenocarbonyl radical anions of the type **5** or the corresponding neutral chalcogenocarbonyls **6** upon oxidation. In this context it is pertinent to note that Le Floch et al. have recently described the isolation of deep purple alkali metal salts of the radical anion [Ph₂C=C(PPh₂S)₂]^{•-} in which the electron-accepting phosphine sulfide substituents exert a stabilising influence on the alkene radical.^[19] Thioketyl radical anions [R₂C=S]^{•-} (e.g., R = *t*Bu, Me) have been characterised in solution by EPR spectroscopy, but salts of these anions have not been isolated.^[20] The effect of the PPh₂S substituents on the stabilities of these radical anions of type **5** was therefore of interest.

In this contribution we report the synthesis of dilithium derivatives of the dianions **4b** and **4c** and the X-ray structure of [Li(TMEDA)]₂**4c** (TMEDA = tetramethylethylenediamine). Investigations of the oxidation of **4b** and **4c** with iodine revealed the formation of **7b** and **7c** (Scheme 1),



Scheme 1. Synthesis and oxidation of the chalcogenocarbonyl dianions **4b** and **4c**.

which are formally dimers of the corresponding anion radicals **5b** and **5c**, respectively, upon one-electron oxidation. The X-ray structures of [Li(L)]₂**7b** (L=TMEDA, (THF)₂) and [Li(TMEDA)]₂**7c** have been determined and the possible dissociation of these dimers into the paramagnetic species **5b** and **5c** has been investigated by EPR spectroscopy. Interestingly, the two-electron oxidation of **4c** with I₂ produces the unusual selone **6c**^[21] as a LiI adduct, whereas the attempted two-electron oxidation of **4b** with I₂ generates the protonated monoanion **8b**; X-ray structures of [Li(L)]**8b** (L=TMEDA, ([12]crown-4)₂) were elucidated. The experimental work is supported by DFT calculations that provide insights into the molecular and electronic structures of the radical anions **5b** and **5c** and of the corresponding dimers **7b** and **7c**, as well as confirmation of the molecular structure of the protonated species **8b**.

Results and Discussion

Synthesis and characterisation of $[\text{Li}(\text{TMEDA})]_2(\text{E})\text{C}(\text{PPh}_2\text{S})_2$ ($[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ ($\text{E}=\text{S}$), $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ ($\text{E}=\text{Se}$)). Because the diseleno PCP-bridged dianion $[\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$ is not accessible (see above), the starting point for the synthesis of tridentate ligands of the type **4** was the known reagent $\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2]$, which is prepared by treatment of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ with two equivalents of MeLi .^[4] Successive addition of two equivalents of TMEDA at 23 °C and then one equivalent of the elemental chalcogen either at –80 °C (S) or at 0 °C (Se) produced dilithium salts of the trichalcogeno dianions, $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ (Scheme 1), as analytically pure, orange-red or red solids in excellent yields (86 and 91 %, respectively). Both compounds exhibit significant air and/or moisture sensitivity even in the solid state, with exposure to ambient conditions resulting in a rapid loss of the red colour.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ in $[\text{D}_8]\text{THF}$ showed the typical patterns for TMEDA and phenyl groups (in the expected intensity ratio); in the latter spectra signals attributable to the PCP carbon were observed at $\delta=141.1$ and 141.2 ppm, respectively. The ^7Li and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibited singlets at $\delta=1.67$ and 44.0 ppm, respectively, for $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ and at $\delta=2.05$ and 43.5 ppm for $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$. In addition, a singlet at $\delta=-4.5$ ppm for the carbon-bound selenium was evident in the ^{77}Se NMR spectrum of $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$, representing a downfield shift of about 300 ppm in relation to that of the CSe resonance observed for the homoleptic Te^{IV} complex $[\text{Te}(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]$ [$\text{Te}(\mathbf{4a})_2$].^[17,22] Taken together, the NMR spectroscopic data are consistent with the formation of the dianions **4b** and **4c**, each incorporating two TMEDA-chelated Li^+ cations symmetrically coordinated to the dianion.

As depicted in Figure 1 a, the solid-state structure of $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ corroborates the formation of a monomeric complex in which the lithium cations are S,Se-chelated by the dianion $[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]^{2-}$, thus resulting in a bicyclic $\text{LiSP}(\text{Se})\text{CPSLi}$ core with the two five-membered rings connected by a common C–Se bond. The P–C and P–S bond

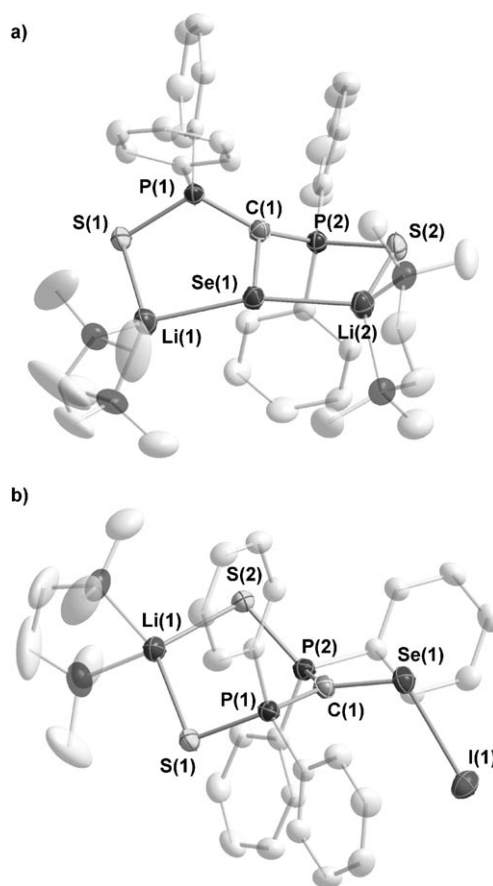


Figure 1. Molecular structures of a) $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$, and b) $[\text{LiI}(\text{TMEDA})]\mathbf{6c}$, with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms and solvate molecules (in $[\text{LiI}(\text{TMEDA})]\mathbf{6c}$) have been omitted for clarity.

lengths of about 1.72 and 2.02 Å, respectively, in $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ (Table 1) are about 0.02 Å shorter, and the C–Se distance of 1.970(3) Å is about 0.05 Å longer, than the corresponding bonds in the lead(II) complex $\text{Pb}\mathbf{4c}$.^[6a] A similar disparity is evident between the P–C and C–Se bond lengths in $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ and those of about 1.73–1.76 and 1.89–1.94 Å, respectively, found in the group 12, 14 and

Table 1. Selected interatomic distances [Å] and angles [°] for $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ and $[\text{LiI}(\text{TMEDA})]\mathbf{6c}$ (calculated values in square brackets).

	$[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$	$[\text{LiI}(\text{TMEDA})]\mathbf{6c}$		$[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$	$[\text{LiI}(\text{TMEDA})]\mathbf{6c}$
C(1)–Se(1)	1.970(3) [1.963]	1.815(4) [1.821]	Li(1)–S(1)	2.416(6) [2.406]	2.416(7) [2.399]
C(1)–P(1)	1.712(3) [1.732]	1.776(4) [1.788]	Li(1)–S(2)	2.390(5) ^[a] [2.373]	2.487(7) [2.399]
C(1)–P(2)	1.716(3) [1.736]	1.782(4) [1.789]	Li(1)–Se(1)	2.551(5) [2.517]	–
P(1)–S(1)	2.020(1) [2.051]	1.989(2) [2.015]	Li(2)–Se(1)	2.500(5) [2.500]	–
P(2)–S(2)	2.011(1) [2.038]	2.005(2) [2.022]	Se(1)–I(1)	–	2.7218(7) [2.705]
P(1)–C(1)–P(2)	135.1(2) [133.3]	122.0(2) [121.6]	C(1)–Se(1)–I(1)	–	109.3(1) [109.4]
P(1)–C(1)–Se(1)	110.2(2) [110.3]	118.2(2) [117.2]	S(1)–Li(1)–S(2)	–	108.7(3) [108.7]
P(2)–C(1)–Se(1)	109.5(2) [112.2]	119.9(2) [121.2]	C(1)–Se(1)–Li(1)	97.4(2) [97.8]	–
C(1)–P(1)–S(1)	118.1(1) [117.9]	115.4(1) [115.6]	C(1)–Se(1)–Li(2)	94.0(4) [96.2]	–
C(1)–P(2)–S(2)	114.8(1) [114.4]	114.4(2) [115.6]	S(1)–Li(1)–Se(1)	98.6(2) [99.9]	–
P(1)–S(1)–Li(1)	93.2(1) [93.2]	100.9(2) [104.9]	S(2)–Li(2)–Se(1)	100.2(2) [99.9]	–
P(2)–S(2)–Li(2)	93.5(1) [96.0]	99.2(2) [102.0]	Li(1)–Se(1)–Li(2)	164.4(2) [159.4]	–

[a] Li(1)=Li(2).

16 complexes of the triseleno ligand **4a**, $\{M_n[(Se)C(PPh_2Se)_2]_2\}$ ($n=1$, $M=Sn$ [**Sn(4a)**]₂, Te [**Te(4a)**]₂; $n=2$, $M=Hg$ [**Hg₂(4a)**]₂), the closest values belonging to the dimeric Hg^{II} complex in which the carbon-bound selenium is also three-coordinate.^[17] The PCP carbon in $\{[Li(TMEDA)]_2\mathbf{4c}\}$ exhibits a slight distortion from planarity with $\Sigma\chi C=354.8^\circ$, which is comparable to that in the mercury complex $Hg_2(\mathbf{4a})_2$ (about 353°), whereas in the **Pb4c**, **Sn(4a)**₂ and **Te(4a)**₂ complexes the corresponding deviation from planarity is more pronounced ($\Sigma\chi C\approx 340^\circ$).

One-electron oxidation of 4b and 4c: crystal structures and NMR spectroscopic examination of $\{[Li(TMEDA)]_2[(SPh_2P)_2CEECPPh_2S]_2\}$ ($E=S$ [Li(TMEDA)**]₂**7b**, Se [**Li(TMEDA)**]₂**7c**):** Initial investigations of the oxidation of the dianions **4b** and **4c** were carried out with a view to the generation of the corresponding chalcogenocarbonyl radical anions **5b** and **5c** and assessment of their stabilities. One-electron oxidation was therefore attempted by the addition of one-half equivalent of iodine to solutions of $\{[Li(TMEDA)]_2\mathbf{4b}\}$ and $\{[Li(TMEDA)]_2\mathbf{4c}\}$, prepared in situ in toluene at $-80^\circ C$ (Scheme 1). After a few minutes, $[Li(TMEDA)]_2\mathbf{7b}$ and $[Li(TMEDA)]_2\mathbf{7c}$ were obtained as yellow and orange powders, respectively, and identified after recrystallisation by single-crystal X-ray structure determinations.

The crystal structures of $[Li(TMEDA)]_2\mathbf{7b}$ and $[Li(TMEDA)]_2\mathbf{7c}$ (Figure 2) revealed the formation of diamagnetic dianions, which are formally dimers of the radical anions $[(E)C(PPh_2S)_2]^{•-}$ ($E=S$ (**5b**), Se (**5c**)) joined by chalcogen–chalcogen ($E-E$) bonds ($E=S, Se$) at a crystallographic symmetry centre. The central S–S and Se–Se bond lengths of 2.222(2) and 2.508(1) Å (Table 2) in $[Li(TMEDA)]_2\mathbf{7b}$ and $[Li(TMEDA)]_2\mathbf{7c}$, respectively, are significantly longer than those of about 2.02–2.06 and 2.29–

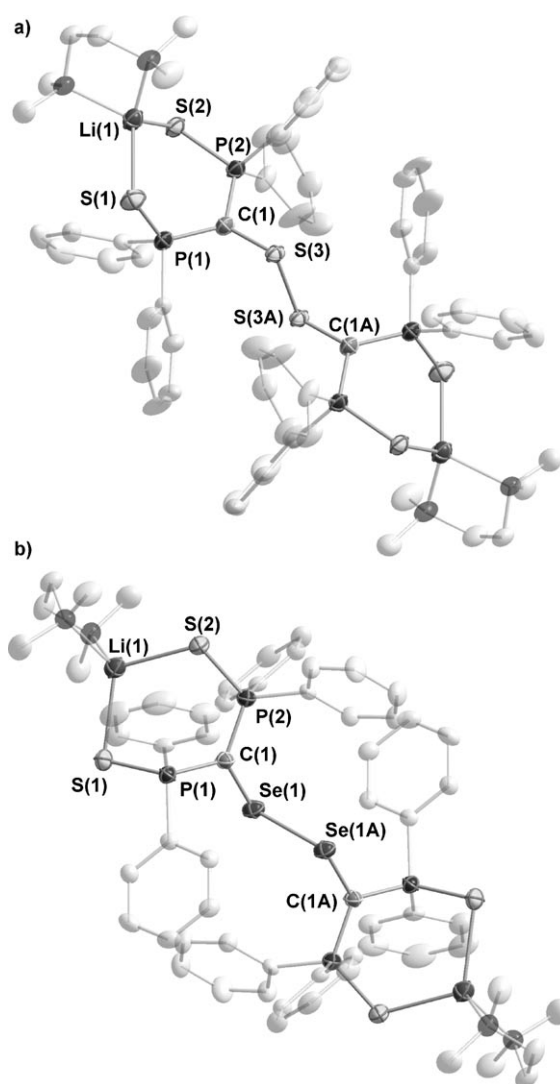


Figure 2. Crystal structures of a) $[Li(TMEDA)]_2\mathbf{7b}$, and b) $[Li(TMEDA)]_2\mathbf{7c}$, with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms and solvate molecules (in $[Li(TMEDA)]_2\mathbf{7b}$) have been omitted for clarity. Only the higher-occupancy portion of the disordered sections is shown. Symmetry operation (A): $1-x, -y, -z$.

Table 2. Selected interatomic distances [Å] and angles [$^\circ$] for $[Li(TMEDA)]_2\mathbf{7b}$, $[Li(THF)]_2\mathbf{7b}$ and $[Li(TMEDA)]_2\mathbf{7c}$ (calculated values in square brackets).

	$[Li(TMEDA)]_2\mathbf{7b}$	$[Li(THF)]_2\mathbf{7b}$	$[Li(TMEDA)]_2\mathbf{7c}$
S(3)–S(3A)	2.222(2) ^[a] [2.281]	2.213(2) ^[b]	2.508(1) ^[a,c] [2.524]
C(1)–S(3)	1.736(3) [1.735]	1.760(3)	1.885(3) ^[a,c] [1.877]
C(1)–P(1)	1.761(3) [1.778]	1.756(3)	1.746(3) [1.770]
C(1)–P(2)	1.753(3) [1.778]	1.753(3)	1.751(3) [1.770]
P(1)–S(1)	2.002(1) [2.034]	2.003(1)	2.003(1) [2.034]
P(2)–S(2)	1.999(2) [2.022]	1.991(1)	1.994(1) [2.022]
Li(1)–S(1)	2.390(6) [2.397]	2.441(7)	2.455(6) [2.399]
Li(1)–S(2)	2.404(6) [2.397]	2.467(7)	2.440(6) [2.397]
P(1)–C(1)–P(2)	119.1(2) [118.4]	119.1(2)	121.7(2) [119.4]
P(1)–C(1)–S(3)	119.0(2) [119.2]	115.9(2)	118.1(2) ^[a,c] [118.8]
P(2)–C(1)–S(3)	118.0(2) [119.0]	117.0(2)	117.2(2) ^[a,c] [118.3]
C(1)–P(1)–S(1)	118.1(1) [117.9]	117.8(1)	117.6(1) [118.1]
C(1)–P(2)–S(2)	115.8(1) [115.1]	114.7(1)	115.0(1) [115.1]
P(1)–S(1)–Li(1)	99.6(2) [98.8]	98.4(2)	95.6(2) [98.7]
P(2)–S(2)–Li(2)	106.2(2) [107.1]	104.4(2)	106.3(2) [107.4]
S(1)–Li(1)–S(2)	108.1(2) [108.6]	106.3(2)	110.3(2) [109.1]
C(1)–S(3)–S(3A)	107.1(1) ^[a] [108.6]	105.9(1) ^[b]	106.3(1) ^[a,c] [106.9]

Symmetry operation (A): [a] $1-x, -y, -z$, [b] $2-x, -y, 2-z$. [c] S(3) = Se(1), S(3A) = Se(1A).

2.35 Å observed in the diaryl dichalcogenides Ar_2E_2 ($E=S$, $Ar=C_6H_5$, C_6F_5 , $4-NO_2C_6H_4$, $2,4,6-iPr_3C_6H_2$; $E=Se$, $Ar=C_6H_5$, C_6F_5 , $4-NO_2C_6H_4$, $2,4,6-tBu_3C_6H_2$).^[23] The S–S distance in $[Li(TMEDA)]_2\mathbf{7b}$ is, however, comparable to the value of 2.177(13) Å reported for an analogous $P_2C-S-S-CP_2$ unit in the neutral dinuclear manganese(I) complex $[(CO)_4Mn\{(Ph_2P)_2CSSC(PPh_2)_2\}Mn(CO)_4]$.^[24] On the other hand, the Se–Se distance in $[Li(TMEDA)]_2\mathbf{7c}$ is about 0.19 Å longer than the corresponding distance in the dication $[(CO)_4Mn\{(Ph_2P)_2C(H)SeSe(H)C(PPh_2)_2\}Mn(CO)_4]^{2+}$.^[25] The P–C and P–S bond lengths in $[Li(TMEDA)]_2\mathbf{7b}$ and $[Li(TMEDA)]_2\mathbf{7c}$ are essentially identical at about 1.75 and 2.00 Å, respectively, although the mean Li–S contacts in the latter compound are about 0.05 Å longer. The Li–S contacts in $[Li(TMEDA)]_2\mathbf{7c}$ are, however, equal to those in the THF-coordinated derivative of **7b**, $[Li(THF)]_2\mathbf{7b}$, obtained

from the THF crystallisation of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$, revealing an unusual lability of the N,N' -chelated TMEDA ligand. The THF- and TMEDA-coordinated lithium complexes of the dianion $\mathbf{7b}$ are isostructural (Figure 2a). The P–C bond lengths in the selenium derivative $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ display an elongation of about 0.04 Å in relation to the precursor $\mathbf{4c}$, whereas the C–Se bond in the former is significantly shorter (by 0.09 Å). The PCP carbon atoms in the anions $\mathbf{7b}$ and $\mathbf{7c}$ exhibit only slight distortions from planarity ($\Sigma\angle\text{C}(1) \approx 356^\circ$, 352° and 357° in $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$, $[\text{Li}(\text{THF})]_2\mathbf{7b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$, respectively). As a consequence of the centre of symmetry, the CSSC fragments in $\mathbf{7b}$ and $\mathbf{7c}$ are planar with *trans* C atoms (compare with $[(\text{CO})_4\text{Mn}[(\text{Ph}_2\text{P})_2\text{CSSC}(\text{PPh}_2)_2]\text{Mn}(\text{CO})_4]^{[24]}$).

The ^7Li and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ in CD_2Cl_2 showed singlets at $\delta = 1.20$ and 50.2 ppm and at $\delta = 1.24$ and 50.5 ppm, respectively. In addition, the characteristic patterns for phenyl and TMEDA resonances were observed in the ^1H NMR spectra. However, the all-sulfur system $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ exhibited broad signals (half-width of 325 Hz for the ^7Li signal and 405 Hz for the ^{31}P signal) and after 30 min the singlet at $\delta = 50.2$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was replaced by two singlets in an approximately 1:1 ratio at $\delta = 48.8$ and 51.8 ppm; these were subsequently shown to arise from $\{[\text{Li}(\text{TMEDA})]-(\text{SPh}_2\text{P})_2\text{CSSC}(\text{H})\text{C}(\text{PPh}_2\text{S})_2\}$ ($[\text{Li}(\text{TMEDA})]_2\mathbf{8b}$; see below).^[26] After 12 h in solution (THF, CH_2Cl_2 or CH_3CN) at 23°C , both $\mathbf{7b}$ and $\mathbf{7c}$ had released their carbon-bound chalcogens to give $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ ($\mathbf{9}$) as the final product (^1H NMR: $\delta = 3.84$ ppm (t); $^{31}\text{P}\{^1\text{H}\}$ NMR at $\delta = 35.8$ ppm (s)).^[27]

Electronic structures of the dianions $[(\text{SPh}_2\text{P})_2\text{CEEC}(\text{PPh}_2\text{S})_2]^{2-}$ (E=S ($\mathbf{7b}$), Se ($\mathbf{7c}$)) and the radical anions $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^-$ (E=S ($\mathbf{5b}$), Se ($\mathbf{5c}$)): DFT-level electronic structure calculations were performed for the dimers $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ and for the paramagnetic monoanions $[\text{Li}(\text{TMEDA})]\mathbf{5b}$ and $[\text{Li}(\text{TMEDA})]\mathbf{5c}$. Pertinent optimised structural parameters are given in Table 2 and Table 3, respectively; there is an excellent agreement between the theoretical and the experimental results. Notably, there is almost no change in the interatomic distances and angles of the radicals $\mathbf{5b}$ and $\mathbf{5c}$ upon formation of the corresponding diamagnetic dimers $\mathbf{7b}$ and $\mathbf{7c}$.

An inspection of the frontier orbitals of $\mathbf{5b}$ and $\mathbf{5c}$ and of those of $\mathbf{7b}$ and $\mathbf{7c}$ reveals that the net chalcogen–chalcogen bonding interaction in the dianions is solely due to the (somewhat poor) overlap of the SOMOs of the monoanionic radicals, which are themselves composed of an antibonding combination of *p*-orbitals on the C=E bond (Figure 3). Consequently, the calculated binding energies of $\mathbf{7b}$ and $\mathbf{7c}$ (with respect to the monomers $\mathbf{5b}$ and $\mathbf{5c}$ in the geometry they adopt in the dimers) are particularly small: 72 and 90 kJ mol^{-1} , respectively, in accord with the elongated chalcogen–chalcogen bonds observed in the solid-state structures.

The morphologies of the SOMOs of the monoanionic radicals $\mathbf{5b}$ and $\mathbf{5c}$ (Figure 3a) parallel those of the structurally

Table 3. Selected interatomic distances [Å] and angles [$^\circ$] calculated for $[\text{Li}(\text{TMEDA})]\mathbf{5b}$ and $[\text{Li}(\text{TMEDA})]\mathbf{5c}$.

	$[\text{Li}(\text{TMEDA})]\mathbf{5b}$	$[\text{Li}(\text{TMEDA})]\mathbf{5c}^{[a]}$
C(1)–S(3)	1.700	1.841
C(1)–P(1)	1.793	1.781
C(1)–P(2)	1.787	1.786
P(1)–S(1)	2.024	2.025
P(2)–S(2)	2.018	2.019
Li(1)–S(1)	2.400	2.402
Li(1)–S(2)	2.400	2.402
P(1)–C(1)–P(2)	121.4	121.4
P(1)–C(1)–S(3)	121.5	116.6
P(2)–C(1)–S(3)	117.0	121.5
C(1)–P(1)–S(1)	117.0	116.7
C(1)–P(2)–S(2)	116.0	115.7
P(1)–S(1)–Li(1)	101.0	100.9
P(2)–S(2)–Li(1)	104.1	104.2
S(1)–Li(1)–S(2)	109.9	109.6

[a] S(3) = Se(1).

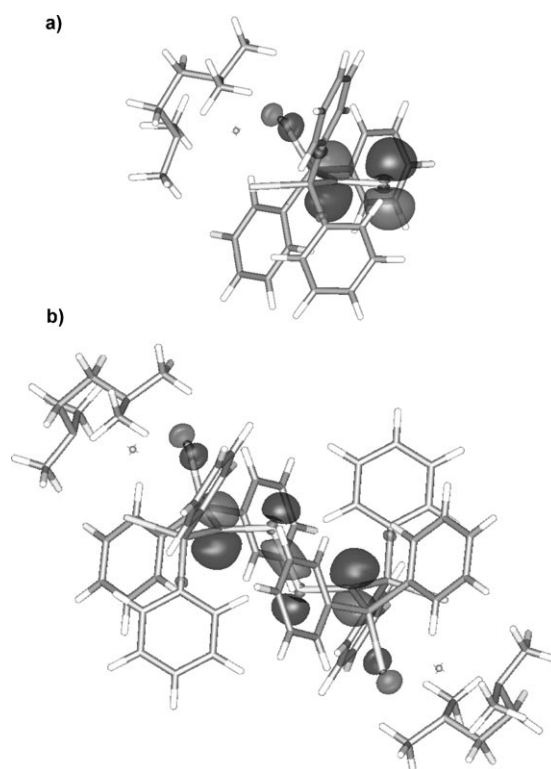


Figure 3. Frontier molecular orbitals of $[\text{Li}(\text{TMEDA})]^+$ salts of a) $\mathbf{5b}$ (SOMO), and b) $\mathbf{7b}$ (HOMO). Isosurfaces are drawn at contour values ± 0.05 .

related radical anions $[\text{R}_2\text{C}=\text{S}]^{\cdot-}$ ^[20] and $[\text{Ph}_2\text{C}=\text{C}(\text{PPh}_2\text{S})_2]^{\cdot-}$.^[19] Although the *p* orbital at the carbon-bound chalcogen atom makes significant contributions to the SOMOs, the predicted hyperfine couplings (hfc) to these nuclei are small due to the vanishing *s*-wave contributions: 4.6 and 20.6 G for $\mathbf{5b}$ and $\mathbf{5c}$, respectively (compared with $a^{33}\text{S} \approx 2$ G for thioketyl anion radicals $[\text{R}_2\text{C}=\text{S}]^{\cdot-}$).^[20a] Consequently, the largest hfc in $\mathbf{5b}$ ($\mathbf{5c}$) of -19.4 (17.8) and

–19.8 (18.1) G are due to spin polarisation and involve the two slightly inequivalent phosphorus centres. The interactions of the unpaired electron with the two sulfur atoms and with the protons at the four phenyl rings are considerably smaller and do not give rise to any significant splitting of the signal. The EPR spectra of **5b** and **5c** are hence expected each to be dominated by a broadened binomial triplet with minor contributions from ^{33}S and ^{77}Se satellites.

Attempts to detect the radical anions **5b** and **5c** by monitoring CH_2Cl_2 solutions of the $[\text{Li}(\text{TMEDA})]^+$ salts of the dimeric dianions **7b** and **7c** by EPR spectroscopy resulted in each case in the observation of two radical species. However, the observed signal patterns could not be assigned to **5b** and **5c** with certainty.^[28]

Two-electron oxidation of **4c**: synthesis and crystal structure of $[\{\text{Li}(\text{TMEDA})\}[\text{I}(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]]$ ($[\{\text{Li}(\text{TMEDA})\}6\text{c}]$):

The two-electron oxidation of the dianions **4b** and **4c** was investigated with a view to producing the neutral chalcogenocarbonyls $\text{EC}(\text{PPh}_2\text{S})_2$ (**6b**, $\text{E}=\text{S}$; **6c**, $\text{E}=\text{Se}$). Treatment of the Se-containing derivative $[\{\text{Li}(\text{TMEDA})\}_24\text{c}]$ with one equivalent of iodine in toluene at -80°C produced a dark red powder. The ^1H NMR spectrum of this red product in CD_2Cl_2 displayed the characteristic signal patterns for both phenyl and TMEDA groups with integrated intensities consistent with the presence of one TMEDA ligand for each $[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]$ molecule. The ^7Li NMR spectrum showed the presence of a Li^+ cation with a singlet at 1.64 ppm, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibited a single resonance at 54.2 ppm. The NMR spectroscopy data therefore indicated the incorporation of $(\text{TMEDA})\text{LiI}$ in the red product.

The dark red powder was recrystallised from toluene/pentane and shown by an X-ray structural determination to be the TMEDA-solvated LiI adduct of the selone $[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]$ (**6c**, Scheme 1 and Figure 1b). The Li^+ cation is S,S' -chelated by the neutral selone ligand and the iodide anion is bonded to the carbon-bound selenium atom. Selenocarbonyl compounds have attracted increasing attention as a result of their applications in conducting materials and biological systems.^[21a,30] The stability of selenoketones $\text{R}_2\text{C}=\text{Se}$ is enhanced if the substituents R (preferably both) contain heteroatoms, especially R_2N groups.^[21a] The thiophosphoryl derivative **6c** is a rare example of a selone in which a phosphorus substituent is attached to the $\text{C}=\text{Se}$ functionality.^[18] We note, however, that the iodide ion in the adduct $[\{\text{LiI}(\text{TMEDA})\}6\text{c}]$ appears to provide a necessary stabilising influence on this unusual selone.^[31,32]

The $\text{Se}-\text{I}$ distance of $2.7218(7) \text{ \AA}$ (Table 1) in $[\{\text{LiI}(\text{TMEDA})\}6\text{c}]$ represents a moderately strong interaction. This value is about $0.20 \text{ \AA}$ longer than the covalent $\text{Se}-\text{I}$ bond lengths in the selenenyl iodides ArSeI ($\text{Ar}=2,4,6\text{-}t\text{Bu}_3\text{-C}_6\text{H}_2$, $2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$;^[33] for comparison, the sum of the covalent radii of selenium and iodine is $2.50 \text{ \AA}$ ^[34]), and it is at the higher end of the distances ($2.56\text{--}2.73 \text{ \AA}$) observed by Devillanova et al. for charge-transfer complexes of selones with I_2 or IBr , which have been described as “strong” $\text{Se}-\text{I}$ bonds.^[35] The $\text{Se}-\text{I}$ distance in $[\{\text{LiI}(\text{TMEDA})\}6\text{c}]$ also

falls in the range of $2.74\text{--}2.78 \text{ \AA}$ reported for organoselenenyl iodides, which are stabilised by an intramolecular $\text{Se}\cdots\text{N}$ interaction that, paradoxically, weakens the $\text{Se}-\text{I}$ bond through electron donation into the $\text{Se}-\text{I} \sigma^*$ orbital.^[36] The $\text{C}-\text{Se}$ distance of $1.815(4) \text{ \AA}$ falls within the $1.77\text{--}1.84 \text{ \AA}$ range reported for a wide variety of selenocarbonyl compounds,^[21,30] with selenoketones falling in the lower end of that range.^[37] It is comparable with the value of $1.817(7) \text{ \AA}$ found for *N*-methylbenzothiadiazole-2(3*H*)-selone.^[38] We note, however, that the $\text{C}-\text{Se}$ distance in the selenium donor is elongated by $0.04\text{--}0.06 \text{ \AA}$ in charge-transfer complexes that contain strong $\text{Se}-\text{I}$ bonds.^[35] It thus seems reasonable to infer that the $\text{C}=\text{Se}$ distance in **6c**, if it can be isolated,^[31] will be significantly shorter than the value of $1.815(4) \text{ \AA}$ found for the LiI adduct. The $\text{C}-\text{Se}$ distance for the π -bonded $\text{C}=\text{Se}$ group in the copper complex of $[(\text{Se})\text{C}(\text{PPh}_2\text{O})_2]$ is $1.846(9) \text{ \AA}$.^[18]

The $\text{Li}-\text{S}$ contacts in $[\{\text{LiI}(\text{TMEDA})\}6\text{c}]$ are comparable to those in $[\{\text{Li}(\text{TMEDA})\}_24\text{c}]$, $[\{\text{Li}(\text{TMEDA})\}_27\text{b}]$, $[\{\text{Li}(\text{TMEDA})\}_27\text{c}]$ and $[\{\text{Li}(\text{TMEDA})\}_28\text{b}]$. The $\text{P}-\text{C}$ bond lengths along the series dianion **4c**, monoanion **5c** in the dimer **7c** and the neutral LiI adduct of **6c** (about 1.71 , 1.75 and $1.78 \text{ \AA}$, respectively) display a steady increase concomitant with the shortening, and enhanced double bond character, of the $\text{C}-\text{Se}$ contact ($1.970(3)$, $1.885(3)$ and $1.815(4) \text{ \AA}$, respectively). A significantly less pronounced trend is noted in the deviation from the planarity for the PCP carbon atoms, with sums of the bond angles of about 355 , 357 and 360° in the dianion **4c**, the dimeric dianion **7c** and neutral **6c**, respectively.

Two-electron oxidation of **4b**: formation and crystal structures of $[\{\text{Li}(\text{L})\}[(\text{SPh}_2\text{P})_2\text{CSS}(\text{H})\text{C}(\text{PPh}_2\text{S})_2]]$ ($[\{\text{Li}(\text{L})\}8\text{b}; \text{L}=\text{TMEDA}, ([12]\text{crown-4})_2$):

The attempted two-electron oxidation of the all-sulfur dianion in $[\{\text{Li}(\text{TMEDA})\}_24\text{b}]$ by addition of one equivalent of iodine to an Et_2O solution at -80°C produced a pale yellow powder. In contrast with the observations made with the Se analogue **4c**, the ^1H NMR spectrum of this product in CD_2Cl_2 revealed the presence of phenyl and TMEDA groups with integrated intensities consistent with only one TMEDA group per two $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]$ units. In addition, the ^7Li NMR spectrum exhibited a singlet at 1.32 ppm and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two singlets in an approximately 1:1 ratio at $\delta=48.8$ and 51.8 ppm . The chemical shifts of the latter resonances were notably similar to those observed for the initial decomposition product of $[\{\text{Li}(\text{TMEDA})\}_27\text{b}]$ in various solvents (see above) and the product from the reaction between $[\{\text{Li}(\text{TMEDA})\}_27\text{b}]$ and $[12]\text{crown-4}$ (Scheme 1).^[26] Collectively, these NMR data suggest the formation of an unsymmetrical dimer that incorporates $[\text{Li}(\text{TMEDA})]^+$.

The identity of this yellow product was established by X-ray structural determinations of two derivatives: $[\{\text{Li}(\text{L})\}[(\text{SPh}_2\text{P})_2\text{CSS}(\text{H})\text{C}(\text{PPh}_2\text{S})_2]]$ ($[\{\text{Li}(\text{L})\}8\text{b}; \text{L}=\text{TMEDA}, ([12]\text{crown-4})_2$). As depicted in Figure 4, the anionic component of these monolithium salts is the monoanion $[(\text{SPh}_2\text{P})_2\text{CSS}(\text{H})\text{C}(\text{PPh}_2\text{S})_2]^-$ (**8b**), a “protonated” deriva-

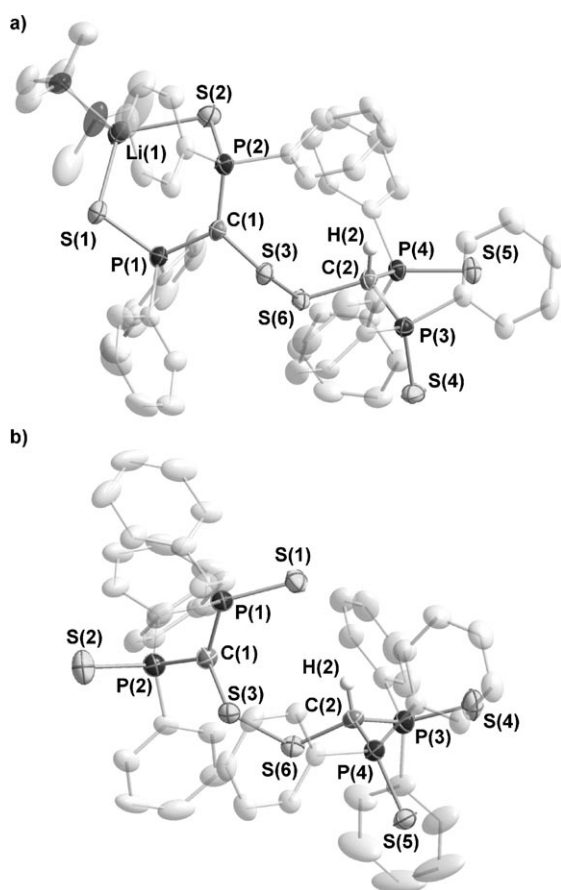


Figure 4. Crystal structures of a) $[\text{Li}(\text{TMEDA})]\mathbf{8b}$ and b) the anion $\mathbf{8b}$ in the ion-separated salt $[\text{Li}([12]\text{crown-4})_2]\mathbf{8b}$, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms of the phenyl and TMEDA groups, and solvate molecules in $[\text{Li}(\text{TMEDA})]\mathbf{8b}$, have been omitted for clarity.

tive of the dianion $\mathbf{7b}$.^[39] The diamagnetic monoanion $\mathbf{8b}$ is formally made up of the radical anion $\mathbf{5b}$, $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^{-\bullet}$ and a neutral radical $[\text{H}(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^\bullet$, connected through an S–S bond that is significantly shorter than that in the di-

anionic precursor $\mathbf{7b}$ (by about 0.09 Å, Table 4). The four-coordinate C(2) atom in $\mathbf{8b}$, as would be expected, displays an elongation in the P–C and C–S bond lengths of about 0.1 Å relative to the three-coordinate C(1) atom in the anionic half of the ligand, whereas the disparity in the P–S distances between the anionic $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^{-\bullet}$ and neutral $[\text{H}(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^\bullet$ units is less pronounced (about 0.03 Å). The difference in P–S bond lengths between the ion-separated salt $[\text{Li}([12]\text{crown-4})_2]\mathbf{8b}$ and $[\text{Li}(\text{TMEDA})]\mathbf{8b}$ is insignificant despite the Li–S contacts in the latter. However, one of the $\text{P}(\text{Ph}_2)\text{S}$ units of the $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^{-\bullet}$ anion in the former complex is situated over the C–S–S–C fragment, resulting in a slight shortening of the S(3)–S(6) distance (0.03 Å) and an inequality of about 28° in the dihedral C(1)–S(3)–S(6)–C(2) angle in relation to $[\text{Li}(\text{TMEDA})]\mathbf{8b}$. The S(1)–H(2) distance of 2.964(4) Å is slightly shorter than those of 3.074(3) and 3.121(3) Å reported for the corresponding contacts in the dication $[(\text{CO})_4\text{Mn}\{(\text{Ph}_2\text{P})_2\text{C}(\text{H})\text{SS}(\text{H})\text{C}(\text{PPh}_2\text{S})_2\}\text{Mn}(\text{CO})_4\}]^{2+}$, indicating a weak C–H⋯S interaction in the solid state.^[24]

In summary, the dianionic all-sulfur system $\mathbf{7b}$ exhibits a pronounced tendency for proton abstraction, which pre-empts the formation of the expected two-electron oxidation product $\text{SC}(\text{PPh}_2\text{S})_2$. In this context we note that the HOMO of $\mathbf{7b}$ exhibits a significant contribution from the p orbitals of the two backbone carbon atoms. In contrast, we were unable to detect the formation of the analogous protonated species $\mathbf{8c}$ as an intermediate of the decomposition process for the selenium-containing system $\mathbf{7c}$ despite the observation that $\text{H}_2\text{C}(\text{PPh}_2\text{S})_2$ is the final product from both $\mathbf{7b}$ and $\mathbf{7c}$ in solution (see above).

Conclusions

We have developed a straightforward and efficient synthesis of the trichalcogeno species $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ ($\text{E} = \text{S}, \text{Se}$) as their dilithium derivatives. One-electron oxidation of these dianions produces the novel dichalcogenides

Table 4. Selected interatomic distances [Å] and angles [°] for $[\text{Li}(\text{TMEDA})]\mathbf{8b}$ and $[\text{Li}([12]\text{crown-4})_2]\mathbf{8b}$ (calculated values in square brackets).

	$[\text{Li}(\text{TMEDA})]\mathbf{8b}$	$[\text{Li}([12]\text{crown-4})_2]\mathbf{8b}$		$[\text{Li}(\text{TMEDA})]\mathbf{8b}$	$[\text{Li}([12]\text{crown-4})_2]\mathbf{8b}$
C(1)–S(3)	1.709(4) [1.721]	1.732(4) [1.727]	C(2)–S(6)	1.831(4) [1.834]	1.827(4) [1.829]
C(1)–P(1)	1.769(4) [1.782]	1.768(4) [1.784]	C(2)–P(3)	1.869(4) [1.890]	1.859(4) [1.880]
C(1)–P(2)	1.752(4) [1.770]	1.758(4) [1.780]	C(2)–P(4)	1.867(4) [1.890]	1.873(4) [1.890]
P(1)–S(1)	1.986(2) [2.028]	1.980(2) [2.000]	P(3)–S(4)	1.949(2) [1.964]	1.947(2) [1.968]
P(2)–S(2)	1.998(2) [2.077]	1.977(2) [2.005]	P(4)–S(5)	1.950(2) [1.965]	1.952(1) [1.973]
S(3)–S(6)	2.140(1) [2.176]	2.112(2) [2.162]	Li(1)–S(1)	2.410(7) [2.412]	–
			Li(1)–S(2)	2.412(7) [2.412]	–
P(1)–C(1)–P(2)	121.8(2) [121.2]	125.5(2) [124.7]	P(3)–C(2)–P(4)	113.6(2) [112.1]	112.5(2) [112.2]
P(1)–C(1)–S(3)	115.1(2) [117.5]	111.8(2) [112.2]	P(3)–C(2)–S(6)	109.4(2) [109.5]	109.2(2) [109.6]
P(2)–C(1)–S(3)	122.9(2) [122.2]	117.3(2) [117.7]	P(4)–C(2)–S(6)	110.0(2) [111.2]	112.2(2) [113.1]
C(1)–P(1)–S(1)	115.5(1) [115.0]	116.3(1) [116.7]	C(2)–P(3)–S(4)	113.6(1) [113.6]	112.3(1) [113.6]
C(1)–P(2)–S(2)	117.5(1) [117.9]	118.6(1) [118.6]	C(2)–P(4)–S(5)	113.7(1) [113.7]	114.5(1) [115.5]
C(1)–S(3)–S(6)	111.9(1) [112.0]	112.0(1) [110.5]	C(2)–S(6)–S(3)	104.9(1) [106.4]	109.4(1) [109.1]
P(1)–S(1)–Li(1)	104.8(2) [104.5]	–	S(1)–Li(1)–S(2)	110.0(3) [108.4]	–
P(2)–S(2)–Li(1)	98.2(2) [86.8]	–	C(1)–S(3)–S(6)–C(2)	117.9(2) [116.6]	90.0(2) [89.2]

$[(\text{SPh}_2\text{P})_2\text{CEEC}(\text{PPh}_2\text{S})_2]^{2-}$, which are formally dimers of the corresponding monoanion radicals $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^\cdot$. The electronic structures of these radical anions and their dimers have been elucidated, but attempts to characterise these short-lived species by EPR spectroscopy were unsuccessful. Two-electron oxidation of the dianion $[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ produces the novel selone $[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]$, which is stabilised as the LiI adduct. In contrast, the attempted two-electron oxidation of the corresponding all-sulfur system produces a protonated species formally made up of the anion radical $[(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^\cdot$ and the neutral radical $[\text{H}(\text{S})\text{C}(\text{PPh}_2\text{S})_2]^\cdot$ connected through an S–S bond.

The tridentate $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ and tetradentate $[(\text{SPh}_2\text{P})_2\text{CEEC}(\text{PPh}_2\text{S})_2]^{2-}$ chalcogen-centred dianions (E = S, Se) are potentially versatile ligands for the construction of a wide variety of metal complexes. More specifically, there is an intriguing possibility that metathesis of either of these dianions with metal halides could, in certain cases, lead to complexes of the elusive monoanion radicals $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^\cdot$, either through an internal redox process (one-electron oxidation) or as a result of E–E bond cleavage. Such studies are in progress.

Experimental Section

General procedures: All reactions and the manipulations of products were performed under argon with use of standard Schlenk techniques or an inert atmosphere glovebox. The compounds $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ (Aldrich, 97%), TMEDA (Aldrich, 99%), MeLi (Aldrich, 1.6 M sol. in Et_2O), I_2 (Aldrich, 99.99+%) and [12]crown-4 (Alfa Aesar, 98%) were used as received. The dianion $\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2]$ (**Li₂2**) was prepared by a literature method and was used in situ.^[4] The solvents *n*-hexane, pentane, toluene, Et_2O and THF were dried by distillation over Na/benzophenone and CH_2Cl_2 over CaH_2 under argon prior to use. Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary.

Spectroscopic methods: The ^1H , ^7Li , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and ^{77}Se NMR spectra were obtained in CD_2Cl_2 or in $[\text{D}_8]\text{THF}$ at 23 °C with a Bruker DRX 400 spectrometer operating at 399.46, 155.24, 100.46, 161.71 and 76.17 MHz, respectively. ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are referenced to the solvent signal and the chemical shifts are reported relative to $(\text{CH}_3)_4\text{Si}$. ^7Li , $^{31}\text{P}\{^1\text{H}\}$ and ^{77}Se NMR spectra are referenced externally and the chemical shifts are reported relative to a solution of LiCl in D_2O (1.0 M), to a solution of H_3PO_4 (85%) and to neat Me_2Se , respectively.

The X-band EPR spectra were recorded with a Bruker EMX 113 spectrometer fitted with a variable-temperature accessory.

Computational details: DFT calculations were performed for $[\{\text{Li}(\text{TMEDA})\}_2\textbf{4c}]$, $[\text{Li}(\text{TMEDA})\textbf{5b}]$, $[\text{Li}(\text{TMEDA})\textbf{5c}]$, $[\{\text{Li}(\text{TMEDA})\}_2\textbf{6c}]$, $[\text{Li}(\text{TMEDA})\textbf{7b}]$, $[\text{Li}(\text{TMEDA})\textbf{7c}]$ and $[\text{Li}(\text{TMEDA})\textbf{8b}]$. The structures were fully optimised by use of a combination of the PBE0 exchange-correlation functional^[40] with the Ahlrichs' triple-zeta valence basis sets augmented by one set of polarisation functions (def-TZVP).^[41] Hyperfine couplings of radicals $[\text{Li}(\text{TMEDA})\textbf{5b}]$ and $[\text{Li}(\text{TMEDA})\textbf{5c}]$ were calculated at the optimised geometries with the same basis set–density functional combination. All calculations were performed with the Gaussian 03^[42] and Turbomole 6.1^[43] program packages. Visualisations for Figure 3 were achieved with gOpenMol.^[44]

X-ray crystallography: Crystallographic data for $[\{\text{Li}(\text{TMEDA})\}_2\textbf{4c}]$, $[\{\text{Li}(\text{TMEDA})\}_2\textbf{6c}] \cdot \text{C}_6\text{H}_8$, $[\text{Li}(\text{TMEDA})\textbf{7b} \cdot (\text{CH}_2\text{Cl}_2)_{0.33}]$, $[\text{Li}(\text{THF})_2\textbf{7b}]$, $[\text{Li}(\text{TMEDA})\textbf{7c}]$, $[\text{Li}(\text{TMEDA})\textbf{8b} \cdot (\text{CH}_2\text{Cl}_2)_2]$ and $[\text{Li}(\text{[12]crown-4})\textbf{8b}]$ are summarised in Table 5 (see Scheme 1 for the identities of **4c**, **6c**, **7b**,

7c and **8b**). The crystals of all compounds were coated with Paratone 8277 oil and mounted on glass fibres. Diffraction data were collected with a Nonius KappaCCD diffractometer with use of monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at -100°C . The data sets were corrected for Lorentz and polarisation effects, and empirical absorption correction was applied to the net intensities. The structures were solved by direct methods by use of SHELXS-97 and refined with SHELXL-97.^[45,46] After full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions ($\text{C}–\text{H} = 0.95 \text{ \AA}$ for $–\text{CH}$, $0.99 \text{ \AA}$ for $–\text{CH}_2$ and $0.98 \text{ \AA}$ for $–\text{CH}_3$ hydrogen atoms). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for $–\text{CH}$ and $–\text{CH}_2$ hydrogen atoms, and 1.5 times for $–\text{CH}_3$ hydrogen atoms. In the structures of **8b** the hydrogen atom bonded to the PCP carbon was located from the Fourier density map and it was refined as isotropic. In the final refinement the remaining hydrogen atoms were riding on their respective carbon atoms.

In the structures of $[\text{Li}(\text{TMEDA})_2\textbf{7b} \cdot (\text{CH}_2\text{Cl}_2)_{0.33}]$ and $[\text{Li}(\text{THF})_2\textbf{7b}]$ the carbon-bound sulfur atoms show positional disorder with site occupancy factors of about 0.93:0.07 and 0.88:0.12, respectively, in the final refinement. In addition, the structure of $[\text{Li}(\text{TMEDA})_2\textbf{7b} \cdot (\text{CH}_2\text{Cl}_2)_{0.33}]$ is partially solvated with an occupancy of 0.33 for the CH_2Cl_2 molecule that results in two orientations for the closest phenyl group in the ratio 0.67:0.33. One of the two solvate molecules in $[\text{Li}(\text{TMEDA})\textbf{8b} \cdot (\text{CH}_2\text{Cl}_2)_2]$ is also disordered, with the refined occupancies of 0.59:0.41.

CCDC-780827, CCDC-780828, CCDC-780829, CCDC-780830, CCDC-780831, CCDC-780832 and CCDC-780833 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.

Synthesis of $[\{\text{Li}(\text{TMEDA})\}_2\textbf{4b}]$: A solution of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ (0.538 g, 1.20 mmol) in toluene (10 mL) was cooled to -80°C and MeLi (1.50 mL of a 1.6 M solution in Et_2O , 2.40 mmol) was added by syringe. The reaction mixture was stirred for 15 min at -80°C and for 2.5 h at 23°C .^[4] A solution of TMEDA (0.279 g, 1.20 mmol) in toluene (5 mL) was added at 23°C to the cloudy solution of $\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2]$. The reaction mixture was stirred for 15 min, after which it was added at -80°C to a suspension of S_8 (0.038 g, 1.20 mmol) in toluene (5 mL). The reaction mixture was stirred for 15 min at -80°C and for 2 h at 23°C . The solvent was evaporated under vacuum and the product was washed with *n*-hexane to afford $[\{\text{Li}(\text{TMEDA})\}_2\textbf{4b}]$ as an orange-red powder (0.748 g, 86%). ^1H NMR ($[\text{D}_8]\text{THF}$, 23°C): $\delta = 6.88–7.97$ (m, 20H; C_6H_5), 2.31 (s, 8H; $–\text{CH}_2$ of TMEDA), 2.16 ppm (s, 24H; $–\text{CH}_3$ of TMEDA); $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 141.1$ (t, $^1J(\text{C},\text{P}) = 43.7 \text{ Hz}$; PCP carbon), 134.3 (m, Ph), 132.1 (m, Ph), 129.5 (s, Ph), 128.7 (s, Ph), 127.8 (m, Ph), 126.9 (m, Ph), 58.7 (s, TMEDA, $–\text{CH}_2$), 46.1 ppm (s, TMEDA, $–\text{CH}_3$); ^7Li NMR: $\delta = 1.67 \text{ ppm}$; $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 44.0 \text{ ppm}$; elemental analysis calcd (%) for $\text{C}_{37}\text{H}_{52}\text{Li}_2\text{N}_4\text{P}_2\text{S}_3$: C 61.31, H 7.23, N 7.73; found: C 60.97, H 7.11, N 7.64.

Synthesis of $[\{\text{Li}(\text{TMEDA})\}_2\textbf{4c}]$: A solution of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ (0.538 g, 1.20 mmol) in toluene (10 mL) was cooled to -80°C and MeLi (1.50 mL of 1.6 M solution in Et_2O , 2.40 mmol) was added by syringe. The reaction mixture was stirred for 15 min at -80°C and for 2.5 h at 23°C .^[4] A solution of TMEDA (0.279 g, 1.20 mmol) in toluene (5 mL) was added at 23°C to the cloudy solution of $\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2]$. The reaction mixture was stirred for 15 min, after which it was added at 0°C to a suspension of elemental selenium (0.095 g, 1.20 mmol) in toluene (5 mL). The reaction mixture was stirred for 15 min at 0°C and for 2 h at 23°C . The solvent was evaporated under vacuum and the product was washed with *n*-hexane to afford $[\{\text{Li}(\text{TMEDA})\}_2\textbf{4c}]$ as a red powder (0.843 g, 91%). ^1H NMR ($[\text{D}_8]\text{THF}$, 23°C): $\delta = 6.88–7.80$ (m, 20H; C_6H_5), 2.32 (s, 8H; $–\text{CH}_2$ of TMEDA), 2.16 ppm (s, 24H; $–\text{CH}_3$ of TMEDA); $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 141.2$ (t, $^1J(\text{C},\text{P}) = 46.2 \text{ Hz}$; PCP carbon), 134.3 (m; Ph), 134.1 (s; Ph), 132.1 (m; Ph), 129.5 (s; Ph), 128.8 (s; Ph), 128.7 (s; Ph), 127.8 (m; Ph), 126.9 (m; Ph), 125.9 (m; Ph), 58.6 (s; TMEDA, $–\text{CH}_2$), 46.2 ppm (s; TMEDA, $–\text{CH}_3$); ^7Li NMR: $\delta = 2.05 \text{ ppm}$; $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 43.5 \text{ ppm}$; ^{77}Se NMR: $\delta = -4.5 \text{ ppm}$; elemental analysis calcd (%) for $\text{C}_{37}\text{H}_{52}\text{Li}_2\text{N}_4\text{P}_2\text{S}_2\text{Se}$: C 57.58, H 6.79, N 7.26; found: C 57.36, H 6.45, N

Table 5. Crystallographic data for $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$, $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$, $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$, $[\text{Li}(\text{TMEDA})]_2\mathbf{8b}$, $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$, $[\text{Li}(\text{THF})]_2\mathbf{7b}$, $[\text{Li}(\text{THF})]_2\mathbf{7b}$, $[\text{Li}(\text{CH}_2\text{Cl}_2)]_2\mathbf{7b}$, $[\text{Li}(\text{CH}_2\text{Cl}_2)]_2\mathbf{8b}$, $[\text{Li}(\text{CH}_2\text{Cl}_2)]_2\mathbf{7c}$ and $[\text{Li}(\text{crown-4})]_2\mathbf{8b}$.

formula	$[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$	$[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$	$[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$	$[\text{Li}(\text{TMEDA})]_2\mathbf{8b}$	$[\text{Li}(\text{THF})]_2\mathbf{7b}$	$[\text{Li}(\text{CH}_2\text{Cl}_2)]_2\mathbf{7b}$	$[\text{Li}(\text{CH}_2\text{Cl}_2)]_2\mathbf{8b}$	$[\text{Li}(\text{CH}_2\text{Cl}_2)]_2\mathbf{7c}$	$[\text{Li}(\text{crown-4})]_2\mathbf{8b}$
Fw.	771.73	867.61	867.61	867.61	867.61	867.61	867.61	867.61	867.61
cryst. system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.365(2)	15.493(3)	15.493(3)	15.493(3)	15.493(3)	15.493(3)	15.493(3)	15.493(3)	15.493(3)
b [Å]	12.324(3)	14.338(3)	14.338(3)	14.338(3)	14.338(3)	14.338(3)	14.338(3)	14.338(3)	14.338(3)
c [Å]	16.424(3)	18.962(4)	18.962(4)	18.962(4)	18.962(4)	18.962(4)	18.962(4)	18.962(4)	18.962(4)
α [°]	92.89(3)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β [°]	102.35(3)	109.76(3)	109.76(3)	109.76(3)	109.76(3)	109.76(3)	109.76(3)	109.76(3)	109.76(3)
γ [°]	112.96(3)	90.00	90.00	90.00	90.00	90.00	90.00	90.00	90.00
V [Å ³]	2046.1(9)	3964(2)	3964(2)	3964(2)	3964(2)	3964(2)	3964(2)	3964(2)	3964(2)
Z	2	4	4	4	4	4	4	4	4
ρ_{calc} [g cm ⁻³]	1.253	1.454	1.454	1.454	1.454	1.454	1.454	1.454	1.454
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	1.128	1.940	1.940	1.940	1.940	1.940	1.940	1.940	1.940
crystal size [mm ³]	0.20 × 0.16 × 0.12	0.32 × 0.12 × 0.08	0.32 × 0.12 × 0.08	0.32 × 0.12 × 0.08	0.32 × 0.12 × 0.08	0.32 × 0.12 × 0.08	0.32 × 0.12 × 0.08	0.32 × 0.12 × 0.08	0.32 × 0.12 × 0.08
$F(000)$	808	1752	1752	1752	1752	1752	1752	1752	1752
θ range [°]	2.06–25.03	2.52–25.02	2.52–25.02	2.52–25.02	2.52–25.02	2.52–25.02	2.52–25.02	2.52–25.02	2.52–25.02
refl. collected	13729	12575	12575	12575	12575	12575	12575	12575	12575
unique refls.	7211	6931	6931	6931	6931	6931	6931	6931	6931
R_{int}	0.0306	0.0344	0.0344	0.0344	0.0344	0.0344	0.0344	0.0344	0.0344
refl. $[I > 2\sigma(I)]$	6238	5748	5748	5748	5748	5748	5748	5748	5748
R_1 [$I > 2\sigma(I)$]	0.0423	0.0422	0.0422	0.0422	0.0422	0.0422	0.0422	0.0422	0.0422
wR_2 (all data)	0.1034	0.0930	0.0930	0.0930	0.0930	0.0930	0.0930	0.0930	0.0930
GoF on F^2	1.043	1.072	1.072	1.072	1.072	1.072	1.072	1.072	1.072
completeness	0.995	0.990	0.990	0.990	0.990	0.990	0.990	0.990	0.990

$$[a] \lambda (\text{MoK}\alpha) = 0.71073 \text{ Å}, [b] T = -100^\circ\text{C}, [c] R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, [d] wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}.$$

7.19. X-ray quality crystals were obtained by layering *n*-hexane onto the toluene solution of $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ after 24 h at -20°C .

Synthesis of $[\text{Li}(\text{TMEDA})]_2\mathbf{6c}$: A solution of $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ (0.60 mmol, prepared in situ from 0.269 g of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$, 0.75 mL of MeLi, 0.139 g of TMEDA and 0.047 g of Se as described above) in toluene (20 mL) was cooled to -80°C and a solution of I_2 (0.152 g, 0.60 mmol) in toluene (20 mL) was added by cannula. The reaction mixture was stirred for 15 min at -80°C and for 2 h at 23°C . The solvent volume was reduced to about 10 mL and *n*-hexane (40 mL) was added by cannula. The resulting white precipitate (LiCl) was removed by filtration and the solution was stored at -20°C for 48 h to afford $[\text{Li}(\text{TMEDA})]_2\mathbf{6c} \cdot \text{C}_7\text{H}_8$ as a dark red, crystalline powder (0.369 g, 71 %). ^1H NMR (CD_2Cl_2 , 23°C): δ = 7.13–7.86 (m, 20H; C_6H_5 and 5H of C_7H_8), 2.38 (s, 4H; $-\text{CH}_2$ of TMEDA), 2.29 (s; 3H of C_7H_8), 2.27 ppm (s, 12H; $-\text{CH}_3$ of TMEDA); ^7Li NMR: δ = 1.64 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 54.2 ppm; elemental analysis calcd (%) for $\text{C}_{38}\text{H}_{44}\text{Li}_2\text{N}_2\text{P}_2\text{S}_2\text{Se}$ ($[\text{Li}(\text{TMEDA})]_2\mathbf{6c}$ + 1 mole of toluene solvate (see NMR spectroscopic and crystallographic data): C 52.6, H 5.11, N 3.23; found: C 52.17, H 5.17, N 3.33. ^{13}C and ^{77}Se NMR spectra were not obtained, due to decomposition of the adduct in solution. X-ray quality crystals were obtained by layering pentane onto the toluene solution of $[\text{Li}(\text{TMEDA})]_2\mathbf{6c}$ after 4 h at 5°C .

Synthesis of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$: A solution of $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ (1.20 mmol, prepared in situ from 0.538 g of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$, 1.50 mL of MeLi, 0.279 g of TMEDA and 0.038 g of S_8 as described above) in toluene (20 mL) was cooled to -80°C and a solution of I_2 (0.152 g, 0.60 mmol) in toluene (10 mL) was added by cannula. The reaction mixture was stirred for 15 min at -80°C and for 2 h at 23°C . The resulting powder was allowed to settle and the solvent was decanted by cannula. The precipitate was washed with toluene to afford $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ as a yellow powder (0.430 g, 60 %). ^1H NMR (CD_2Cl_2 , 23°C): δ = 6.90–7.90 (brs, 40H; C_6H_5), 2.25 (s, 8H; $-\text{CH}_2$ of TMEDA), 1.98 ppm (s, 24H; $-\text{CH}_3$ of TMEDA); ^7Li NMR: δ = 1.20 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 50.2 ppm; elemental analysis calcd (%) for $\text{C}_{62}\text{H}_{72}\text{Li}_2\text{N}_2\text{P}_2\text{S}_6$: C 61.88, H 6.03, N 4.66; found: C 61.37, H 6.16, N 4.64. At room temperature, solutions of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ (THF, CH_2Cl_2 , CH_3CN) form $[\text{Li}(\text{TMEDA})]_2\mathbf{8b}$, followed by decomposition and formation of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ ($\mathbf{9}$) as shown by NMR spectroscopy.^[27] X-ray quality crystals were obtained by layering *n*-hexane on top of the CH_2Cl_2 solution of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ after 3 h at 23°C . When *n*-hexane was layered onto the THF solution of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$, crystals of $[\text{Li}(\text{THF})]_2\mathbf{7b}$ were obtained after 12 h at 5°C .

Synthesis of $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$: A solution of $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ (1.20 mmol, prepared in situ from 0.538 g of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$, 1.50 mL of MeLi, 0.279 g of TMEDA and 0.095 g of selenium as described above) in toluene (20 mL) was cooled to -80°C and a solution of I_2 (0.152 g, 0.60 mmol) in toluene (10 mL) was added by cannula. The reaction mixture was stirred for 15 min at -80°C and for 2 h at 23°C . The resulting powder was allowed to settle and the solvent was decanted by cannula. The precipitate was washed with toluene to afford $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ as an orange powder (0.578 g, 74 %). ^1H NMR (CD_2Cl_2 , 23°C): δ = 7.13–7.63 (m, 40H; C_6H_5), 2.19 (s, 8H; $-\text{CH}_2$ of TMEDA), 1.88 ppm (s, 24H; $-\text{CH}_3$ of TMEDA); ^7Li NMR: δ = 1.24 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 50.5 ppm; elemental analysis calcd (%) for $\text{C}_{62}\text{H}_{72}\text{Li}_2\text{N}_2\text{P}_2\text{S}_4\text{Se}_2$: C 57.40, H 5.59, N 4.32; found: C 57.55, H 5.71, N 4.19. At room temperature, solutions of $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ (THF, CH_2Cl_2 , CH_3CN) decompose and eventually form $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ ($\mathbf{9}$) (NMR spectroscopy).

copy)^[27] and elemental selenium. X-ray quality crystals were obtained by layering Et₂O on top of the CH₂Cl₂ solution of [Li(TMEDA)]₂**7c** after 4 h at 23 °C.

Synthesis of [Li(TMEDA)]₂8b**:** A solution of [[Li(TMEDA)]₂**4b**] (0.60 mmol, prepared in situ from 0.269 g of [H₂C(PPh₂S)₂], 0.75 mL of MeLi, 0.139 g of TMEDA and 0.019 g of S₈ as described above) in Et₂O (20 mL) was cooled to –80 °C and a solution of I₂ (0.152 g, 0.60 mmol) in Et₂O (20 mL) was added by cannula. The reaction mixture was stirred for 15 min at –80 °C and for 2 h at 23 °C. The resulting pale yellow powder was allowed to settle and the solvent was decanted by cannula. The product was washed with pentane and Et₂O and was identified as [Li(TMEDA)]₂**8b** (0.210 g, 65%). ¹H NMR (CD₂Cl₂, 23 °C): δ = 7.02–7.82 (m, 40H; C₆H₅), 2.32 (s, 4H; –CH₂ of TMEDA), 1.93 ppm (s, 12H; –CH₃ of TMEDA); ⁷Li NMR: δ = 1.32 ppm; ³¹P{¹H} NMR: δ = 51.8 (s), 48.8 ppm (s). At room temperature, solutions of [Li(TMEDA)]₂**8b** (THF, CH₂Cl₂, CH₃CN) decompose and eventually form [H₂C(PPh₂S)₂] (**9**) as shown by NMR spectroscopy.^[27] X-ray quality crystals of [Li(TMEDA)]₂**8b** were obtained by layering *n*-hexane onto the CH₂Cl₂ solution of the yellow powder after 3 d at –20 °C.

Synthesis of [Li([12]crown-4)₂]8b**:** A solution of [Li(TMEDA)]₂**7b** (0.241 g, 0.20 mmol) in CH₂Cl₂ (20 mL) was cooled to 0 °C and a solution of [12]crown-4 (0.070 g, 0.40 mmol) in CH₂Cl₂ (5 mL) was added by cannula. The reaction mixture was stirred for 10 min at 0 °C and for 1 h at 23 °C. The solvent was evaporated under vacuum and the product was washed with Et₂O and toluene to afford [Li([12]crown-4)₂]**8b** as a bright yellow powder (0.208 g, 79%). The use of 4 equivalents of [12]crown-4 (0.140 g, 0.80 mmol) also resulted in the formation of [Li([12]crown-4)₂]**8b**, based on the ¹H NMR spectrum. ¹H NMR (CD₂Cl₂, 23 °C): δ = 6.95–8.22 (m, 40H; C₆H₅), 3.66 ppm (s, 32H; –CH₂ of [12]crown-4); ⁷Li NMR: δ = –0.50 ppm; ³¹P{¹H} NMR: δ = 51.0 (s), 47.3 ppm (s). At room temperature, solutions of [Li([12]crown-4)₂]**8b** (THF, CH₂Cl₂, CH₃CN) decompose and eventually form [H₂C(PPh₂S)₂] (**9**) as shown by NMR spectroscopy.^[27] X-ray quality crystals of [Li([12]crown-4)₂]**8b** were obtained by layering *n*-hexane onto the CH₂Cl₂ solution of the yellow powder after 5 h at 5 °C.

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