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Year: 2010

Version:

Please cite the original version:

Konu, J., Chivers, T., & Tuononen, H. (2010). Synthesis and Redox Behaviour of the Chalcogenocarbonyl Dianions, [(E)C(PPh₂S)₂]₂²⁻: Formation and Structures of Chalcogen–Chalcogen Bonded Dimers and a Novel Selone. *Chemistry - A European Journal*, 16(43), 12977-12987. <https://doi.org/10.1002/chem.201001699>

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**Synthesis and Redox Behaviour of the Chalcogenocarbonyl Dianions,
[(E)C(PPh₂S)₂]²⁻ (E = S, Se): Formation and Structures of Chalcogen-
Chalcogen Bonded Dimers and a Novel Selone**

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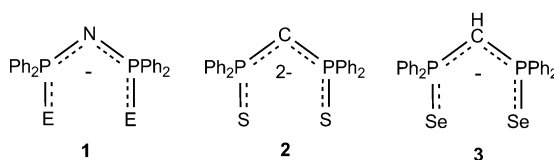
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Abstract: The lithium salts of the chalcogenocarbonyl dianions, $[(E)C(PPh_2S)_2]^{2-}$ [E = S (**4b**), Se (**4c**)], were produced by the reaction between $Li_2[C(PPh_2S)_2]$ and elemental chalcogens in the presence of TMEDA, and the solid-state structure of $\{[Li(TMEDA)]_2[(Se)C(PPh_2S)_2]\}$ $\{[Li(TMEDA)]_2$ **4c** $\}$ was shown to be bicyclic with Li^+ cations bis-*S,Se*-chelated by the dianionic ligand. One-electron oxidation of the dianions **4b,c** with iodine afforded the diamagnetic complexes $\{[Li(TMEDA)]_2[(SPh_2P)_2CEEC(PPh_2S)_2]\}$ (E = S $\{[Li(TMEDA)]_2$ **7b** $\}$, Se $\{[Li(TMEDA)]_2$ **7c** $\}$), which are dimers of the radical anions $[(E)C(PPh_2S)_2]^{-\bullet}$ [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, $\{[Li(TMEDA)][I(Se)C(PPh_2S)_2]\}$ $\{[Li(TMEDA)]$ **6c** $\}$, whereas the analogous reaction with **4b** resulted in the formation of **7b** followed by protonation to give $\{[Li(TMEDA)][(SPh_2P)_2CSS(H)C(PPh_2S)_2]\}$ $\{[Li(TMEDA)]$ **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**, $[Li(TMEDA)]$ **6c**·C₇H₈, $[Li(TMEDA)]_2$ **7b**·(CH₂Cl₂)_{0.33}, $[Li(THF)]_2$ **7b**, $[Li(TMEDA)]_2$ **7c**, $[Li(TMEDA)]$ **8b**·(CH₂Cl₂)₂ and $[Li(12-crown-4)]$ **8b** were determined and salient structural features are discussed.

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

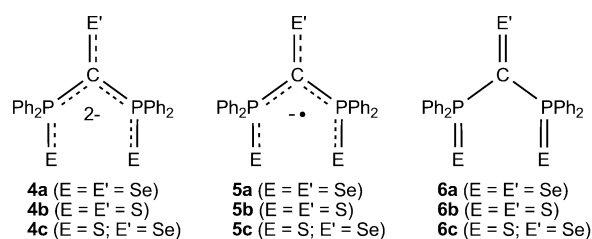
Introduction

In contrast to the extensively studied *N*-bridged, monoanionic ligands $[\text{N}(\text{PPh}_2\text{E})_2]^-$ (**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 $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ (**2**) exhibits strong metal-carbon interactions in 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 derivative 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] early^[7] and late transition metals,^[4, 8] as well as lanthanides^[9] and actinides,^[10] have subsequently been prepared by metathesis of $\text{Li}_2\mathbf{2}$ 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 **2**. In contrast to the formation of chalcogen-chalcogen bonds upon oxidation of *N*-bridged ligands of the type **1**,^[11] treatment of $\text{Li}_2\mathbf{2}$ with the mild oxidising agents C_2Cl_6 or I_2 produces remarkably stable monomeric or dimeric carbenoids, respectively.^[12, 13] The nucleophilic reactivity of **2** is also illustrated by the reaction with CS_2 to give the 1,1-ethylenedithiolate $[\text{S}_2\text{C}=\text{C}(\text{PPh}_2\text{S})_2]^{2-}$.^[4b]

The diseleno *C*-bridged monoanion $[\text{HC}(\text{PPh}_2\text{Se})_2]^-$ (**3**), isoelectronic with **1** ($\text{E} = \text{Se}$), was first prepared from the neutral ligand $[\text{H}_2\text{C}(\text{PPh}_2\text{Se})_2]$ and *n*BuLi and used as an *in situ* metathetical reagent for the preparation of homoleptic M(II) ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$) 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-yield synthesis of Li**3** 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 MCl_2 ($\text{M} = \text{Sn}, \text{Te}$) with Li**3** in a 1:2 molar ratio produce homoleptic M(IV) complexes of the *triseleno dianion* $[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$ (**4a**) via a redox process that formally involves selenium-proton exchange.^[17] A dinuclear Hg(II) complex of **4a** is formed on mild heating of $\text{Hg}(\text{3})_2$.^[17] Very recently, homoleptic Pb(II) complexes of the related trichalcogeno dianions **4b** and **4c** were obtained by chalcogen insertion into the Pb–C bond of dimeric, homoleptic Pb(II) complexes of **2**.^[6a]



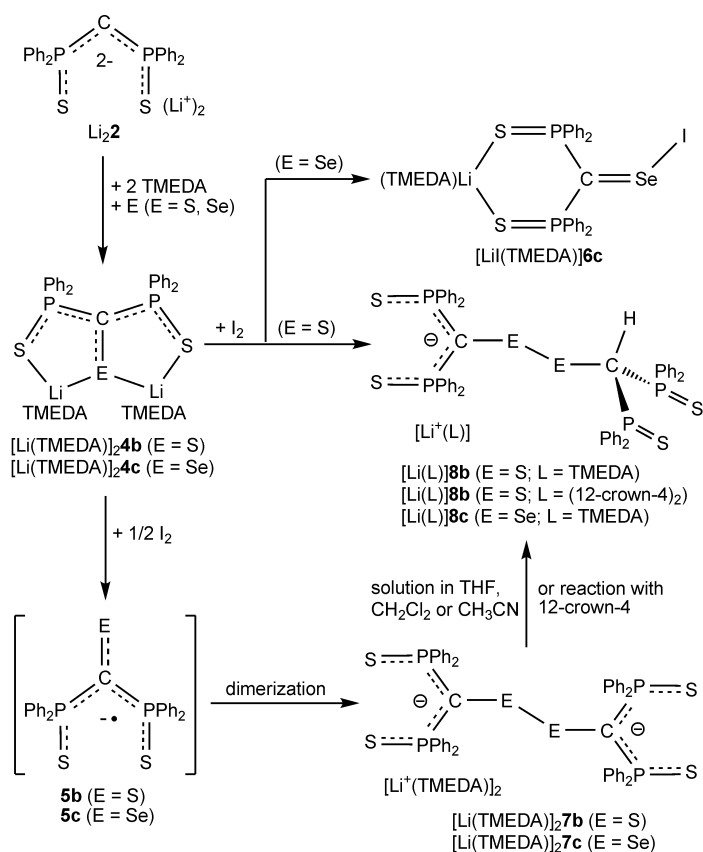
The first examples of metal complexes of ligands of the type **4** exhibit notably different structural features suggesting a rich coordination chemistry.^[6a, 17, 18] With this in mind, we sought to develop an efficient synthesis of alkali-metal derivatives of these novel tridentate ligands that can be used as metathetical reagents. Concomitantly, we considered that investigations of the redox behaviour of these dianions 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 $[\text{Ph}_2\text{C}=\text{C}(\text{PPh}_2\text{S})_2]^{-\bullet}$ in which the electron-accepting phosphine sulfide substituents exert a stabilising influence on the alkene radical.^[19] Thioketyl radical anions $[\text{R}_2\text{C}=\text{S}]^{-\bullet}$ (e.g. $\text{R} = t\text{Bu}, \text{Me}$) have been characterised in solution by EPR spectroscopy, but salts of these anions have not been isolated.^[20] The effect of the PPh_2S substituents on the stability of these radical anions of the 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 $[\text{Li}(\text{TMEDA})]_2\text{4c}$. Investigations of the oxidation of the **4b** and **4c** with iodine revealed the formation of **7b** and **7c**, which are formally dimers of the corresponding anion radicals **5b** and **5c**, respectively, upon one-electron oxidation (Scheme 1). The X-ray structures of $[\text{Li}(\text{L})]_2\text{7b}$ [$\text{L} = \text{TMEDA}, (\text{THF})_2$] and $[\text{Li}(\text{TMEDA})]_2\text{7c}$ 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 I_2 produces the unusual selone **6c**^[21] as a LiI adduct, whereas the attempted two-electron oxidation of **4b** with I_2 generates the protonated monoanion **8b**; the X-ray structures of $[\text{Li}(\text{L})]\text{8b}$ [$\text{L} = \text{TMEDA}, (12\text{-crown-}4)_2$] were elucidated. The experimental work is supported by DFT calculations which provide insights into the molecular and electronic structures of the radical anions **5b** and **5c**, and the corresponding dimers **7b** and **7c**, as well as confirmation of the molecular structure of the protonated species **8b**.

Results and Discussion

Synthesis and characterization of $\{[\text{Li}(\text{TMEDA})]_2[\text{(E)C}(\text{PPh}_2\text{S})_2]\}$ (E = S $\{[\text{Li}(\text{TMEDA})]_2\mathbf{4b}\}$, Se $\{[\text{Li}(\text{TMEDA})]_2\mathbf{4c}\}$). Since the diseleno PCP-bridged dianion $[\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$ is not accessible (*vide supra*), 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 elemental chalcogen at -80 °C (S) or 0 °C (Se) produced dilithium salts of the trichalcogeno dianions, $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$, as analytically pure, orange-red or red solids in excellent yields (86 and 91%, respectively) (Scheme 1). Both compounds exhibit significant air and/or moisture sensitivity even in the solid state and exposure to ambient conditions results in a rapid loss of the red colour.



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

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 spectrum signals attributable to the PCP carbon were observed at 141.1 and 141.2 ppm, respectively. The ^7Li and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibited singlets at 1.67 and 44.0 ppm, respectively, for $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ and at 2.05 and 43.5 ppm for $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$. In addition, a singlet at -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 ca. 300 ppm compared to that of the CSe resonance observed for the homoleptic Te(IV) complex $\{\text{Te}[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]_2\}$ $[\text{Te}(\mathbf{4a})_2]$.^[17, 22] Taken together, the

NMR spectroscopic data are consistent with the formation of the dianions **4b** and **4c** incorporating two TMEDA-chelated Li⁺ cations symmetrically coordinated to the dianion.

As depicted in Figure 1a, the solid-state structure of [Li(TMEDA)]₂**4c** corroborates the formation of a monomeric complex in which the lithium cations are *S*,*Se*-chelated by the dianion [(Se)C(PPh₂S)₂]²⁻ thus resulting in a bicyclic LiSP(Se)CPSLi core with the two five-membered rings connected by a common C-Se bond. The P-C and P-S bond lengths of ca. 1.72 and 2.02 Å, respectively, in [Li(TMEDA)]₂**4c** (Table 2) are ca. 0.02 Å shorter, and the C-Se distance of 1.970(3) Å is ca. 0.05 Å longer, than the corresponding bonds in the lead(II) complex Pb**4c**.^[6a] A similar disparity is evident between the P-C and C-Se bond lengths in [Li(TMEDA)]₂**4c** and those of ca. 1.73-1.76 and 1.89-1.94 Å, respectively, found in the group 12, 14 and 16 complexes of the triseleno ligand **4a**, {M_n[(Se)C(PPh₂Se)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**4c** exhibits a slight distortion from planarity with Σ ∠ C = 354.8°, which is comparable to that in the mercury complex Hg₂(**4a**)₂ (ca. 353°), while in the Pb**4c**, Sn(**4a**)₂ and Te(**4a**)₂ complexes the corresponding deviation from planarity is more pronounced (Σ ∠ C is ca. 340°).

One-electron oxidation of 4b and 4c; crystal structures and NMR spectroscopy of {[Li(TMEDA)]₂[(SPh₂P)₂CEEC(PPh₂S)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 generating and assessing the stability of the corresponding chalcogenocarbonyl radical anions **5b** and **5c**. Thus, one-electron oxidation was attempted by the addition of *one-half equivalent* of iodine to solutions of $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$, respectively, prepared in situ in toluene at -80°C (Scheme 1). After a few minutes, $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ and $\{[\text{Li}(\text{TMEDA})]_2\mathbf{7c}\}$ were obtained as yellow and orange powders, respectively, and identified after recrystallisation by single-crystal X-ray structure determinations.

The crystal structures of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ and $\{[\text{Li}(\text{TMEDA})]_2\mathbf{7c}\}$ (Figure 2) revealed the formation of dimers of the radical anions $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^\bullet$ [$\text{E} = \text{S}$ (**5b**), Se (**5c**)], joined by chalcogen-chalcogen (E-E) bonds ($\text{E} = \text{S}, \text{Se}$) at a crystallographic symmetry centre. The central S-S and Se-Se bond lengths of 2.222(2) and 2.508(1) Å (Table 3) in $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$, respectively, are significantly longer than those of ca. 2.02-2.06 Å and 2.29-2.35 Å observed in diaryl dichalcogenides, Ar_2E_2 ($\text{E} = \text{S}, \text{Ar} = \text{C}_6\text{H}_5, \text{C}_6\text{F}_5, 4\text{-NO}_2\text{C}_6\text{H}_4, 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$; $\text{E} = \text{Se}, \text{Ar} = \text{C}_6\text{H}_5, \text{C}_6\text{F}_5, 4\text{-NO}_2\text{C}_6\text{H}_4, 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2$).^[23] The S-S distance in $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ is, however, comparable with the value of 2.177(13) Å reported for an analogous $\text{P}_2\text{C-S-S-CP}_2$ unit in the neutral dinuclear manganese(I) complex $[(\text{CO})_4\text{Mn}\{(\text{Ph}_2\text{P})_2\text{CSSC}(\text{PPh}_2)_2\}\text{Mn}(\text{CO})_4]$.^[24] On the other hand, the Se-Se distance in $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ is ca. 0.19 Å longer than the corresponding distance in the dication $[(\text{CO})_4\text{Mn}\{(\text{Ph}_2\text{P})_2\text{C}(\text{H})\text{SeSe}(\text{H})\text{C}(\text{PPh}_2)_2\}\text{Mn}(\text{CO})_4]^{2+}$.^[25] The P-C and P-S bond lengths in $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ are essentially identical at ca. 1.75 and 2.00 Å, respectively, while the mean Li-S contacts in the latter are ca. 0.05 Å longer. The Li-S contacts in $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ are, however, equal to those in the THF-coordinated

derivative of **7b**, $[\text{Li}(\text{THF})_2]_2\mathbf{7b}$, which was 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 **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 ca. 0.04 Å compared to the precursor **4c**, while the C-Se bond in the former is significantly shorter (by 0.09 Å). The PCP carbon in the anions **7b** and **7c** exhibits only a slight distortion from planarity ($\Sigma\angle\text{C}(1)$ is ca. 356°, 352° and 357° in $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$, $[\text{Li}(\text{THF})_2]_2\mathbf{7b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$, respectively). As a consequence of the centre of symmetry, the CSSC fragment in **7b** and **7c** is planar with *trans* C atoms, *cf.* $[(\text{CO})_4\text{Mn}\{(\text{Ph}_2\text{P})_2\text{CSSC}(\text{PPh}_2)_2\}\text{Mn}(\text{CO})_4]$.^[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 1.20 and 50.2 ppm, and at 1.24 and 50.5 ppm, respectively. In addition, the characteristic patterns for phenyl and TMEDA resonances were observed in the ^1H NMR spectrum. However, the all-sulfur system $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ exhibited broad signals (half-width of 325 Hz for the ^7Li and 405 Hz for the ^{31}P signal) and after 30 minutes the singlet at δ 50.2 in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was replaced by two singlets at 48.8 and 51.8 ppm in an approximately 1:1 ratio.^[26] After 12 h in solution (THF, CH_2Cl_2 or CH_3CN) at 23 °C both **7b** and **7c** had released the carbon-bound chalcogen to give $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ (**9**) as the final product (^1H NMR: δ 3.84 (t); $^{31}\text{P}\{^1\text{H}\}$ NMR at δ 35.8 (s)).^[27]

Electronic structures of the dianions $[(\text{SPh}_2\text{P})_2\text{CEEC}(\text{PPh}_2\text{S})_2]^{2-}$ [E = S (7b**), Se (**7c**)] and the radical anions $[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]^\cdot$ [E = S (**5b**), Se (**5c**)].** DFT-level electronic

structure calculations were performed for the dimers $[\text{Li}(\text{TMEDA})]_2\mathbf{7b,c}$ and for the paramagnetic monoanions $[\text{Li}(\text{TMEDA})]\mathbf{5b,c}$. Pertinent optimised structural parameters are given in Tables 3 and 4; there is an excellent agreement between the theoretical and experimental results. Notably, there is almost no change in the bond lengths and angles of the radicals $\mathbf{5b,c}$ upon formation of the corresponding diamagnetic dimers $\mathbf{7b,c}$.

An inspection of the frontier orbitals of $\mathbf{5b,c}$ and $\mathbf{7b,c}$ 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 themselves are comprised of an anti-bonding 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 monomers $\mathbf{5b,c}$ in the geometry they adopt in the dimer) 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 morphology of the SOMOs of the monoanionic radicals $\mathbf{5b,c}$ (Figure 3a) parallels that of the structurally 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 a significant contribution to the SOMO, the predicted hyperfine couplings (hfc) to these nuclei are small due to the vanishing s -wave contribution; 4.6 and 20.6 G for $\mathbf{5b}$ and $\mathbf{5c}$, respectively (*cf.* $a^{33}\text{S} \sim 2\text{G}$ for thioketyl anion radicals $[\text{R}_2\text{C}=\text{S}]^{\cdot-}$). [20a] Consequently, the largest hfc in $\mathbf{5b}$ ($\mathbf{5c}$), -19.4 (17.8) and -19.8 (18.1) G, are due to spin polarization 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. Hence, the EPR spectra of **5b** and **5c** are expected to be dominated by a broadened binomial triplet with minor contributions from ^{33}S and ^{77}Se satellites.

When solutions of the $[\text{Li}(\text{TMEDA})]^+$ salts of the dimeric dianions **7b** and **7c** in CH_2Cl_2 were monitored by EPR spectroscopy, two radical species were detected in both cases. A very broad binomial triplet with an hfc of ca. 18 G ($g = 2.0622$, Figure S5a) was detected for the selenium-containing system **7c** that is consistent with coupling to two equivalent ^{31}P ($I = 1/2$) centres. Since the ^{77}Se satellites ($I = 1/2$, 7.6 %) are not observable due to the weakness of the broad signals, the assignment of this signal pattern to **5c** is tentative. The all-sulfur dianion **7b**, on the other hand, showed a broad singlet ($g = 2.0260$, Figure S5b) with a width of ca. 24 G, which cannot be attributed to radical anion **5b** (cf. calculated $a(^{31}\text{P}) = 19$ G for **5b**). Significantly, the *major* radical species in the EPR spectra of CH_2Cl_2 solutions of *both 7b and 7c* exhibited a very strong 1:2:1 triplet with ^{33}S ($I = 3/2$, 0.75 %) satellites as judged by the relative intensities of the signals ($g = 2.0132$, Figure S5c).^[28] This signal pattern can be simulated with hfc's of 19.2 and 5.70 G arising from coupling to two equivalent ^{31}P and two ^{33}S centres, respectively. Since this *persistent* signal is detected in solutions of the $[\text{Li}(\text{TMEDA})]^+$ salts of both **7b** and **7c**, it must arise from a paramagnetic species that no longer contains the carbon-bound chalcogen (cf. formation of $\text{H}_2\text{C}(\text{PPh}_2\text{S})_2$ as the final decomposition product of **7b** and **7c**). However, the calculated EPR parameters for the anion radicals $[(\text{H})\text{C}(\text{PPh}_2\text{S})_2]^-$ and $[\text{C}(\text{PPh}_2\text{S})_2]^-$ are not consistent with the experimental data and the identity of the paramagnetic species could not be established.^[28]

Two-electron oxidation of 4c; synthesis and crystal structure of $\{[\text{Li}(\text{TMEDA})][\text{I}(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]\}$ $\{[\text{LiI}(\text{TMEDA})]\mathbf{6c}\}$. 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**, E = S; **6c**, E = Se). The treatment of the Se-containing derivative $[\text{Li}(\text{TMEDA})]_2\mathbf{4c}$ with *one equivalent* of iodine in toluene at $-80\text{ }^\circ\text{C}$ 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. Thus the NMR data indicated the incorporation of $(\text{TMEDA})\text{LiI}$ in the red product.

The dark red powder was recrystallised from toluene/pentane and shown to be the TMEDA-solvated LiI adduct of the selone $[(\text{Se})\text{C}(\text{PPh}_2\text{S})_2]$ (**6c**) by an X-ray structural determination (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 a heteroatom, 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 $[\text{LiI}(\text{TMEDA})]\mathbf{6c}$ appears to provide a necessary stabilising influence on this unusual selone.^[31, 32]

The Se-I distance of 2.7218(7) Å (Table 2) in [LiI(TMEDA)]**6c** represents a moderately strong interaction. This value is ca. 0.20 Å longer than the covalent Se-I bond lengths in the selenenyl iodides, ArSeI (Ar = 2,4,6-*t*Bu₃-C₆H₂, 2,4,6-Me₃-C₆H₂);^[33] *cf.* sum of covalent radii for selenium and iodine is 2.50 Å^[34]), and it is at the higher end of the distances (2.56-2.73 Å) observed by Devillanova et al. for charge-transfer complexes of selones with I₂ or IBr, which have been described as “strong” Se-I bonds.^[35] The Se-I distance in [LiI(TMEDA)]**6c** also falls in the range of 2.74-2.78 Å reported for organoselenenyl iodides, which are stabilised by an intramolecular Se⋯N interaction that, paradoxically, weakens the Se-I bond through electron donation into the Se-I σ* orbital.^[36] The C-Se distance of 1.815(4) Å falls within the range 1.77-1.84 Å 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) Å found for *N*-methylbenzothiadiazole-2(3*H*)-selone.^[38] We note, however, that the C-Se distance in the selenium donor is elongated by 0.04-0.06 Å in charge-transfer complexes that contain strong Se-I bonds.^[35] Thus, it seems reasonable to infer that the C=Se distance in **6c**, if it can be isolated,^[31] will be significantly shorter than the value of 1.815(4) Å found for the LiI adduct. The C-Se distance for the π-bonded C=Se group in the copper complex of [(Se)C(PPh₂O)₂] is 1.846(9) Å.^[18]

The Li-S contacts in [LiI(TMEDA)]**6c** are comparable to those in [Li(TMEDA)]₂**4c**, [Li(TMEDA)]₂**7b**, [Li(TMEDA)]₂**7c** and [Li(TMEDA)]₂**8b**. The P-C bond lengths along the series dianion **4c**, monoanion **5c** in the dimer **7c** and the neutral LiI adduct of **6c** (ca. 1.71 Å, 1.75 Å and 1.78 Å, respectively) display a steady increase concomitant with the shortening, and enhanced double bond character, of the C-Se

contact (1.970(3) Å, 1.885(3) Å and 1.815(4) Å, respectively). A significantly less pronounced trend is noted in the deviation from the planarity for the PCP carbon with the sum of bond angles of ca. 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 $\{[\text{Li}(\text{L})][(\text{SPh}_2\text{P})_2\text{CSS}(\text{H})\text{C}(\text{PPh}_2\text{S})_2]\} \{[\text{Li}(\text{L})]_2\mathbf{8b}; \text{L} = \text{TMEDA}, (12\text{-crown-4})_2\}$. The attempted two-electron oxidation of the all-sulfur dianion in $[\text{Li}(\text{TMEDA})]_2\mathbf{4b}$ by addition of *one equivalent* of iodine to an Et₂O solution at -80 °C produced a pale yellow powder. By contrast to the observations for the Se analogue **4c**, the ¹H NMR spectrum of this product in CD₂Cl₂ revealed the presence of phenyl and TMEDA groups with integrated intensities consistent with only *one* TMEDA group per *two* [(S)C(PPh₂S)₂] units. In addition, the ⁷Li NMR spectrum exhibited a singlet at 1.32 ppm, and the ³¹P{¹H} NMR spectrum showed two singlets at δ 48.8 and 51.8 in an approximately 1:1 ratio. The chemical shifts of the latter resonances were notably similar to those observed for the initial decomposition product of $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ in various solvents (*vide supra*) and the product from the reaction between $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$ and 12-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, $\{[\text{Li}(\text{L})][(\text{SPh}_2\text{P})_2\text{CSS}(\text{H})\text{C}(\text{PPh}_2\text{S})_2]\} \{[\text{Li}(\text{L})]_2\mathbf{8b}; \text{L} = \text{TMEDA}, (12\text{-crown-4})_2\}$. As depicted in Figure 4, the anionic part 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”

derivative of the dianion **7b**.^[39] The diamagnetic monoanion **8b** is formally constructed from the radical anion **5b**, [(S)C(PPh₂S)₂]^{-•}, and a neutral radical [H(S)C(PPh₂S)₂][•] connected through an S-S bond, which is significantly shorter than that in the dianionic precursor **7b** (by ca. 0.09 Å, Table 5). The four-coordinate C(2) atom in **8b** expectedly displays an elongation in the P-C and C-S bond lengths of ca. 0.1 Å compared to the three-coordinate C(1) atom in the anionic half of the ligand, while the disparity in the P-S distances between the anionic [(S)C(PPh₂S)₂]^{-•} and neutral [H(S)C(PPh₂S)₂][•] units is less pronounced (ca. 0.03 Å). The difference in P-S bond lengths between the ion-separated salt [Li(12-crown-4)₂]**8b** and [Li(TMEDA)]**8b** is insignificant despite the Li-S contacts in the latter. However, one of the P(Ph₂)S units of the [(S)C(PPh₂S)₂]^{-•} 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 ca. 28° in the dihedral C(1)-S(3)-S(6)-C(2) angle compared to [Li(TMEDA)]**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 [(CO)₄Mn{(Ph₂P)₂C(H)SS(H)C(PPh₂)₂}Mn(CO)₄]²⁺ indicating a weak C-H⋯S interaction in the solid state.^[24]

In summary, the dianionic all-sulfur system **7b** exhibits a pronounced tendency for proton abstraction which preempts the formation of the expected two-electron oxidation product SC(PPh₂S)₂. In this context we note that the HOMO of **7b** exhibits a significant contribution from the *p*-orbitals of the two backbone carbon atoms. By contrast, we were unable to detect the formation of the analogous protonated species from **7c** despite the observation that H₂C(PPh₂S)₂ is the final decomposition product from both **7b** and **7c** (*vide supra*).

Conclusions

We have developed a straightforward and efficient synthesis of the trichalcogeno species $[(E)C(PPh_2S)_2]^{2-}$ [E = S, Se] as their dilithium derivatives. The one-electron oxidation of these dianions produces novel dichalcogenides $[(SPh_2P)_2CEEC(PPh_2S)_2]^{2-}$ that are dimers of the corresponding monoanion radicals $[(E)C(PPh_2S)_2]^{-\bullet}$. 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. The two electron-oxidation of the dianion $[(Se)C(PPh_2S)_2]^{2-}$ produces the novel selone $[(Se)C(PPh_2S)_2]$, which is stabilised as the LiI adduct. By contrast, the attempted two-electron oxidation of the corresponding all-sulfur system produces a protonated species that is formally comprised of the anion radical $[(S)C(PPh_2S)_2]^{-\bullet}$ and the neutral radical $[H(S)C(PPh_2S)_2]^{\bullet}$ connected through an S-S bond.

The tridentate $[(E)C(PPh_2S)_2]^{2-}$ and tetradentate $[(SPh_2P)_2CEEC(PPh_2S)_2]^{2-}$ 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 $[(E)C(PPh_2S)_2]^{-\bullet}$ either via an internal redox process (one-electron oxidation) or as a result of E-E bond cleavage. Such studies are in progress.

Acknowledgments. The authors gratefully acknowledge financial support from the Academy of Finland (H.M.T) and the Natural Sciences and Engineering Research

Council (Canada). We thank Dr T. L. Roemmele (University of Lethbridge) for carrying out the CV and SEEPR experiments.

Experimental Section

General Procedures. All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glove box. The compounds [H₂C(PPh₂)₂] (Aldrich, 97%), TMEDA (Aldrich, 99%), MeLi (Aldrich, 1.6 M sol. in Et₂O), I₂ (Aldrich, 99.99+%) and 12-crown-4 (Alfa Aesar, 98%) were used as received. The dianion Li₂[C(PPh₂S)₂] (Li₂2) was prepared by a literature method and was used *in situ*.^[4] The solvents *n*-hexane, pentane, toluene, Et₂O and THF were dried by distillation over Na/benzophenone and CH₂Cl₂ over CaH₂ under an argon atmosphere prior to use. Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary.

Spectroscopic methods. The ¹H, ⁷Li, ¹³C{¹H}, ³¹P{¹H} and ⁷⁷Se NMR spectra were obtained in CD₂Cl₂ or in [D₈]THF at 23 °C on a Bruker DRX 400 spectrometer operating at 399.46, 155.24, 100.46, 161.71 and 76.17 MHz, respectively. ¹H and ¹³C{¹H} spectra are referenced to the solvent signal and the chemical shifts are reported relative to (CH₃)₄Si. ⁷Li, ³¹P{¹H} and ⁷⁷Se NMR spectra are referenced externally and the chemical shifts are reported relative to a 1.0 M solution of LiCl in D₂O, to an 85% solution of H₃PO₄, and to neat Me₂Se, respectively.

The X-band EPR spectra were recorded on a Bruker EMX 113 spectrometer

equipped with a variable-temperature accessory.

Computational Details. DFT calculations were performed for [Li(TMEDA)]**4c**, [Li(TMEDA)]**5b,c**, [Li(TMEDA)]**6c**, [Li(TMEDA)]₂**7b,c** and [Li(TMEDA)]**8b**. The structures were fully optimized by using a combination of the PBE0 exchange-correlation functional^[40] with the Ahlrichs' triple-zeta valence basis sets augmented by one set of polarization functions (def-TZVP).^[41] Hyperfine couplings of radicals [Li(TMEDA)]**5b,c** were calculated at the optimized geometries using the same basis set-density functional combination. All calculations were performed with Gaussian 03^[42] and Turbomole 6.1^[43] program packages. Visualizations for Figure 3 were done with gOpenMol.^[44]

X-ray crystallography. Crystallographic data for {[Li(TMEDA)]₂**4c**}, {[Li(TMEDA)]**6c**·C₇H₈}, {[Li(TMEDA)]₂**7b**·(CH₂Cl₂)_{0.33}}, {[Li(THF)₂]₂**7b**}, {[Li(TMEDA)]₂**7c**}, {[Li(TMEDA)]**8b**·(CH₂Cl₂)₂} and {[Li(12-crown-4)]₂**8b**} are summarized in Table 1 (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 a glass fibre. Diffraction data were collected on a Nonius KappaCCD diffractometer using monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at -100 °C. The data sets were corrected for Lorentz and polarization effects, and empirical absorption correction was applied to the net intensities. The structures were solved by direct methods using SHELXS-97 and refined using 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 (C-H = 0.95 Å for -CH, 0.99 Å for -CH₂ and

0.98 Å for -CH₃ hydrogens). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for -CH and -CH₂ hydrogens, and 1.5 times for -CH₃ hydrogens. 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 [Li(TMEDA)]₂**7b**·(CH₂Cl₂)_{0.33} and [Li(THF)]₂**7b** the carbon bound sulfur atoms show positional disorder with the site occupancy factors of ca. 0.93:0.07 and 0.88:0.12, respectively, in the final refinement. In addition, the structure of [Li(TMEDA)]₂**7b**·(CH₂Cl₂)_{0.33} is partially solvated with an occupancy of 0.33 for the CH₂Cl₂ 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 [Li(TMEDA)]**8b**·(CH₂Cl₂)₂ is also disordered with the refined occupancies of 0.59:0.41. CCDC-780827-780833 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 {[Li(TMEDA)]₂4b**}. A solution of [H₂C(PPh₂S)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 Et₂O, 2.40 mmol) was added via syringe. The reaction mixture was stirred for 15 min. at -80 °C and 2 ½ h at 23 °C.^[4] To the cloudy solution of Li₂[C(PPh₂S)₂] a solution of TMEDA (0.279 g, 1.20 mmol) in toluene (5 mL) was added at 23 °C. The reaction mixture was stirred for 15 min. after which it was added to a suspension of S₈ (0.038 g, 1.20 mmol) in toluene (5**

mL) at -80 °C. The reaction mixture was stirred for 15 min. at -80 °C and 2 h at 23 °C. The solvent was evaporated under vacuum and the product was washed with *n*-hexane affording [Li(TMEDA)]₂**4b** as an orange-red powder (0.748 g, 86%). ¹H NMR ([D₈]THF, 23 °C): δ 6.88-7.97 [m, 20H, C₆H₅], 2.31 [s, 8H, -CH₂ of TMEDA], 2.16 [s, 24H, -CH₃ of TMEDA]; ¹³C{¹H}: δ 141.1 [t, PCP carbon, ¹J(¹³C,³¹P) = 43.7 Hz], 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, -CH₂], 46.1 [s, TMEDA, -CH₃]; ⁷Li: δ 1.67; ³¹P{¹H}: δ 44.0; elemental analysis calcd (%) for C₃₇H₅₂Li₂N₄P₂S₃: C 61.31, H 7.23, N 7.73; found: C 60.97, H 7.11, N 7.64.

Synthesis of {[Li(TMEDA)]₂4c}. A solution of [H₂C(PPh₂S)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 Et₂O, 2.40 mmol) was added via syringe. The reaction mixture was stirred for 15 min. at -80 °C and 2 ½ h at 23 °C.^[41] To the cloudy solution of Li₂[C(PPh₂S)₂] a solution of TMEDA (0.279 g, 1.20 mmol) in toluene (5 mL) was added at 23 °C. The reaction mixture was stirred for 15 min. after which it was added to a suspension of elemental selenium (0.095 g, 1.20 mmol) in toluene (5 mL) at 0 °C. The reaction mixture was stirred for 15 min. at 0 °C and 2 h at 23 °C. The solvent was evaporated under vacuum and the product was washed with *n*-hexane affording [Li(TMEDA)]₂**4c** as a red powder (0.843 g, 91%). ¹H NMR ([D₈]THF, 23 °C): δ 6.88-7.80 [m, 20H, C₆H₅], 2.32 [s, 8H, -CH₂ of TMEDA], 2.16 [s, 24H, -CH₃ of TMEDA]; ¹³C{¹H}: δ 141.2 [t, PCP carbon, ¹J(¹³C,³¹P) = 46.2 Hz], 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, -CH₂], 46.2 [s, TMEDA, -CH₃]; ⁷Li: δ 2.05; ³¹P{¹H}: δ 43.5; ⁷⁷Se: δ -4.5; elemental analysis calcd (%) for C₃₇H₅₂Li₂N₄P₂S₂Se:

C 57.58, H 6.79, N 7.26; found: C 57.36, H 6.45, N 7.19. X-ray quality crystals were obtained by layering *n*-hexane onto the toluene solution of [Li(TMEDA)]₂**4c** after 24 h at -20 °C.

Synthesis of {[Li(TMEDA)]_{6c}}. A solution of [Li(TMEDA)]₂4c** (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 0.047 g of Se as described above) in toluene (20 mL) was cooled to -80 °C and a solution of I₂ (0.152 g, 0.60 mmol) in toluene (20 mL) was added via cannula. The reaction mixture was stirred for 15 min. at -80 °C and 2 h at 23 °C. The solvent volume was reduced to ca. 10 mL and 40 mL of *n*-hexane was added via cannula. The resulting white precipitate (LiCl) was removed by filtration and the solution was stored at -20 °C for 48 h affording [Li(TMEDA)]_{6c}·C₇H₈ as a dark red, crystalline powder (0.369 g, 71%). ¹H NMR (CD₂Cl₂, 23 °C): δ 7.13-7.86 [m, 20H, C₆H₅, and 5H of C₇H₈], 2.38 [s, 4H, -CH₂ of TMEDA], 2.29 [s, 3H of C₇H₈], 2.27 [s, 12H, -CH₃ of TMEDA]; ⁷Li: δ 1.64; ³¹P{¹H}: δ 54.2; elemental analysis calcd (%) for C₃₈H₄₄ILiN₂P₂S₂Se ([Li(TMEDA)]_{6c} + 1 mole of toluene solvate, *cf.* NMR spectroscopic and crystallographic data): C 52.6, H 5.11, N 3.23; found: C 52.17, H 5.17, N 3.33. ¹³C and ⁷⁷Se 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 [Li(TMEDA)]_{6c} after 4 h at 5 °C.**

Synthesis of {[Li(TMEDA)]₂7b**}. A solution of [Li(TMEDA)]₂**4b** (1.20 mmol, prepared in situ from 0.538 g of [H₂C(PPh₂S)₂], 1.50 mL of MeLi, 0.279 g of TMEDA and 0.038 g of S₈ as described above) in toluene (20 mL) was cooled to -80 °C and a solution of I₂**

(0.152 g, 0.60 mmol) in toluene (10 mL) was added via cannula. The reaction mixture was stirred for 15 min. at -80 °C and 2 h at 23 °C. The resulting powder was allowed to settle and the solvent was decanted via cannula. The precipitate was washed with toluene affording [Li(TMEDA)]₂**7b** as a yellow powder (0.430 g, 60%). ¹H NMR (CD₂Cl₂, 23 °C): δ 6.90-7.90 [s, br, 40H, C₆H₅], 2.25 [s, 8H, -CH₂ of TMEDA], 1.98 [s, 24H, -CH₃ of TMEDA]; ⁷Li: δ 1.20; ³¹P{¹H}: δ 50.2; elemental analysis calcd (%) for C₆₂H₇₂Li₂N₄P₄S₆: C 61.88, H 6.03, N 4.66; found: C 61.37, H 6.16, N 4.64. At room temperature, the solutions of [Li(TMEDA)]₂**7b** (THF, CH₂Cl₂, CH₃CN) form [Li(TMEDA)]₂**8b** followed by decomposition and formation of [H₂C(PPh₂S)₂] (**9**) as proven by the NMR spectroscopy.^[27] X-ray quality crystals were obtained by layering *n*-hexane on top of the CH₂Cl₂ solution of [Li(TMEDA)]₂**7b** after 3 h at 23 °C. When *n*-hexane was layered onto the THF solution of [Li(TMEDA)]₂**7b**, crystals of [Li(THF)₂]₂**7b** were obtained after 12 h at 5 °C.

Synthesis of {[Li(TMEDA)]₂7c**}. A solution of [Li(TMEDA)]₂**4c** (1.20 mmol, prepared in situ from 0.538 g of [H₂C(PPh₂S)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 I₂ (0.152 g, 0.60 mmol) in toluene (10 mL) was added via cannula. The reaction mixture was stirred for 15 min. at -80 °C and 2 h at 23 °C. The resulting powder was allowed to settle and the solvent was decanted via cannula. The precipitate was washed with toluene affording [Li(TMEDA)]₂**7c** as an orange powder (0.578 g, 74%). ¹H NMR (CD₂Cl₂, 23 °C): δ 7.13-7.63 [m, 40H, C₆H₅], 2.19 [s, 8H, -CH₂ of TMEDA], 1.88 [s, 24H, -CH₃ of TMEDA]; ⁷Li: δ 1.24; ³¹P{¹H}: δ 50.5; elemental analysis calcd (%) for**

C₆₂H₇₂Li₂N₄P₄S₄Se₂: C 57.40, H 5.59, N 4.32; found: C 57.55, H 5.71, N 4.19. At room temperature, the solutions of [Li(TMEDA)]₂**7c** (THF, CH₂Cl₂, CH₃CN) decompose and eventually form [H₂C(PPh₂S)₂] (**9**) (NMR spectroscopy)^[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)]8b**}. 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 via cannula. The reaction mixture was stirred for 15 min. at -80 °C and 2 h at 23 °C. The resulting pale yellow powder was allowed to settle and the solvent was decanted via cannula. The product was washed with pentane and Et₂O, and it was identified as [Li(TMEDA)]**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 [s, 12H, -CH₃ of TMEDA]; ⁷Li: δ 1.32; ³¹P{¹H}: δ 51.8 (s), 48.8 (s). At room temperature, the solutions of [Li(TMEDA)]**8b** (THF, CH₂Cl₂, CH₃CN) decompose and eventually form [H₂C(PPh₂S)₂] (**9**) as proven by the NMR spectroscopy.^[27] X-ray quality crystals of [Li(TMEDA)]**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)]8b**}. A solution of [Li(TMEDA)]₂**7b** (0.241g, 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 via cannula. The reaction mixture was stirred for 10**

min. at 0 °C and 1 h at 23 °C. The solvent was evaporated under a vacuum and the product was washed with Et₂O and toluene affording [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 [s, 32H, -CH₂ of 12-crown-4]; ⁷Li: δ -0.50; ³¹P{¹H}: δ 51.0 (s), 47.3 (s). At room temperature, solutions of [Li(12-crown-4)₂]**8b** (THF, CH₂Cl₂, CH₃CN) decompose and eventually form [H₂C(PPh₂S)₂] (**9**) as proven by the 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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Table 1. Crystallographic data for [Li(TMEDA)]₂**4c**, [Li(TMEDA)]**6c**·C₇H₈, [Li(TMEDA)]₂**7b**·(CH₂Cl₂)_{0.33}, [Li(THF)₂]₂**7b**, [Li(TMEDA)]₂**7c**, [Li(TMEDA)]**8b**·(CH₂Cl₂)₂ and [Li(12-crown-4)]₂**8b**.^{[a], [b]}

	[Li(TMEDA)] ₂ 4c	[Li(TMEDA)] 6c ·C ₇ H ₈	[Li(TMEDA)] ₂ 7b ·(CH ₂ Cl ₂) _{0.33}	[Li(THF) ₂] ₂ 7b	[Li(TMEDA)] ₂ 7c	[Li(TMEDA)] 8b ·(CH ₂ Cl ₂) ₂	[Li(12-c-4)] ₂ 8b
emp. formula	C ₃₇ H ₅₂ Li ₂ N ₄ P ₂ S ₂ Se	C ₃₈ H ₄₄ LiN ₂ P ₂ S ₂ Se	C _{62.33} H _{72.67} Cl _{0.67} Li ₂ N ₄ P ₄ S ₆	C ₆₆ H ₇₂ Li ₂ O ₄ P ₄ S ₆	C ₆₂ H ₇₂ Li ₂ N ₄ P ₄ S ₄ Se ₂	C ₅₈ H ₆₁ Cl ₄ LiN ₂ P ₄ S ₆	C ₆₆ H ₇₃ LiO ₈ P ₄ S ₆
Fw.	771.73	867.61	1231.02	1259.36	1297.16	1251.07	1317.42
cryst. system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	P -1	P2 ₁ /c	P -1	P2 ₁ /n	P2 ₁ /n	P -1	P2 ₁ /c
<i>a</i> , Å	11.365(2)	15.493(3)	9.195(2)	11.912(2)	9.446(2)	13.602(3)	21.060(4)
<i>b</i> , Å	12.324(3)	14.338(3)	13.743(3)	16.931(3)	21.577(4)	13.810(3)	17.647(4)
<i>c</i> , Å	16.424(3)	18.962(4)	13.953(3)	16.006(3)	16.073(3)	17.859(4)	19.872(4)
<i>α</i> , deg.	92.89(3)	90.00	104.66(3)	90.00	90.00	107.71(3)	90.00
<i>β</i> , deg.	102.35(3)	109.76(3)	100.87(3)	90.94	103.61(3)	100.51(3)	117.42(3)
<i>γ</i> , deg.	112.96(3)	90.00	104.04(3)	90.00	90.00	90.92(3)	90.00
<i>V</i> , Å ³	2046.1(9)	3964(2)	1595.1(8)	3228(1)	3184(1)	3133(1)	6556(2)
<i>Z</i>	2	4	1	2	2	2	4
<i>ρ</i> _{calcd} , g/cm ³	1.253	1.454	1.281	1.296	1.353	1.326	1.335
<i>μ</i> (Mo K α), mm ⁻¹	1.128	1.940	0.384	0.358	1.434	0.529	0.360

crystal size, mm ³	0.20×0.16×0.12	0.32×0.12×0.08	0.16×0.12×0.04	0.24×0.20×0.16	0.08×0.08×0.02	0.16×0.12×0.08	0.16×0.12×0.10
<i>F</i> (000)	808	1752	648.4	1324	1340	1300	2768
Θ range, deg	2.06-25.03	2.52-25.02	2.37-25.03	2.15-25.02	2.29-25.03	2.13-25.03	2.18-25.03
reflns collected	13729	12575	10359	9022	21185	20887	42112
unique reflns	7211	6931	5560	5609	5616	11008	11551
<i>R</i> _{int}	0.0306	0.0344	0.0367	0.0307	0.0570	0.0409	0.1070
reflns [<i>I</i> >2σ(<i>I</i>)]	6238	5748	4639	4808	4703	8591	8998
<i>R</i> ₁ [<i>I</i> >2σ(<i>I</i>)] ^[c]	0.0423	0.0422	0.0583	0.0593	0.0423	0.0600	0.0679
<i>wR</i> ₂ (all data) ^[d]	0.1034	0.0930	0.1253	0.1455	0.0942	0.1517	0.1707
GOF on <i>F</i> ²	1.043	1.072	1.089	1.045	1.065	1.056	1.093
completeness	0.995	0.990	0.988	0.985	0.999	0.993	0.998

^[a] λ (MoKα) = 0.71073 Å. ^[b] T = -100 °C. ^[c] $R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$. ^[d] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for [Li(TMEDA)]₂**4c** and [Li(TMEDA)]**6c** (calculated values in square brackets).

	[Li(TMEDA)] ₂ 4c	[Li(TMEDA)] 6c		[Li(TMEDA)] ₂ 4c	[Li(TMEDA)] 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).

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] for $[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$, $[\text{Li}(\text{THF})_2]_2\mathbf{7b}$ and $[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$ (calculated values in square brackets).

	$[\text{Li}(\text{TMEDA})]_2\mathbf{7b}$	$[\text{Li}(\text{THF})_2]_2\mathbf{7b}$	$[\text{Li}(\text{TMEDA})]_2\mathbf{7c}$
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).

Table 4. Selected bond lengths [\AA] and angles [$^\circ$] calculated for $[\text{Li}(\text{TMEDA})]\mathbf{5b}$, and $[\text{Li}(\text{TMEDA})_2]\mathbf{5c}$.

	$[\text{Li}(\text{TMEDA})]\mathbf{5b}$	$[\text{Li}(\text{TMEDA})]\mathbf{5c}$
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(2)	104.1	104.2
S(1)-Li(1)-S(2)	109.9	109.6

Table 5. Selected bond lengths [\AA] and angles [$^\circ$] 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(2)	98.2(2) [86.8]	-	C(1)-S(3)-S(6)-C(2)	117.9(2) [116.6]	90.0(2) [89.2]

Figure Captions

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

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

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 .

Figure 4. Crystal structure of (a) $[\text{Li}(\text{TMEDA})]\mathbf{8b}$ and (b) the anion $\mathbf{8b}$ in the ion-separated salt $[\text{Li}(\text{12-crown-4})_2]\mathbf{8b}$ with thermal ellipsoids drawn at 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.

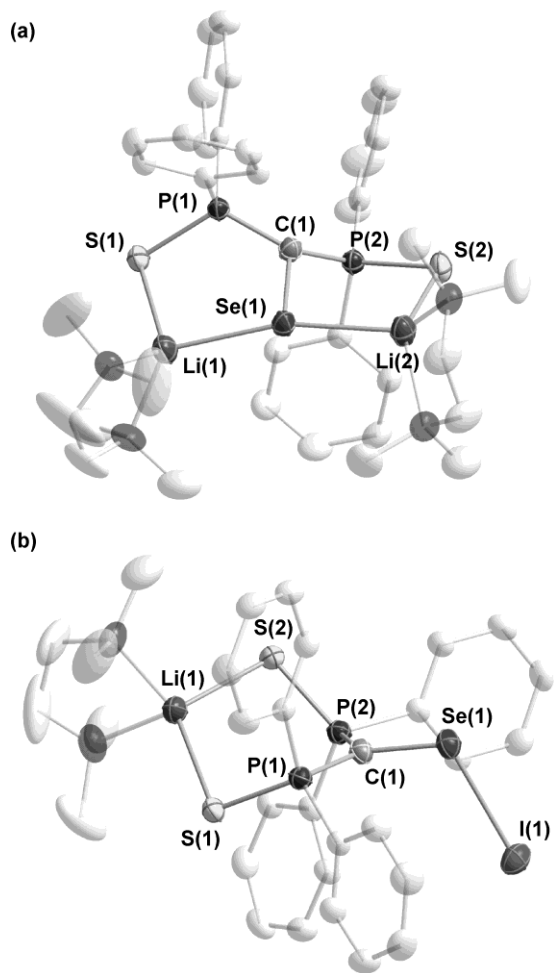


Figure 1.

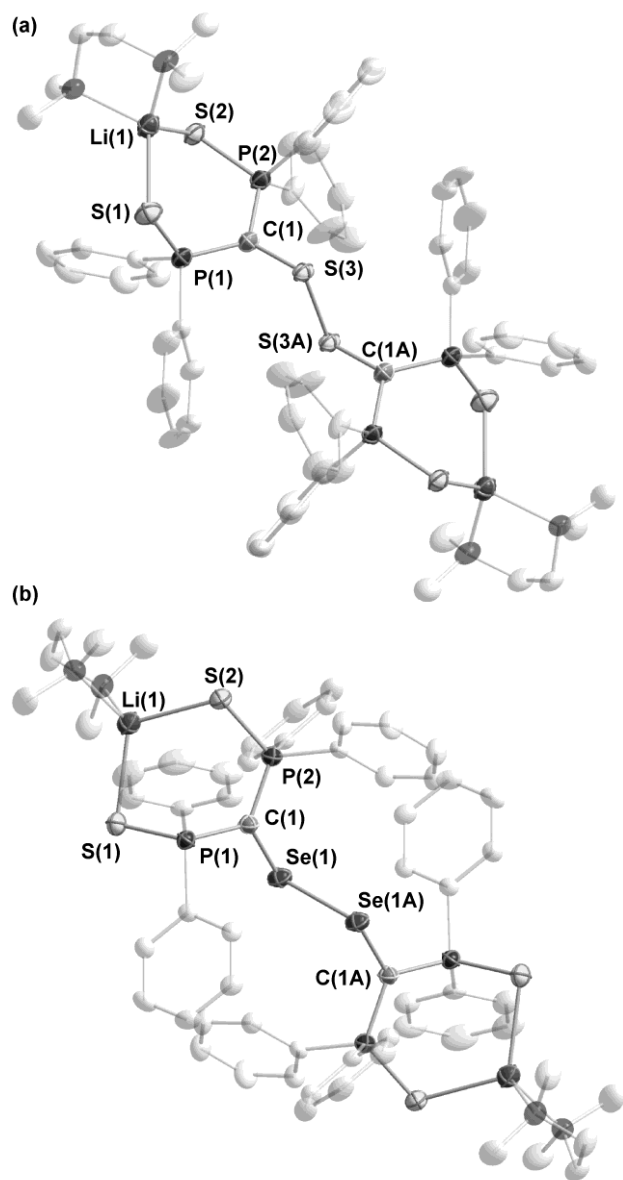


Figure 2.

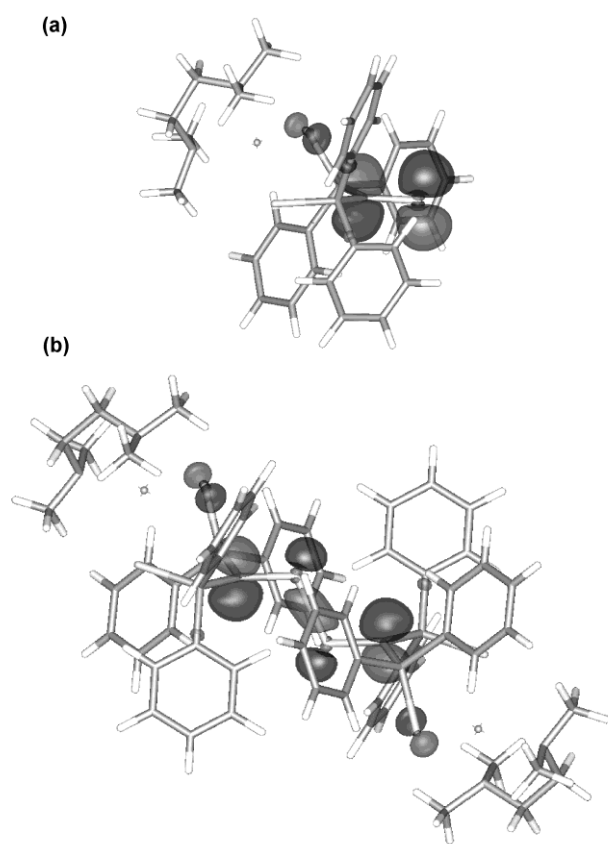


Figure 3.

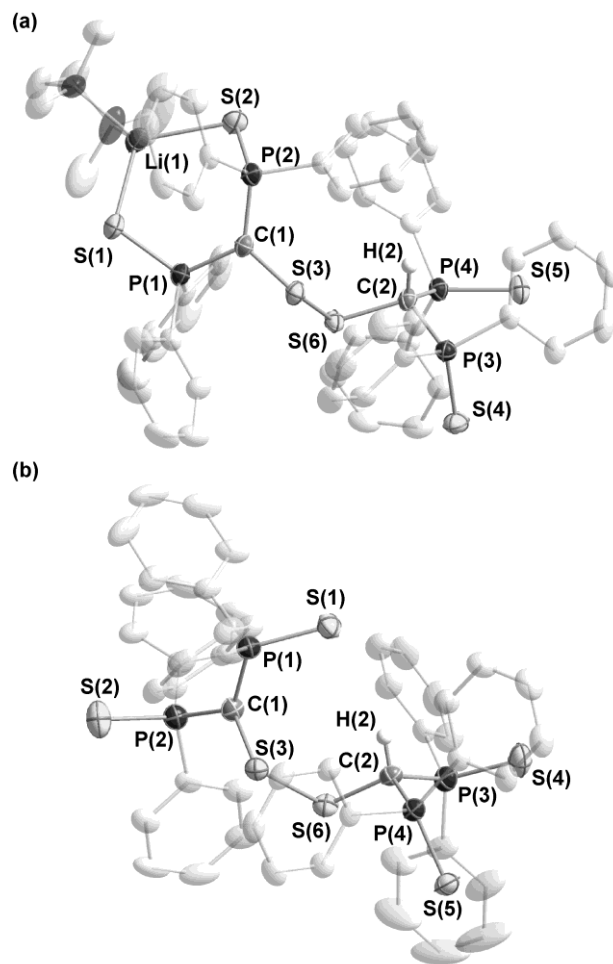


Figure 4.