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Structural and Spectroscopic Studies of the PCP-Bridged Heavy Chalcogen-Centered Monoanions, $[\text{HC}(\text{PPh}_2\text{E})(\text{PPh}_2)]^-$ (E = Se, Te) and $[\text{HC}(\text{PR}_2\text{E})_2]^-$ (E = Se, Te, R = Ph; E = Se, R = *i*Pr): Homoleptic Group 12 Complexes and One-electron Oxidation of $[\text{HC}(\text{PR}_2\text{Se})_2]^-$

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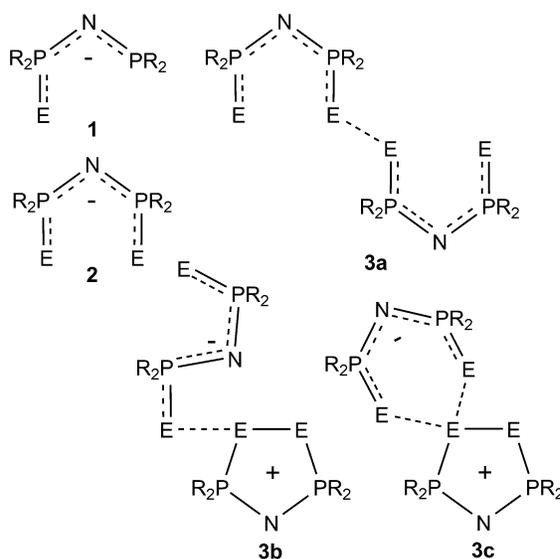
Abstract:

Selenium- and tellurium-containing bis(diphenylphosphinoyl)methane monoanions were prepared by oxidation of the anion $[\text{HC}(\text{PPh}_2)_2]^-$ with elemental chalcogens. The selenium-containing *iso*-propyl derivative was synthesized by generating $[\text{H}_2\text{C}(\text{P}^i\text{Pr}_2)_2]$ via a reaction between $[\text{H}_2\text{C}(\text{PCl}_2)_2]$ and four equivalents of $^i\text{PrMgCl}$ prior to *in situ* oxidation with selenium followed by deprotonation with LiN^iPr_2 . The solid-state structures of the lithium salts of the monochalcogeno anions $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PPh}_2\text{E})(\text{PPh}_2)]$ [E = Se (**Li7a**), E = Te (**Li7b**)] and the dichalcogeno anions $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PR}_2\text{Se})_2]$ [R = Ph (**Li8a**), ^iPr (**Li8c**)] revealed five- and six-membered LiEPCP and LiSePCPSe rings, respectively. The homoleptic group 12 complexes $\{\text{M}[\text{HC}(\text{PPh}_2\text{Se})_2]_2\}$ [M = Zn (**9a**); Hg (**9b**)] were prepared from **Li8a** and MCl_2 and shown to have distorted tetrahedral structures; the non-planarity of the carbon center in the $\text{PC}(\text{H})\text{P}$ unit of the Zn complex **9a** is attributed to crystal packing effects. The complexes **Li7a**, **Li7b**, **Li8a**, $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PPh}_2\text{Te})_2]$ (**Li8b**), **Li8c**, **9a** and **9b** were characterized in solution by multinuclear (^1H , ^7Li , ^{13}C , ^{31}P , ^{77}Se , ^{125}Te and ^{199}Hg) NMR spectroscopy. One-electron oxidation of **Li8a** and **Li8c** with iodine in a variety of organic solvents produced $[\text{H}_2\text{C}(\text{PR}_2\text{Se})_2]$ (R = ^iPr , Ph) as the final product, presumably owing to hydrogen abstraction from the solvent. DFT calculations revealed a significant contribution from the *p*-orbital on carbon to the SOMO of the radicals $[\text{HC}(\text{PR}_2\text{Se})_2]^\cdot$ (R = ^iPr , Ph).

Introduction

Mono- and dichalcogenoimidodiphosphinate monoanions, $[\text{N}(\text{PR}_2\text{E})(\text{PR}_2)]^-$ (**1**) and $[\text{N}(\text{PR}_2\text{E})_2]^-$ (**2**) ($\text{R} = \textit{i}\text{Pr}, \textit{t}\text{Bu}, \text{Ph}$; $\text{E} = \text{S}, \text{Se}, \text{Te}$), are versatile acyclic ligands that have attracted considerable interest over decades.^{1, 2} While the monochalcogeno ligands **1** and the sulfur- and selenium-containing dichalcogeno ligands **2** are readily prepared by deprotonating the neutral precursors,^{1, 3} the synthesis of the tellurium congener **2** requires generation of the P(III)NP(III) anion $[\text{N}(\text{PR}_2)_2]^-$ prior to oxidation with the elemental chalcogen.⁴

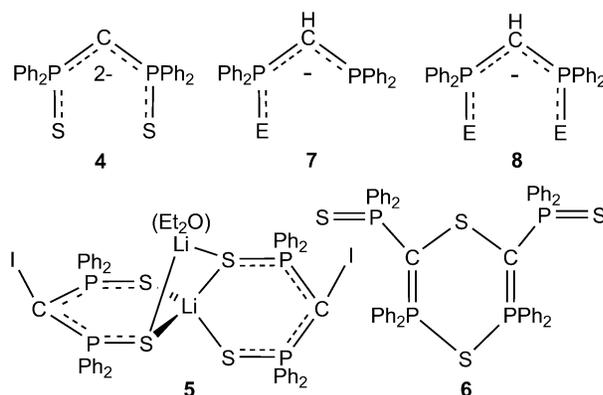
Of particular interest is the recent utilization of the *dichalcogenoimidodiphosphinate* monoanions **2** ($\text{E} = \text{S}, \text{Se}, \text{Te}$; $\text{R} = \textit{i}\text{Pr}, \textit{t}\text{Bu}$) in redox reactions that have revealed new and unanticipated aspects of the fundamental chemistry of these well-studied anions. One-electron oxidation with iodine produces neutral dimers $[\text{EPR}_2\text{NR}_2\text{PE}-\text{EPR}_2\text{NR}_2\text{PE}]$ (**3a**), formally involving the association of two $[\text{EPR}_2\text{NR}_2\text{PE}]^\bullet$ radicals with elongated central E-E bonds.^{5, 6} Intriguingly, in addition to the neutral form **3a** these dimers can also exist as contact ion pairs where the $[\text{N}(\text{PR}_2\text{E})_2]^-$ anion exhibits either an acyclic, mono-dentate (**3b**) or *E,E'*-chelated (**3c**) coordination to one of the chalcogens of the incipient cyclic cation $[\text{N}(\text{PR}_2\text{E})_2]^+$; the calculated energy differences between the forms **3a-c** are small especially when $\text{E} = \text{S}$ or Se .^{5, 6}



Furthermore, the formally 6π -electron five-membered cations $[\text{N}(\text{PR}_2\text{E})_2]^+$ ($\text{E} = \text{S}, \text{Se}$,

Te; R = *i*Pr, *t*Bu) are obtained as iodide salts by two-electron oxidation of the corresponding anions (**2**).^{6a, 7} By contrast, the oxidation of the phenyl-substituted derivatives [N(PPh₂E)₂]⁻ (E = Se, Te) with one equivalent of iodine was found to be chalcogen-dependent; the five-membered ring [N(PPh₂Te)₂]⁺ was obtained for tellurium, whereas the unusual six-membered ring [N(PPh₂Se)₂(μ-Se)]⁺ was the major product in the case of selenium.^{7b}

These intriguing and diverse results redirected our attention to the oxidative behavior of the isoelectronic, sulfur-containing [C(PPh₂S)₂]²⁻ dianion (**4**), which is prepared from [H₂C(PPh₂S)₂] by treatment with two equivalents of methyl-lithium.⁸ In this context, we recently reported that the two-electron oxidation of the dianion **4** with iodine results in the formation of a remarkably stable dicarbenoid [(Et₂O)(μ-Li)][(μ₄-Li){IC(PPh₂S)₂]₂] (**5**).⁹ In the absence of the combination of LiI with the initially formed [:C(PPh₂S)₂] carbene, the novel, unsaturated six-membered C₂P₂S₂ ring in [(SPh₂P)₂C₂(PPh₂)₂S₂] (**6**) is obtained.⁹ Prior to our study, Le Floch and co-workers had noted that the mild oxidation of Li₂**4** with hexachloroethane produces a monomeric form of **5**, *i.e.* [ClC(PPh₂S)₂Li(OEt₂)₂].¹⁰



While the sulfur-containing dianion **4** has attracted considerable interest lately, primarily due to the exciting work of Le Floch *et al.*,⁸⁻¹¹ the heavier chalcogen (Se, Te) analogues of **4** have not been reported. Furthermore, even information on the related monoanions [HC(PPh₂E)(PPh₂)]⁻ (**7**, E = Se, Te) and [HC(PPh₂E)₂]⁻ (**8**, E = Se, Te) is sparse. The former are isoelectronic with the monochalcogenoimidodiphosphinate anions **1**, while the dichalcogeno anions **8** are isoelectronic

with the monoanions **2** and the dianion **4**. A search of the the Cambridge Crystallographic Database revealed only two complexes of **7** or **8**, viz. the group 14 monoseleno compound $\{\text{Ge}[(\text{Me}_3\text{Si})\text{C}(\text{PMe}_2)(\text{PMe}_2\text{Se})_2]\}^{12}$ and the diseleno complex $\{\text{Cp}^*\text{Rh}[\text{HC}(\text{PPh}_2\text{Se})_2]\text{ClO}_4\}^{13}$ in which the rhodium center is connected to the anionic PCP-carbon. No solid-state structures of complexes of the tellurium-containing anions **7** or **8** ($\text{E} = \text{Te}$) or their neutral precursors have been reported.

In this contribution we report the synthesis, spectroscopic and structural characterization of the lithium salts $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PPh}_2\text{E})(\text{PPh}_2)]$ [$\text{E} = \text{Se}$ (**Li7a**); $\text{E} = \text{Te}$ (**Li7b**)] and $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PPh}_2\text{E})_2]$ [$\text{E} = \text{Se}$ (**Li8a**), Te (**Li8b**)]. In addition, we describe a one-step reaction to generate the *iso*-propyl derivative of the PCP ligand, $[\text{H}_2\text{C}(\text{P}^i\text{Pr}_2)_2]$, for the subsequent production of $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{P}^i\text{Pr}_2\text{Se})_2]$ (**Li8c**). The utility of **Li8a** as a metathetical reagent is demonstrated by the preparation of the homoleptic group 12 complexes $\{\text{M}[\text{HC}(\text{PPh}_2\text{Se})_2]_2\}$ [$\text{M} = \text{Zn}$ (**9a**); Hg (**9b**)] which were structurally characterized. The one-electron oxidation of **Li8a** and **Li8c** with iodine was investigated for comparison with the analogous reactions reported for the PNP-bridged monoanions **2** (*vide supra*). DFT calculations were carried out in order to explain the different behavior of the transient radicals $[\text{HC}(\text{PR}_2\text{Se})_2]^{\bullet}$ (**10a**, $\text{R} = \text{Ph}$; **10c**, $\text{R} = ^i\text{Pr}$) (hydrogen abstraction) compared to that of $[\text{N}(\text{PR}_2\text{Se})_2]^{\bullet}$ ($\text{R} = ^i\text{Pr}, ^t\text{Bu}$) (dimerization).^{5, 6}

Experimental section

Reagents and 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 $[\text{H}_2\text{C}(\text{PPh}_2)_2]$ (Aldrich, 97%), $[\text{H}_2\text{C}(\text{P}^i\text{Pr}_2)_2]$ (Strem Chemicals, >90%), $^i\text{PrMgCl}$ (Aldrich, 2.0 M sol. in THF), TMEDA (Aldrich, 99%), MeLi (Aldrich, 1.6 M sol. in Et_2O), ZnCl_2 (Acros Organics,

99.99%) and HgCl₂ (Strem Chemicals, 99+%) were used as received. TMEDA·Li[HC(PPh₂)₂] was prepared by the reaction between H₂C(PPh₂)₂ and MeLi in the presence of TMEDA in Et₂O.¹⁴ The solvents *n*-hexane, toluene, Et₂O and THF were dried by distillation over Na/benzophenone 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, ³¹P, ⁷⁷Se, ¹²⁵Te and ¹⁹⁹Hg NMR spectra were obtained in d₈-THF at 23 °C on a Bruker DRX 400 spectrometer operating at 399.46, 155.24, 100.46, 161.71, 76.17, 125.90 and 71.49 MHz, respectively. ¹H and ¹³C spectra are referenced to the solvent signal and the chemical shifts are reported relative to (CH₃)₄Si. ⁷Li and ³¹P NMR spectra are referenced externally and the chemical shifts are reported relative to a 1.0 M solution of LiCl in D₂O and to an 85% solution of H₃PO₄. Similarly, the ⁷⁷Se, ¹²⁵Te and ¹⁹⁹Hg NMR spectra are reported relative to neat Me₂Se, Me₂Te and Me₂Hg, respectively.

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

X-ray crystallography

Crystallographic data for Li**7a**, Li**7b**, Li**8a**, Li**8c**, **9a** and **9b** are summarized in Table 1 (see also supplementary data). Crystals of TMEDA·Li[HC(PPh₂Se)(PPh₂)] (Li**7a**), TMEDA·Li[HC(PPh₂Te)(PPh₂)] (Li**7b**), TMEDA·Li[HC(PPh₂Se)₂] (Li**8a**), TMEDA·Li[HC(P^{*i*}Pr₂Se)₂] (Li**8c**), {Zn[HC(PPh₂Se)₂]₂} (**9a**) and {Hg[HC(PPh₂Se)₂]₂} (**9b**) 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 (λ = 0.71073 Å) 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.^{15, 16} 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 final refinement the hydrogen atoms were riding on their respective carbon atoms. In the structure of **Li7b** the hydrogen atom bonded to the PCP carbon was located from the Fourier density map and it was refined.

Computational Details

Theoretical calculations on the neutral radicals **10** were done with the Gaussian 03 program using density functional theory.¹⁷ Molecular structures were optimized with the hybrid PBE1PBE exchange-correlation functional¹⁸ together with the Ahlrichs' TZVP basis sets.¹⁹ Hyperfine coupling constants were then calculated by single-point calculations employing the optimized structures and the basis set combination used to for the optimizations. The orbital plots were obtained by the program gOpenMol.²⁰

Synthesis of TMEDA·Li[HC(PPh₂Se)(PPh₂)] (**Li7a**).

A mixture of TMEDA·Li[HC(PPh₂)₂] (0.507 g, 1.00 mmol) and elemental selenium (0.079 g, 1.00 mmol) in 30 mL of toluene was stirred for 10 min at -80 °C and 2 ½ h at 23 °C. The solvent was evaporated under vacuum and the resulting oily product was treated with 10 mL of Et₂O affording **Li7a** as a yellow powder (0.556 g, 95%). Anal. Calcd for C₃₁H₃₇LiN₂P₂Se: C 63.59; H 6.37; N 4.78. Found: C 63.38; H 6.34; N 4.58. ¹H NMR (d₈-THF, 23 °C): δ 6.83-7.66 [m, 20H, C₆H₅], 2.06 [s, 4H, -CH₂ of TMEDA], 1.90 [s, 12H, -CH₃ of TMEDA], 1.44 [dd, 1H, -CH of the

PCP carbon, $^2J(^1\text{H}, ^{31}\text{P}) = 7.6$ and 12.4 Hz]. ^{13}C NMR (23 °C): δ 147.5 [dd, Ph, C_{ipso} , $^1J(^{13}\text{C}, ^{31}\text{P}) = 10.6$ Hz, $^3J(^{13}\text{C}, ^{31}\text{P}) = 1.6$ Hz], 144.6 [dd, Ph, C_{ipso} , $^1J(^{13}\text{C}, ^{31}\text{P}) = 74.7$ Hz, $^3J(^{13}\text{C}, ^{31}\text{P}) = 3.5$ Hz], 132.4 [d, Ph, C_{ortho} , $^2J(^{13}\text{C}, ^{31}\text{P}) = 16.5$ Hz], 132.2 [d, Ph, C_{ortho} , $^2J(^{13}\text{C}, ^{31}\text{P}) = 10.2$ Hz], 129.0 [d, Ph, C_{para} , $^4J(^{13}\text{C}, ^{31}\text{P}) = 2.8$ Hz], 127.9 [d, Ph, C_{meta} , $^3J(^{13}\text{C}, ^{31}\text{P}) = 6.6$ Hz], 127.5 [d, Ph, C_{meta} , $^3J(^{13}\text{C}, ^{31}\text{P}) = 11.6$ Hz], 126.7 [s, Ph, C_{para}], 58.7 [s, TMEDA, $-\text{CH}_2$], 46.1 [s, TMEDA, $-\text{CH}_3$], 20.1 [dd, PCP carbon, $^1J(^{13}\text{C}, ^{31}\text{P}) = 107.7$ Hz, $^1J(^{13}\text{C}, ^{31}\text{P}) = 20.4$ Hz]. ^7Li NMR (23 °C): δ 1.41. ^{31}P NMR (23 °C): δ 33.2 [d, $^2J(^{31}\text{P}, ^{31}\text{P}) = 173.7$ Hz, $^1J(^{31}\text{P}, ^{77}\text{Se}) = 556$ Hz], -10.9 [d, br, $^2J(^{31}\text{P}, ^{31}\text{P}) = 173.7$ Hz]. ^{77}Se NMR (23 °C): δ -203 [dd, $^1J(^{77}\text{Se}, ^{31}\text{P}) = 557$ Hz, $^2J(^{77}\text{Se}, ^{31}\text{P}) = 12.6$ Hz]. X-ray quality crystals of **Li7a** were obtained by dissolving the yellow powder in boiling toluene and then allowing the solution to cool down to room temperature in *ca.* 10 h.

Synthesis of TMEDA·Li[HC(PPh₂Te)(PPh₂)] (**Li7b**).

A mixture of TMEDA·Li[HC(PPh₂)₂] (0.253 g, 0.50 mmol) and elemental tellurium (0.064 g, 0.50 mmol) in 40 mL of toluene was stirred for 10 min at -80 °C and 2 ½ h at 23 °C. A small amount of unreacted tellurium was removed by filtration and the solvent was evaporated under vacuum. Washing with *n*-hexane afforded **Li7b** as a bright yellow powder (0.260 g, 82%, calculated as **Li7b**) in *ca.* 97% purity; removal of the spectroscopically detectable by-products [H₂C(PPh₂)₂] and TMEDA·Li[HC(PPh₂Te)₂] (**Li8b**) was not possible due to the extreme moisture-sensitivity of **Li7b**. ^1H NMR (*d*₈-THF, 23 °C): δ 7.12-7.92 [m, 20H, C₆H₅], 2.34 [s, 4H, $-\text{CH}_2$ of TMEDA], 2.17 [s, 12H, $-\text{CH}_3$ of TMEDA], 1.61 [s, br, 1H, $-\text{CH}$ of the PCP carbon]. ^{13}C NMR (23 °C): δ 148.3 [s, br Ph, C_{ipso}], 144.2 [s, br, Ph, C_{ipso}], 132.9 [s, br, Ph, C_{ortho}], 128.9 [s, br, Ph, C_{para}], 127.3 [s, br, Ph, C_{meta}], 126.5 [s, br, Ph, C_{para}], 58.7 [s, TMEDA, $-\text{CH}_2$], 46.2 [s, TMEDA, $-\text{CH}_3$], 22.0 [s, br, PCP carbon]. ^7Li NMR (23 °C): δ 1.01. ^{31}P NMR (23 °C): δ -4.4 [d, $^2J(^{31}\text{P}, ^{31}\text{P}) = 181.9$ Hz], -14.2 [d, $^2J(^{31}\text{P}, ^{31}\text{P}) = 181.9$ Hz, $^1J(^{31}\text{P}, ^{125}\text{Te}) = 1359$ Hz]. ^{125}Te NMR (23 °C): δ -374 [d, br, $^1J(^{125}\text{Te}, ^{31}\text{P}) =$

1358 Hz]. X-ray quality crystals of Li**7b** were obtained by dissolving the yellow powder in boiling *n*-hexane and then allowing the solution to cool down to room temperature in *ca.* 2 h.

Synthesis of TMEDA·Li[HC(PPh₂Se)₂] (Li**8a**).

A mixture of TMEDA·Li[HC(PPh₂)₂] (0.507 g, 1.00 mmol) and elemental selenium (0.166 g, 2.10 mmol, slight excess) in 50 mL of toluene was stirred for 10 min. at -80 °C, ½ h at 23 °C and 2 ½ h at 55 °C. The excess selenium was removed by filtration and the solvent was evaporated under vacuum. The resulting amorphous product was washed with 20 mL of *n*-hexane affording Li**8a** as a pale yellow powder (0.618 g, 93%). Anal. Calcd for C₃₁H₃₇LiN₂P₂Se₂: C 56.04; H 5.61; N 4.22. Found: C 55.73; H 5.54; N 4.05. ¹H NMR (d₈-THF, 23 °C): δ 7.25-8.01 [m, 20H, C₆H₅], 2.32 [s, 4H, -CH₂ of TMEDA], 2.14 [s, 12H, -CH₃ of TMEDA], 1.54 [t, 1H, -CH of the PCP carbon, ²J(¹H, ³¹P) = 2.2 Hz]. ¹³C NMR (23 °C): δ 141.5 [dd, Ph, C_{ipso}, ¹J(¹³C, ³¹P) = 90.7 Hz, ³J(¹³C, ³¹P) = 6.6 Hz], 132.6 [m, Ph, C_{ortho}, ²J(¹³C, ³¹P) = 5.5 Hz], 129.7 [s, Ph, C_{para}], 127.8 [m, Ph, C_{meta}, ³J(¹³C, ³¹P) = 6.0 Hz], 58.5 [s, TMEDA, -CH₂], 46.2 [s, TMEDA, -CH₃], 18.4 [t, PCP carbon, ¹J(¹³C, ³¹P) = 100.4 Hz]. ⁷Li NMR (23 °C): δ 1.20. ³¹P NMR (23 °C): δ 25.1 [s, ¹J(³¹P, ⁷⁷Se) = 585 Hz, ²J(³¹P, ³¹P) = 30.1 Hz]. ⁷⁷Se NMR (23 °C): δ -166.2 [d, ¹J(⁷⁷Se, ³¹P) = 585 Hz]. X-ray quality crystals of Li**8a** were obtained by dissolving the yellow powder in boiling toluene and then allowing the solution to cool down to room temperature in *ca.* 3 h.

Attempted Synthesis of TMEDA·Li[HC(PPh₂Te)₂] (Li**8b**).

A mixture of TMEDA·Li[HC(PPh₂)₂] (0.253 g, 0.50 mmol) and elemental tellurium (0.128 g, 1.00 mmol) in 40 mL of toluene was stirred for 10 min. at -80 °C and 24 h at 23 °C. After 3 h the ³¹P NMR spectrum showed a *ca.* 2:1:1 mixture of TMEDA·Li[HC(PPh₂Te)(PPh₂)] (Li**7b**), [H₂C(PPh₂)₂] and TMEDA·Li[HC(PPh₂Te)₂] (Li**8b**). Increased reaction time (up to 24 h) and/or

elevated temperature resulted in decomposition and, eventually, the formation of $[\text{H}_2\text{C}(\text{PPh}_2)_2]$ as the sole product containing the PCP unit (^{31}P NMR). NMR data for $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PPh}_2\text{Te})_2]$ (**Li8b**): ^{31}P NMR (d_8 -THF, 23 °C): δ -27.0 [s, $^1J(^{31}\text{P},^{125}\text{Te}) = 1376$ Hz, $^2J(^{31}\text{P},^{31}\text{P}) = 40.3$ Hz]. ^{125}Te NMR (23 °C): δ -245 [d, br, $^1J(^{125}\text{Te},^{31}\text{P}) = 1380$ Hz].

Synthesis of $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{P}^i\text{Pr}_2\text{Se})_2]$ (**Li8c**).

A solution of $[\text{H}_2\text{C}(\text{PCl}_2)_2]$ (0.871 g, 4.00 mmol) in 40 mL of THF was cooled to -80 °C and a solution of $^i\text{PrMgCl}$ (8.0 mL of 2.0 M sol. in THF) was added via syringe. The reaction mixture was stirred for 10 minutes at -80 °C, ½ h at 23 °C and 3 h at 50 °C. Solvent was evaporated under vacuum and the oily product, $[\text{H}_2\text{C}(\text{P}^i\text{Pr}_2)_2]$, was extracted with *ca.* 100 mL of Et_2O . After filtration through a PTFE-disk (to remove MgCl_2) solvent was evaporated and the product was dissolved in 40 mL of THF (^{31}P NMR of $[\text{H}_2\text{C}(\text{P}^i\text{Pr}_2)_2]$: δ -1.3 in THF, *cf.* lit. value of 1.3 ppm in CDCl_3 ²¹). This solution was added to a flask containing 0.632 g of elemental selenium (4.00 mmol), and the reaction mixture was stirred for 5 h at 23 °C. The full conversion of both P(III) centers to P(V) in $[\text{H}_2\text{C}(\text{P}^i\text{Pr}_2\text{Se})_2]$ was confirmed by ^{31}P NMR spectroscopy [δ 56.8, $^1J(^{31}\text{P},^{77}\text{Se}) = 726$ Hz and $^2J(^{31}\text{P},^{31}\text{P}) = 17.0$ Hz in THF].

A solution of LiN^iPr_2 (0.450 g, 4.20 mmol, 5% excess) in 20 mL of THF was added to the solution of $[\text{H}_2\text{C}(\text{P}^i\text{Pr}_2\text{Se})_2]$ at 23 °C. The reaction mixture was stirred for ½ h, and then a solution of TMEDA (0.488 g, 4.20 mmol, 5% excess) was added via cannula and stirring was continued for an additional 3 h. The solvent was evaporated under a vacuum and the product was dissolved in 70 mL of toluene followed by filtration to remove the remaining LiN^iPr_2 . Solvent removal gave a sticky product, which was washed with pentane to give **Li8c** as a pale yellow powder (1.776 g, 84 %). Anal. Calcd for $\text{C}_{19}\text{H}_{45}\text{LiN}_2\text{P}_2\text{Se}_2$: C 43.19; H 8.58; N 5.30. Found: C 42.81; H 8.31; N 5.36. ^1H NMR (d_8 -THF, 23 °C): δ 2.67 [s, 4H, $-\text{CH}_2$ of TMEDA], 2.53 [s, 12H, $-\text{CH}_3$ of TMEDA], 2.27 [m,

4H, -CH of *i*Pr], 1.47 [m, 24H, -CH₃ of *i*Pr], 0.59 [s, 1H, -CH of the PCP carbon]. ¹³C NMR (23 °C): δ 58.4 [s, TMEDA, -CH₂], 46.3 [s, TMEDA, -CH₃], 32.33 [d, *i*Pr, -CH, ¹J(¹³C, ³¹P) = 55.0 Hz], 17.8 [d, *i*Pr, -CH₃, ²J(¹³C, ³¹P) = 4.1 Hz], 4.0 [t, PCP carbon, ¹J(¹³C, ³¹P) = 97.5 Hz]. ⁷Li NMR (23 °C): δ 1.05. ³¹P NMR (23 °C): δ 52.5 [s, ¹J(³¹P, ⁷⁷Se) = 563 Hz, ²J(³¹P, ³¹P) = 13.1 Hz]. ⁷⁷Se NMR (23 °C): δ -355.2 [d, ¹J(⁷⁷Se, ³¹P) = 563 Hz]. X-ray quality crystals of Li**8c** were obtained from Et₂O solution at 5 °C in 12 h.

Synthesis of {Zn[HC(PPh₂Se)₂]₂} (**9a**).

A solution of ZnCl₂ (0.034 g, 0.25 mmol) in 15 mL of THF was cooled to -80 °C and a solution of TMEDA·Li[HC(PPh₂Se)₂] (Li**8a**) (0.332 g, 0.50 mmol) in 20 mL of THF was added via cannula. The reaction mixture was stirred for ½ h at -80 °C and 2 h at 23 °C. The solvent was evaporated under vacuum and the product was washed with cold Et₂O (0 °C) to remove H₂C(PPh₂Se)₂ by-product and then dissolved in toluene. TMEDA·LiCl was filtered from the toluene solution followed by solvent evaporation to afford **9a** as a pale yellow powder (0.138 g, 48%). Anal. Calcd for C₅₀H₄₂P₄Se₄Zn: C 52.31; H 3.69. Found: C 52.42; H 3.83. ¹H NMR (d₈-THF, 23 °C): δ 7.26-7.87 [m, 20H, C₆H₅], 1.72 [s, 1H, -CH of the PCP carbon]. ¹³C NMR (23 °C): δ 137.0 [d, Ph, C_{ipso}, ¹J(¹³C, ³¹P) = 89.9 Hz], 132.7 [m, Ph, C_{ortho}, ²J(¹³C, ³¹P) = 5.5 Hz], 131.1 [s, Ph, C_{para}], 128.5 [m, Ph, C_{meta}, ³J(¹³C, ³¹P) = 6.5 Hz], 15.5 [t, PCP carbon, ¹J(¹³C, ³¹P) = 88.0 Hz]. ³¹P NMR (23 °C): δ 25.4 [s, ¹J(³¹P, ⁷⁷Se) = 502 Hz, ²J(³¹P, ³¹P) = 22.3 Hz]. ⁷⁷Se NMR (23 °C): δ -124.2 [d, ¹J(⁷⁷Se, ³¹P) = 501 Hz]. X-ray quality crystals were obtained by layering *n*-hexane on top of the toluene solution of **9a** after 24 h at +5 °C.

Synthesis of {Hg[HC(PPh₂Se)₂]₂} (**9b**).

A solution of HgCl₂ (0.081 g, 0.30 mmol) in 15 mL of THF was cooled to -80 °C and a solution of TMEDA·Li[HC(PPh₂Se)₂] (**Li8a**) (0.399 g, 0.60 mmol) in 20 mL of THF was added via cannula. The reaction mixture was stirred for ½ h at -80 °C and 2 h at 23 °C. The solvent was evaporated under vacuum and the product was dissolved in toluene. TMEDA·LiCl was removed by filtration followed by solvent removal to afford **9b** as a pale yellow powder (0.298 g, 77%). Anal. Calcd for C₅₀H₄₂P₄Se₄Hg: C 46.80; H 3.30. Found: C 47.10; H 3.49. ¹H NMR (d₈-THF, 23 °C): δ 7.30-7.86 [m, 20H, C₆H₅], 1.76 [s, 1H, -CH of the PCP carbon]. ¹³C NMR (23 °C): δ 137.4 [d, Ph, C_{ipso}, ¹J(¹³C,³¹P) = 89.8 Hz], 132.7 [m, Ph, C_{ortho}, ²J(¹³C,³¹P) = 5.6 Hz], 131.2 [s, Ph, C_{para}], 128.6 [m, Ph, C_{meta}, ³J(¹³C,³¹P) = 6.3 Hz], 16.1 [t, PCP carbon, ¹J(¹³C,³¹P) = 89.6 Hz]. ³¹P NMR (23 °C): δ 26.0 [s, ¹J(³¹P,⁷⁷Se) = 510 Hz, ²J(³¹P,³¹P) = 20.5 Hz, ²J(³¹P,¹⁹⁹Hg) = 109.2 Hz]. ⁷⁷Se NMR (23 °C): δ -82.3 [d, ¹J(⁷⁷Se,³¹P) 510 Hz]. ¹⁹⁹Hg NMR (23 °C): δ -793.2 (s, br). X-ray quality crystals were obtained by layering Et₂O on top of a THF solution of **9b** for 4 h at +5 °C.

Oxidation of TMEDA·Li[HC(PPh₂Se)₂] (**Li8a**) and TMEDA·Li[HC(PⁱPr₂Se)₂] (**Li8c**) with I₂.

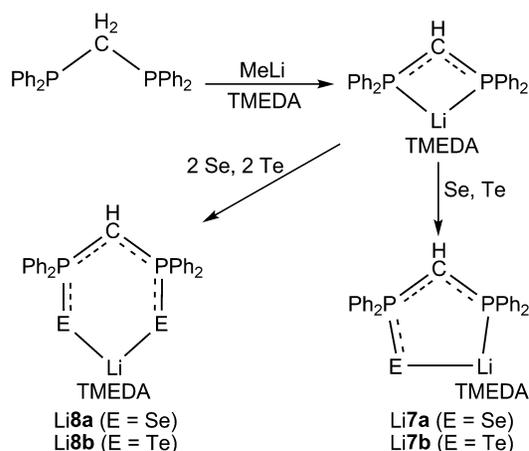
A solution of TMEDA·Li[HC(PPh₂Se)₂] (**Li8a**) (0.066 g, 0.10 mmol) in 30 mL of THF was cooled to -80 °C and a solution of I₂ (0.013 g, 0.05 mmol) in 30 mL of THF was added via cannula. The reaction mixture was allowed to warm up to *ca.* -50 °C at which point the red solution became bright red (cherry) in color. This solution was used for EPR spectroscopic measurements. The remaining reaction solution was allowed to reach room temperature, which resulted in the disappearance of the red color to give a pale yellow solution. NMR spectroscopy revealed the formation of [H₂C(PPh₂Se)₂]; ¹H NMR (d₈-toluene, 23 °C): δ 6.92-7.87 [m, 20H, C₆H₅], 4.20 [t, 2H, -CH of the PCP carbon, ²J(¹H,³¹P) = 13.2 Hz]. ³¹P NMR (23 °C): δ 26.3 [s, ¹J(³¹P,⁷⁷Se) = 763 Hz, ²J(³¹P,³¹P) = 18.6 Hz].²²

The one-electron oxidation of TMEDA·Li[HC(PⁱPr₂Se)₂] (**Li8c**) was performed similarly as described above for **Li8a** by using 0.106 g of **Li8c** (0.20 mmol) and 0.025 g of I₂ (0.10 mmol) in 70 mL of THF. In this case, however, only a steady darkening of the initial red color of the solution was observed when the reaction mixture slowly warmed up. Similarly to **Li8a**, the ³¹P NMR spectrum of the reaction solution showed the neutral [H₂C(PⁱPr₂Se)₂] as the sole product after 1 h at 23 °C; [δ 56.8 with $^1J(^{31}\text{P},^{77}\text{Se}) = 726$ Hz and $^2J(^{31}\text{P},^{31}\text{P}) = 17.0$ Hz in THF]. Samples for EPR spectroscopy were taken at -80 °C and at -50 °C, and the spectra were run in the temperature range -70 °C - +20 °C.

Results and discussion

Synthesis and Spectroscopic Characterization of TMEDA·Li[HC(PPh₂E)(PPh₂)] [E = Se (Li7a**), Te (**Li7b**)] and TMEDA·Li[HC(PPh₂E)₂] [E = Se (**Li8a**), Te (**Li8b**)]**. The synthesis of the monoanions **7** and **8** entails two major challenges that, in part, may provide an explanation for the lack of information for these compounds in the literature. First, similar to the behavior of [HN(PPh₂)₂],⁴ elemental tellurium *does not* react with the neutral bis(diphenylphosphinoyl)methane, [H₂C(PPh₂)₂]. Secondly, a limited spectroscopic study of the monochalcogeno anions **7** showed that, in contrast to the analogous sulfur compounds, organolithium reagents (RLi) react with the P-Se functionality in [H₂C(PPh₂Se)(PPh₂)] with the subsequent formation of RSeLi and/or R₂Se.²³ Consequently, we adopted the synthetic strategy that was successful for the production of the related tellurium-containing anion, [N(PR₂Te)₂]⁻ (**1**).⁴ In this procedure the anion [HC(PR₂)₂]⁻ ¹⁴ is generated *prior to* oxidation of the phosphorus(III) center(s) with elemental chalcogen(s).

Scheme 1. Formation of the monoanions **7** and **8**.



The reactions of $\text{TMEDA} \cdot \text{Li}[\text{HC}(\text{PPh}_2)_2]$ with one equivalent of elemental selenium or tellurium in toluene at room temperature to produce **Li7a** and **Li7b**, respectively, are complete after 2½ hours. The ^{31}P NMR spectra of these lithium derivatives (d_8 -THF, 23 °C) show the expected inequivalence of the P(III) and P(V) centers in the form of two mutually coupled doublets at 33.2 and -10.9 ppm (**Li7a**), and at -4.4 and -14.2 ppm (**Li7b**). The $^2J(^{31}\text{P}, ^{31}\text{P})$ coupling constants show unusually high values of *ca.* 175-180 Hz, *cf.* 50-85 Hz in the neutral P(III)CH₂P(V) systems [$\text{H}_2\text{C}(\text{PPh}_2\text{E})(\text{PPh}_2)$] (E = O, S, Se).²² In these asymmetric, neutral compounds the large coupling constants have been attributed to a combination of increased s character in the phosphorus bonds and to a change in the difference of effective nuclear charge between the phosphorus atoms.²⁴ The larger coupling constants in the anions **7** therefore suggest even greater charge difference between the phosphorus centers than in the analogous neutral systems. The ^{77}Se and ^{125}Te satellites are observable in the ^{31}P NMR resonances at 33.2 (**Li7a**) and -14.2 ppm (**Li7b**). The magnitude of the coupling constants of $^1J(^{31}\text{P}, ^{77}\text{Se}) = 556$ Hz and $^1J(^{31}\text{P}, ^{125}\text{Te}) = 1359$ Hz is significantly smaller than the values of *ca.* 760 and 1650 Hz typically observed for terminal P=Se and P=Te bonds, respectively, thus suggesting a considerable Li-E interaction (E = Se, Te) and formation of a five-membered ring in **Li7a** and **Li7b** as illustrated in Scheme 1 (*cf.* for example $^1J(^{31}\text{P}, ^{77}\text{Se}) = 763$ Hz in

$[\text{H}_2\text{C}(\text{PPh}_2\text{Se})_2]$ ²² and $^1J(^{31}\text{P}, ^{125}\text{Te}) = 1654$ Hz in $[\text{N}(\text{P}^i\text{Pr}_2\text{Te})(\text{P}^i\text{Pr}_2\text{H})]$ ⁵). Furthermore, the two notably different $^1J(^{13}\text{C}, ^{31}\text{P})$ coupling constants of 108 and 20 Hz obtained for the PCP carbon from the ^{13}C NMR spectrum of **Li7a** indicates a substantial inequality in the P-C bond lengths. Interestingly, the selenium-bound $^{31}\text{P}(\text{Se})$ chemical shift in **Li7a** is markedly downfield from the value of -3.7 ppm observed for the anion $[\text{HC}(\text{PPh}_2)_2]^-$ ²⁵ whereas the $^{31}\text{P}(\text{Te})$ signal in **Li7b** exhibits a high field shift compared to the starting material.

While the monoseleno anion **Li7a** is isolated as a relatively stable compound, the tellurium analogue **Li7b** exhibits thermal instability; the yellow powder starts to darken in a few minutes even in an inert atmosphere glove box (with oxygen levels less than 3 ppm) at room temperature. In addition, the ^{31}P NMR spectrum of the reaction solution of **Li7b** after 2½ hours shows two minor signals (*ca.* 3%) attributed to $[\text{H}_2\text{C}(\text{PPh}_2)_2]$ (δ -21.4) and $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PPh}_2\text{Te})_2]$ (**Li8b**, δ -27.0, *vide infra*); after prolonged standing only the former by-product is observed in the ^{31}P NMR spectrum. A similar disproportionation of the related P(III)/P(V) system, $\text{Li}[\text{N}(\text{P}^i\text{Pr}_2\text{Te})(\text{P}^i\text{Pr}_2)]$, to give the symmetrical P(III)/P(III) and P(V)/P(V) compounds, $[\text{HN}(\text{P}^i\text{Pr}_2)_2]$ and $\text{Li}[\text{N}(\text{P}^i\text{Pr}_2\text{Te})_2]$, respectively, has been previously reported.³ This disproportionation, presumably, also contributes to the broadness of the signals in the NMR spectra of **Li7b**. The $^1J(^{13}\text{C}, ^{31}\text{P})$ coupling constants could not be obtained from the ^{13}C NMR spectrum and only a very broad doublet is observed in the ^{125}Te NMR spectrum, whereas the ^{77}Se NMR spectrum of **Li7a** displays a well-resolved doublet of doublets due to the $^1J(^{77}\text{Se}, ^{31}\text{P})$ and $^2J(^{77}\text{Se}, ^{31}\text{P})$ couplings.

The oxidation of $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PPh}_2)_2]$ with two equivalents of elemental selenium in toluene requires moderate heating (55 °C) to complete the formation of **Li8a** (Scheme 1). The ^{31}P NMR spectrum of **Li8a** (d_8 -THF, 23 °C) exhibits a singlet at 25.1 ppm with ^{77}Se satellites showing $^1J(^{77}\text{Se}, ^{31}\text{P})$ and $^2J(^{31}\text{P}, ^{31}\text{P})$ coupling constants of 585 and 30.1 Hz, respectively. The latter value is considerably smaller than that observed for **Li7a**, indicative of the change in the difference of effective nuclear charge between the two phosphorus centers,²⁴ *i.e.* Li-P contact in the asymmetric

Li**7a** has likely been replaced by a P-Se bond in Li**8a**. The ^{77}Se NMR spectrum of Li**8a** exhibits a doublet at -166 ppm, *ca.* 35 ppm downfield from the signal observed for Li**7a**, and the $^1J(^{13}\text{C}, ^{31}\text{P})$ coupling constant of 100 Hz, obtained from the PCP carbon resonance at 18.4 ppm in the ^{13}C NMR spectrum of Li**8a**, is close to one of the two inequivalent couplings resolved for Li**7a**. Taken together, these NMR data suggest formation of the expected LiSePCPSe six-membered ring with equivalent P(V) atoms for Li**8a**.

The reaction between elemental tellurium and TMEDA·Li[HC(PPh₂)₂] in a 2:1 molar ratio is more complicated than the corresponding reaction with selenium. After 3 hours at 23 °C the ^{31}P NMR spectrum of the reaction mixture shows resonances attributed to Li**7b** (doublets at -4.4 and -14.2 ppm) and [H₂C(PPh₂)₂] (δ -21.4), in addition to a singlet at -27.0 ppm. The last signal exhibits ^{125}Te satellites with the $^1J(^{31}\text{P}, ^{125}\text{Te})$ and $^2J(^{31}\text{P}, ^{31}\text{P})$ coupling constants of 1376 and 40.3 Hz, respectively. The former coupling is somewhat bigger than that obtained for the asymmetric monotelluro compound Li**7b**, and the latter coupling is in the same range as that observed for the diseleno anion in Li**8a**. In addition, a broad doublet is resolved in the ^{125}Te NMR spectrum of the reaction mixture at -245 ppm, *ca.* 130 ppm downfield from that of Li**7b**, with a $^1J(^{31}\text{P}, ^{125}\text{Te})$ coupling constant of 1380 Hz. Comparison of these NMR data with those of the monotelluro compound Li**7b**, and the selenium congeners Li**7a** and Li**8a**, is consistent with the formation of ditelluro anion in Li**8b**. However, longer reaction times or even moderate heating leads to decomposition to yield neutral [H₂C(PPh₂)₂]; consequently, we have not been able to isolate a pure sample of Li**8b**.

Synthesis and Spectroscopic Characterization of TMEDA·Li[HC(PⁱPr₂Se)₂] (Li8c**).** While the parent PCP backbone in **7** and **8** as the phenyl derivative, [H₂C(PPh₂)₂], is easily available from commercial sources, the preparation of other (especially alkyl) derivatives is hampered by multi-step and/or low-yield processes.²⁶ However, by using commercially available

bis(dichlorophosphinoyl)methane, $[\text{H}_2\text{C}(\text{PCl}_2)_2]$, in a reaction with four equivalents of the Grignard reagent, ${}^i\text{PrMgCl}$, the *iso*-propyl derivative is readily obtained in quantitative yield (>95%, Eq. 1). The purity of this colorless oil was confirmed by ${}^{31}\text{P}$ NMR spectroscopy²¹ prior to *in situ* reaction with 2 equivalents of elemental selenium (Eq. 2) followed by (*in situ*) deprotonation with $\text{LiN}{}^i\text{Pr}_2$ in the presence of TMEDA (Eq. 3). This three-step process affords analytically pure $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{P}{}^i\text{Pr}_2\text{Se})_2]$ (**Li8c**) in excellent yield (84%, calculated from $[\text{H}_2\text{C}(\text{PCl}_2)_2]$).



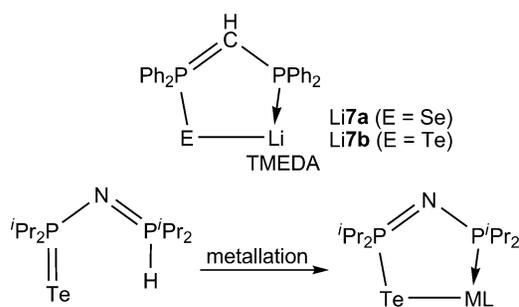
(Li8c)

The ${}^{31}\text{P}$ NMR spectrum of **Li8c** shows a singlet at 52.5 ppm with ${}^1J({}^{31}\text{P}, {}^{77}\text{Se})$ of 563 Hz and ${}^2J({}^{31}\text{P}, {}^{31}\text{P})$ of 13.1 Hz, indicative of only a slight change in the P-Se bond length compared to the phenyl-derivative **Li8a**. The triplet resolved at 4.0 ppm for the PCP carbon in the ${}^{13}\text{C}$ NMR spectrum of **Li8c** exhibits ${}^1J({}^{13}\text{C}, {}^{31}\text{P})$ coupling constant of 97.5 Hz, *cf.* 100.4 Hz in **Li8a**, and a singlet is observed at 0.59 ppm for the corresponding hydrogen in the ${}^1\text{H}$ NMR spectrum. In both of these spectra the typical signal patterns are also seen for the *i*Pr and TMEDA groups. In addition, a doublet is found at -355.2 ppm in the ${}^{77}\text{Se}$ NMR spectrum of **Li8c** with the ${}^1J({}^{77}\text{Se}, {}^{31}\text{P})$ of 563 Hz, which is *ca.* 160 Hz smaller than that in the neutral precursor, $[\text{H}_2\text{C}(\text{P}{}^i\text{Pr}_2\text{Se})_2]$ (see experimental), thus indicating the expected coordination of the lithium atom to two selenium centers.

Crystal structures of TMEDA·Li[HC(PPh₂E)(PPh₂)] [E = Se (Li7a), Te (Li7b)] and TMEDA·Li[HC(PR₂Se)₂] [R = Ph (Li8a), ⁱPr (Li8c)]. The X-ray structural determinations of Li7a and Li7b confirm the formation of the 5-membered ELiPCP ring (E = Se, Te) inferred from the NMR data (Figure 1). In the crystal lattice both structures appear as centrosymmetric dimers created by an intermolecular E···E close contact that is somewhat stronger for the tellurium compound Li7b [3.514(1) Å (Li7b) vs. 3.6407(6) Å (Li7a), Table 2] (*cf.* sum of the van der Waals radii for Se and Te is 4.00 Å and 4.40 Å, respectively).²⁷ Presumably the steric strain between TMEDA and phenyl units is reduced in Li7b compared to Li7a as a result of the longer Te-P and Te-Li bonds. The five-membered ring in Li7a and Li7b displays a moderate distortion from planarity with the dihedral angles spanning a range of 1-19°. The change of chalcogens between Li7a and Li7b results in a difference of *ca.* 4° in the bond angles at the E1 (E = Se, Te) and P2 atoms, while the remaining bond angles are approximately equal.

As indicated by the calculated bond orders (Table 2),²⁸ the Li-E contact in both Li7a and Li7b (E = Se, Te) approaches a covalent bond with the value of 0.9 whereas the Li-P bond is somewhat weaker with the bond order of 0.5. Furthermore, consistent with the two inequivalent ¹J(¹³C, ³¹P) coupling constants resolved for the PCP carbon in Li7a, the P-C bond lengths in both Li7a and Li7b show a disparity of *ca.* 0.04 Å, the shorter bond involving the chalcogen-bound phosphorus(V) atom. These data are indicative of substantial contribution from a resonance structure in which the phosphorus(III) center forms a dative bond with lithium and the phosphorus(V) atom is connected to the PCP carbon with a double bond (Scheme 2). A similar bonding arrangement has been suggested in monotelluroimidodiphosphate monoanions **1** after metallation of the P-H unit in the neutral [N(P^{*i*}Pr₂Te)(P^{*i*}Pr₂H)] (Scheme 2).³

Scheme 2. Major resonance form in Li7a and in the analogous monotelluroimidodiphosphinates.



The crystal structures of Li8a and Li8c are illustrated in Figure 2 and the pertinent bond parameters are summarized in Table 3. The structures of Li8a and Li8c corroborate the formation of the expected six-membered ring with two P-Se bonds and Li-Se contacts (Scheme 1). The P-Se and Li-Se bond lengths in the structure of the diseleno derivative Li8a are analogous to those seen in the monoseleno analogue Li7a, while the P-C distances are intermediate between the two values observed in the PCP unit for Li7a. The change of substituents on phosphorus atoms in Li8c has virtually no effect on the bond lengths compared to Li8a. The dihedral angles reveal a slightly more puckered six-membered ring in Li8a than in the *iso*-propyl derivative Li8c, and the P-C-P angle shows a widening of *ca.* 6° for the latter compound. The bond angles at selenium atoms are also somewhat wider in Li8c while the angles at the phosphorus centers in Li8a and Li8c are equal.

Synthesis and Characterization of {M[HC(PPh₂Se)₂]₂} [M = Zn (9a); Hg (9b)]. The monochalcogeno compounds Li7a and Li7b have been used as *in situ* reagents in metathetical reactions with HgCl₂ to generate homoleptic complexes, which were inferred to involve *P,E* chelation of the ligand to the metal center on the basis of solution NMR data.²³ Alkali derivatives of diselenoimidodiphosphinate anions of the type **1** (E = Se) have been widely used in the synthesis of a variety of metal complexes of main group and transition metal elements,¹ which have subsequently been used as single-source precursors of metal selenides.³⁰ In this initial study of the dichalcogeno

bis(phosphinoyl)methane anion **8**, the reactions between Li**8a** and MCl_2 ($M = Zn, Hg$) were conducted in a 2:1 molar ratio in order to establish the viability of the new reagent in metathesis with metal halides. The reaction with $HgCl_2$ in toluene at $-80\text{ }^\circ\text{C}$ proceeded cleanly to produce $\{Hg[HC(PPh_2Se)_2]_2\}$ (**9b**) in good yield, whereas the synthesis of the zinc congener, $\{Zn[HC(PPh_2Se)_2]_2\}$ (**9a**), afforded also a significant amount of the neutral $H_2C(PPh_2Se)_2$ (^{31}P NMR) regardless of the reaction conditions or the source of $ZnCl_2$.

The ^1H NMR spectra of **9a** and **9b** show a broad singlet at 1.72 and 1.76 ppm, respectively, for the hydrogen in the PCP unit, and a triplet at 15.5 and 16.1 ppm with $^1J(^{13}\text{C}, ^{31}\text{P})$ of *ca.* 90 Hz is resolved for the corresponding carbon in the ^{13}C NMR spectra. The former resonances exhibit a high field shift of *ca.* 1.2 ppm and the latter signals are *ca.* 50 ppm to lower field with the $^1J(^{13}\text{C}, ^{31}\text{P})$ coupling constant *ca.* 45 Hz larger than the value observed for the only structurally characterized complex of the $[HC(PPh_2Se)_2]^-$ anion, $\{Cp^*Rh[HC(PPh_2Se)_2]ClO_4\}$.¹³ Together with the absence of ^{199}Hg satellites for the PCP carbon resonance in the ^{13}C NMR spectrum of **9b** these data indicate that, in contrast to the rhodium complex, the compounds **9a** and **9b** do not contain a significant M-C contact ($M = Zn, Hg$); the larger value of $^1J(^{13}\text{C}, ^{31}\text{P})$ is consistent with somewhat shorter P-C bond lengths than those in the rhodium complex (*vide infra*). The ^{31}P NMR spectra of **9a** and **9b** display a singlet with ^{77}Se satellites at 25.4 and 26.0 ppm, respectively. The $^2J(^{31}\text{P}, ^{31}\text{P})$ and $^1J(^{31}\text{P}, ^{77}\text{Se})$ coupling constants are somewhat smaller than those in Li**8a** indicating a small change in the geometry of PCP unit and slightly stronger M-Se contacts in **9a** and **9b** resulting in longer P-Se bonds (*vide infra*). Due to the low solubility of the mercury compound **9b**, only a weak, broad singlet is observed in the ^{199}Hg NMR spectrum instead of the expected quintet arising from the coupling to four equivalent phosphorus atoms. The chemical shift of -793 ppm is, however, comparable with that of the quintet observed at -785 ppm for a related cationic Hg(II) complex of the neutral ligand, $\{Hg[H_2C(PPh_2Se)_2]_2[ClO_4]_2\}$.³¹ In addition, a doublet is visible at -124 and -82

ppm in the ^{77}Se NMR spectra of **9a** and **9b**, respectively, both at somewhat lower field than the corresponding signal for **Li8a**.

As illustrated in Figure 3, the molecular structures of **9a** and **9b** display the expected *Se,Se'*-chelation of the anions to the metal center affording a distorted tetrahedral environment for the group 12 metals. While the zinc complex **9a** exhibits a centrosymmetric arrangement of the ligands, the symmetry center in the mercury compound **9b** is located between the molecules in the crystal lattice resulting in different crystal systems for the two compounds. As indicated by the NMR spectra, neither of the complexes show a significant M-C contact (M = Zn, Hg). Interestingly, however, the CH-unit in the PCP region in the zinc compound **9a** is bent towards the metal centre resulting in a boat conformation for the ZnSePCPSe six-membered ring and a significant distortion from planarity for the carbon atom ($\Sigma \angle\text{C1 } 352^\circ$, Table 4). By contrast, the planar CH-unit in **9b** is pointed away from the metal center and the analogous six-membered ring is notably twisted as manifested by the dihedral M-Se-P-C angles (Table 4), cf. the pseudo-boat conformation observed in the comparable diselenoimidodiphosphinate complexes, $\{\text{M}[\text{N}(\text{PR}_2\text{Se})_2]_2\}$ (M = Zn, R = *i*Pr, Ph,^{30d} M = Hg, R = *i*Pr,^{30e} Ph³²). Since the disparity in the ring conformations for **9a** and **9b** is not apparent in the solution NMR spectra, we attribute this structural difference to crystal packing effects resulting from the influence of the different orientation of phenyl groups in the two metal complexes on the PC(H)P unit, rather than the difference in size between the two metals or electronic factors. This view is supported by the structures of zinc(II) and mercury(II) halide complexes of the corresponding neutral ligand $[\text{H}_2\text{C}(\text{PPh}_2\text{Se})_2]$.^{33, 34} In all of these complexes the PCP unit is bent towards the metal centre affording a boat conformation similar to that obtained for **9a**.

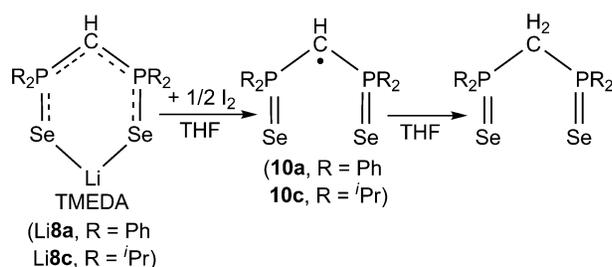
Consistent with the lower (by 75-85 Hz) values of $^1J(^{31}\text{P}, ^{77}\text{Se})$, the P-Se bonds in **9a** and **9b** are *ca.* 0.04 Å longer than those in the lithium reagent **Li8a**; the P-C bond lengths in **9a**, **9b** and **Li8a** are equal. In the structure of **9b**, the twisted six-membered ring results in disparity of 0.03 and 0.06

Å in the P-Se and Se-Hg bonds, respectively. The M-Se bonds in **9a** and **9b** are, expectedly, *ca.* 0.05-0.08 Å shorter than those in metal halide complexes of the neutral ligand $\{\text{ZnI}_2[\text{H}_2\text{C}(\text{PPh}_2\text{Se})_2]\}$ ³³ and $\{\text{HgX}_2[\text{H}_2\text{C}(\text{PPh}_2\text{Se})_2]\}$ (X = Br, I)³⁴ due to the stronger ionic interaction between the anionic ligand and the metal centre. As deduced from the values of $^1J(^{13}\text{C}, ^{31}\text{P})$, the absence of a M-C contact (M = Zn, Hg) in **9a** and **9b** results in somewhat shorter P-C bonds (by *ca.* 0.05 Å) than those in the rhodium complex $\{\text{Cp}^*\text{Rh}[\text{HC}(\text{PPh}_2\text{Se})_2]\text{ClO}_4\}$.¹³ The Se-M-Se bond angles at the metal center in both **9a** and **9b** show a similar range of 99-118°, which is somewhat broader than the range of 103-115° observed in the analogous diselenoimidodiphosphinate complexes, $\{\text{M}[\text{N}(\text{PR}_2\text{Se})_2]_2\}$ (M = Zn, R = *i*Pr, Ph,^{30d} M = Hg, R = *i*Pr,^{30e} Ph³²), despite the virtually identical M-Se and P-Se bond lengths. Finally, while the bond angles at the phosphorus atoms are essentially equal in complexes **9** and **Li8a**, the angles at the selenium atoms are somewhat wider in **9a** and **9b**, presumably owing to the longer M-Se bonds.

One-electron Oxidation of TMEDA·Li[HC(PPh₂Se)₂] (Li8a) and TMEDA·Li[HC(P^{*i*}Pr₂Se)₂] (Li8c) with I₂. The one-electron oxidation of **Li8a** with iodine was performed in order to compare the outcome with similar reactions conducted for the isoelectronic N-bridged anions **2**, which produce dimers of the type **3**, $[\text{N}(\text{PR}_2\text{E})_2]_2$ (E = Se, Te; R = *i*Pr, *t*Bu).^{5,6} The reaction of **Li8a** with iodine was conducted at -80 °C in THF. A subtle change in the color of the solution from red (unreacted iodine) into *bright cherry* red was observable at *ca.* -50 °C, and a further change into pale yellow took place at *ca.* -20 °C. As indicated by the second color change (at *ca.* -20 °C), the initially formed neutral radical **10a** (cherry red solution) is a thermally unstable, short-lived species. NMR spectroscopy revealed that the final product is $[\text{H}_2\text{C}(\text{PPh}_2\text{Se})_2]$,²² presumably formed from **10a** via hydrogen abstraction from the solvent (Scheme 3). The same product was also obtained when the oxidation was carried out in toluene, dichloromethane or diethyl ether.

Subsequently to the somewhat surprising outcome of the one-electron oxidation of Li**8a**, the reaction of the *iso-propyl* derivative Li**8c** with one-half equivalent of I₂ was carried out under the same conditions to determine the effect of changing the substituents on phosphorus and to gain a more direct comparison with the dichalcogenoimidodiphosphinates **2** in which ⁱPr and ^tBu substituents were utilized.^{5, 6} In the case of Li**8c**, the reaction solution showed only a steady darkening of the red color when the temperature was raised; there was no indication of a second color change. However, consistently with the observations for Li**8a**, NMR spectroscopy showed the formation of [H₂C(PⁱPr₂Se)₂] as the final product (Scheme 3).

Scheme 3. One-electron oxidation of Li**8a** and Li**8c**.



DFT calculations of the neutral radicals **9** were carried out in order to provide (a) a comparison of the composition of the SOMO with that of the isoelectronic radicals [N(PR₂E)₂][•],^{5, 6} and (b) an estimate of the EPR parameters. The DFT-optimized structures of the neutral radicals **9** are depicted in Figure 4 along with the calculated singly-occupied molecular orbitals (SOMOs). The minimum geometries found for the Ph and ⁱPr-substituted systems differ significantly with respect to the relative orientation of the phosphorus-bound organic groups that leads to a SOMO consisting of *p*-orbitals either on both or on only one of the selenium centers (**10a** and **10c**, respectively). Most notably, however, the SOMO in both derivatives has a large contribution from the *p*-orbital on the PCP carbon therefore making it susceptible to hydrogen abstraction. This composition differs from

that of the calculated SOMO of the N-bridged systems, $[\text{N}(\text{PR}_2\text{E})_2]^*$, which is almost solely localized on the p -orbitals on the two chalcogen atoms E, thus giving rise to formation of the dimers **3**, $[\text{N}(\text{PR}_2\text{E})_2]_2$, by favorable orbital overlap.^{5, 6} This disparity in the spatial morphology of the frontier orbitals provides a probable explanation for the preference for hydrogen abstraction over dimerization in the one-electron oxidation of the PCP-bridged anions **8**.

DFT calculations for **10a** and **10c** predict that both radicals will display large (ca. 30 G) hyperfine coupling constants (hfccs) to the two phosphorus nuclei (arising from spin polarization) along with a slightly smaller (16 G) coupling to the $-\text{CH}$ of the PCP carbon; couplings to the two selenium atoms as well as the PCP carbon are also significant, but they will have only minor contributions to the expected spectra because of the low natural abundance of the ^{77}Se and ^{13}C isotopes. The attempted identification of the transient radicals **10a** and **10c** at low temperature (ca. -40 °C) by EPR spectroscopy was inconclusive. The EPR spectrum of the bright cherry red solution formed upon oxidation of **Li8a** displayed a broad doublet ($g = 2.0046$) with an hfcc of ca. 11.5 G while the EPR spectrum of the oxidized solution of **Li8c** exhibited a doublet of binomial triplets at $g = 2.0045$ with hfccs of 11.3 and 1.6 G, respectively. In view of (a) the *very poor* signal-to-noise ratio for both EPR spectra and (b) the disparity in the experimental and calculated hfccs constants, no definitive conclusions regarding the identities of the radicals formed upon oxidation of **Li8a** and **Li8c** can be made.³⁵

Conclusions

Synthetic routes to the heavy chalcogen-centered anionic ligands, $[\text{HC}(\text{PPh}_2\text{E})(\text{PPh}_2)]^-$ and $[\text{HC}(\text{PPh}_2\text{E})_2]^-$ (E = Se, Te), have been developed. The selenium-containing monoanions $[\text{HC}(\text{PPh}_2\text{Se})(\text{PPh}_2)]^-$ (**7a**) and $[\text{HC}(\text{PPh}_2\text{Se})_2]^-$ (**8a**) were structurally characterized as Li^+ salts and the application of the new reagent **Li8a** in metathetical reactions was exemplified by the preparation of the homoleptic group 12 complexes, $\text{M}[\text{HC}(\text{PPh}_2\text{Se})_2]_2$ (M = Zn, Hg). By contrast, the tellurium

congeners Li**7b** and Li**8b** are thermally unstable. Consequently, although the solid-state structure of the monotelluro anion Li**7b** was determined, its use as a reagent is limited to *in situ* reactions.

The outcome of the one-electron oxidation of the monoanions $[\text{HC}(\text{PR}_2\text{Se})_2]^-$ (**8**, R = Ph, *i*Pr) revealed somewhat surprising differences compared to the analogous reactions with the isoelectronic N-bridged anions, $[\text{N}(\text{PR}_2\text{E})_2]^-$ (**2**, E = S, Se, Te, R = *i*Pr, *t*Bu). In contrast to the dimerization processes observed upon oxidation of **2**, the treatment of **8** with iodine produces $[\text{H}_2\text{C}(\text{PR}_2\text{Se})_2]$ (R = Ph, *i*Pr) via hydrogen abstraction. This difference in behavior is attributed to the strong contribution from a *p*-orbital on carbon to the SOMO of $[\text{HC}(\text{PR}_2\text{Se})_2]^\cdot$.

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Supporting information available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Table 1. Crystallographic data for **Li7a**, **Li7b**, **Li8a**, **Li8c**, **9a** and **9b**.^a

	Li7a	Li7b	Li8a	Li8c	9a	9b
emp. formula	C ₃₁ H ₃₇ LiN ₂ P ₂ Se	C ₃₁ H ₃₇ LiN ₂ P ₂ Te	C ₃₁ H ₃₇ LiN ₂ P ₂ Se ₂	C ₁₉ H ₄₅ LiN ₂ P ₂ Se ₂	C ₅₀ H ₄₂ P ₄ Se ₄ Zn	C ₅₀ H ₄₂ HgP ₄ Se ₄
Fw	585.47	634.11	664.43	528.37	1147.93	1283.15
cryst. system	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	triclinic
space group	P2 ₁ /c	P2 ₁ /c	Pna2 ₁	P-1	C2/c	P-1
<i>a</i> , Å	8.859(2)	8.915(2)	19.730(4)	10.329(2)	26.195(5)	10.354(2)
<i>b</i> , Å	19.149(4)	19.407(4)	17.919(4)	11.919(2)	11.379(2)	14.489(3)
<i>c</i> , Å	18.131(4)	18.249(4)	9.025(2)	12.019(2)	18.610(4)	16.695(3)
α , deg.	90.00	90.00	90.00	93.99(3)	90.00	111.45(2)
β , deg.	100.31(3)	99.91(3)	90.00	95.60(3)	122.58(3)	94.92(3)
γ , deg.	90.00	90.00	90.00	112.56(3)	90.00	93.71(3)
<i>V</i> , Å ³	3026(1)	3110(1)	3191(1)	1350.5(5)	4674(2)	2310.0(9)
<i>Z</i>	4	4	4	2	4	2
<i>T</i> , °C	-100	-100	-100	-100	-100	-100
ρ_{calcd} , g/cm ³	1.285	1.354	1.383	1.299	1.631	1.845
$\mu(\text{Mo K}\alpha)$, mm ⁻¹	1.368	1.080	2.440	2.862	3.812	6.656
crystal size, mm ³	0.48x0.40x0.28	0.20x0.12x0.10	0.12x0.08x0.06	0.32x0.28x0.24	0.24x0.20x0.16	0.20x0.04x0.02
<i>F</i> (000)	1216	1288	1352	548	2272	1236
Θ range, deg	2.98-25.03	3.35-25.03	2.27-25.02	2.86-25.03	2.87-25.02	2.37-25.03
reflns collected	10492	10112	5409	8815	14646	15466
unique reflns	5341	5481	5409	4743	4109	8106

R_{int}	0.0227	0.0426	0.0436	0.0266	0.0381	0.0525
reflns [$I > 2\sigma(I)$]	4594	4004	4239	4253	3780	6502
R_1 [$I > 2\sigma(I)$] ^b	0.0265	0.0345	0.0460	0.0323	0.0241	0.0554
wR_2 (all data) ^c	0.0656	0.0717	0.0911	0.0841	0.0603	0.1389
GOF on F^2	1.029	1.015	1.065	1.064	1.066	1.061
completeness	0.997	0.996	0.996	0.993	0.998	0.993

^a λ (MoK α) = 0.71073 Å. ^b $R_1 = \Sigma | |F_o| - |F_c| | / \Sigma |F_o|$. ^c $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) in **Li7a** and **Li7b** [calculated bond orders in square brackets].²⁸

	Li7a^a	Li7b^b		Li7a^a	Li7b^b
E1-P1	2.1591(6) [1.43]	2.404(1) [1.16]	P1-C1	1.704(2)	1.693(4)
E1-Li1	2.510(3) [0.91]	2.700(6) [0.88]	P2-C1	1.739(2)	1.743(4)
Li1-P2	2.554(3) [0.52]	2.578(6) [0.48]	E1⋯E1'	3.6407(6) ^c	3.514(1) ^d
P1-E1-Li1	98.2(1)	94.1(1)	Li1-E1-P1-C1	12.0(1)	12.2(2)
C1-P1-E1	116.7(1)	115.9(1)	E1-P1-C1-P2	2.7(2)	0.9(3)
P2-C1-P1	123.2(1)	124.6(2)	P1-C1-P2-Li1	15.9(2)	14.8(3)
Li1-P2-C1	105.2(1)	109.5(2)	C1-P2-Li1-E1	18.9(1)	18.6(2)
E1-Li1-P2	92.5(1)	92.2(2)	P2-Li1-E1-P1	15.9(1)	14.9(2)

^a E = Se, ^b E = Te. Symmetry operation for the atoms marked with a single quote ('): ^c -x, 1-y, -z; ^d 1-x, 1-y, 1-z.

Table 3. Selected bond lengths (Å) and angles (°) in Li**8a** and Li**8c**.

	Li 8a	Li 8c		Li 8a	Li 8c
Se1-P1	2.144(2)	2.155(1)	Se2-Li1	2.59(1)	2.553(5)
Se1-Li1	2.54(1)	2.539(5)	P1-C1	1.720(6)	1.717(3)
Se2-P2	2.162(2)	2.158(1)	P2-C1	1.718(6)	1.717(3)
Li1-Se1-P1	98.7(2)	105.7(1)	Li1-Se1-P1-C1	56.8(4)	44.2(2)
Se1-P1-C1	118.0(2)	119.6(1)	Se1-P1-C1-P2	40.5(5)	-29.9(3)
P1-C1-P2	127.2(3)	133.6(2)	P1-C1-P2-Se2	36.3(6)	-25.3(3)
C1-P2-Se2	118.6(2)	119.5(1)	C1-P2-Se2-Li1	62.4(4)	45.7(2)
P2-Se2-Li1	94.7(2)	105.0(1)	P2-Se2-Li1-Se1	30.1(4)	-21.4(2)
Se2-Li1-Se1	113.6(4)	110.4(2)	Se2-Li1-Se1-P1	16.4(4)	-15.3(2)

Table 4. Selected bond lengths (Å) and angles (°) in **9a** and **9b**.

	9a^a	9b^b		9a^a	9b^b
M1-Se1	2.4568(7)	2.647(1)	Se3-P3	-	2.195(3)
M1-Se2	2.4522(5)	2.679(1)	Se4-P4	-	2.173(3)
M1-Se3	-	2.615(1)	P1-C1	1.718(2)	1.732(10)
M1-Se4	-	2.660(2)	P2-C1	1.724(2)	1.717(10)
Se1-P1	2.1937(7)	2.197(3)	P3-C2	-	1.699(10)
Se2-P2	2.2026(9)	2.161(3)	P4-C2	-	1.727(9)
Se1-M1-Se2	116.45(2)	110.88(4)	Se3-P3-C2	-	118.8(3)
Se1-M1-Se3	98.67(3) ^d	114.97(4)	Se4-P4-C2	-	118.1(4)
Se1-M1-Se4	102.90(3) ^e	108.72(4)	P1-C1-P2	125.1(1)	123.7(6)
Se2-M1-Se3	102.90(3) ^d	112.15(4)	P1-C1-H1	116(2)	118.1
Se2-M1-Se4	118.26(3) ^e	99.13(4)	P2-C2-H1	111(2)	118.1
Se3-M1-Se4	116.45(2) ^{d, e}	109.79(4)	P3-C2-P4	-	128.6(6)
M1-Se1-P1	99.06(2)	91.67(7)	P3-C2-H2	-	115.7
M1-Se2-P2	101.06(4)	96.40(7)	P4-C2-H2	-	115.7
M1-Se3-P3	-	94.98(7)	M1-Se1-P1-C1	19.8(1)	71.2(4)
M1-Se4-P4	-	101.00(7)	M1-Se2-P2-C1	8.1(1)	63.7(4)
Se1-P1-C1	119.52(8)	117.7(3)	M1-Se3-P3-C2	-	65.8(4)
Se2-P2-C1	118.27(9)	116.5(3)	M1-Se4-P4-C2	-	50.9(4)

^a M = Zn. ^b M = Hg. ^c Symmetry operation: -x, y, 0.5-z. ^d Se3 = Se1^c, ^e Se4 = Se2^c.

Figure Captions

Figure 1. Crystal structure of TMEDA·Li[HC(PPh₂Se)(PPh₂)] (**Li7a**) with thermal ellipsoids at 50% probability level. Hydrogen atoms in the phenyl groups and in TMEDA have been omitted for clarity. The tellurium analogue **Li7b** is isostructural with **Li7a**. Symmetry operation: ^a -x, 1-y, -z (**Li7a**) and 1-x, 1-y, 1-z (**Li7b**).

Figure 2. Molecular structure of (a) TMEDA·Li[HC(PPh₂Se)₂] (**Li8a**) and (b) TMEDA·Li[HC(P^{*i*}Pr₂Se)₂] (**Li8c**) with thermal ellipsoids at 50% probability level. Hydrogen atoms in the phenyl and *iso*-propyl groups, and in TMEDA have been omitted for clarity.

Figure 3. Crystal structures of (a) {Zn[HC(PPh₂Se)₂]₂} (**9a**) and (b) {Hg[HC(PPh₂Se)₂]₂} (**9b**). Hydrogen atoms in the phenyl groups have been omitted for clarity. ^a Symmetry operation: -x, y, 0.5-z.

Figure 4. Geometries and SOMOs of the neutral radicals [HC(PR₂Se)₂][•]; (a) R = Ph (**10a**), and (b) R = ^{*i*}Pr (**10c**).

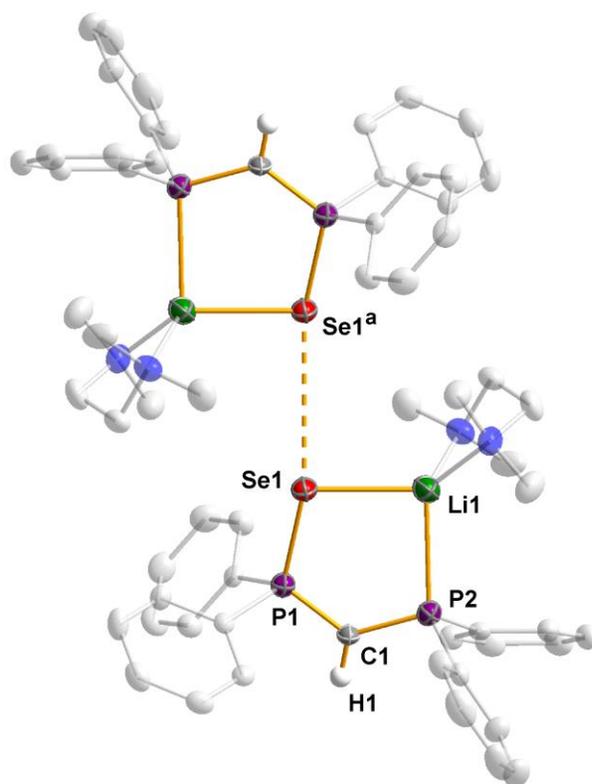


Figure 1.

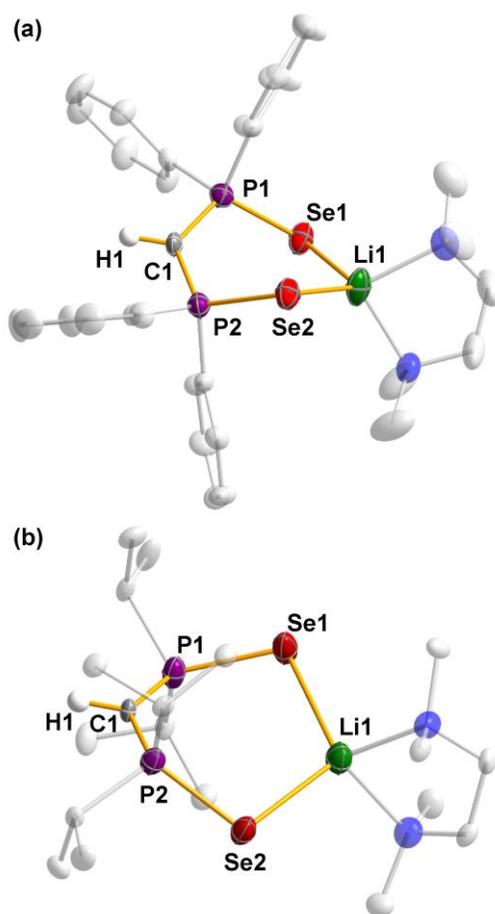


Figure 2.

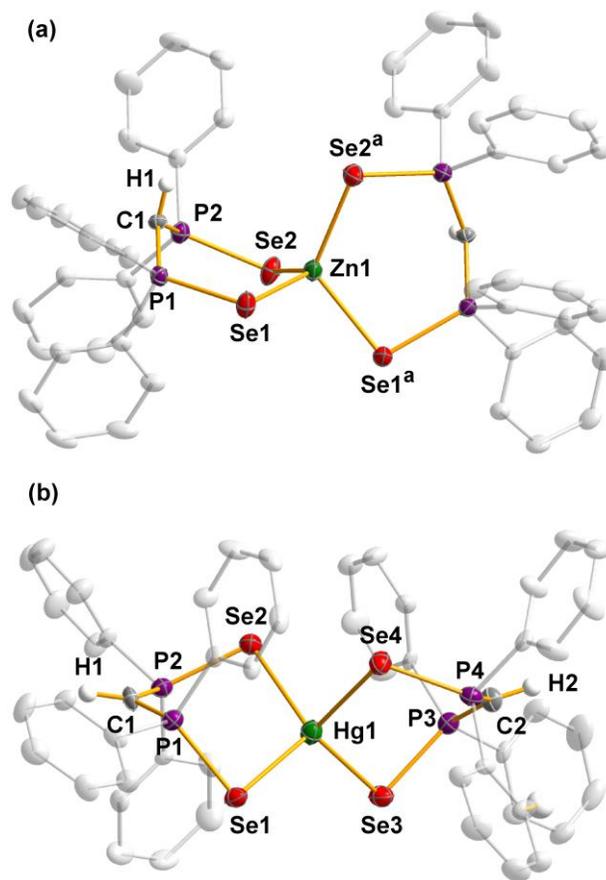


Figure 3.

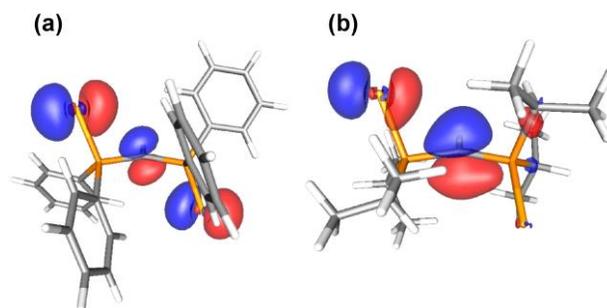


Figure 4.