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Structural and Spectroscopic Studies of the PCP-Bridged Heavy Chalcogen-Centered Monoanions, [HC(PPh₂E)(PPh₂)]⁻ (E = Se, Te) and [HC(PR₂E)₂]⁻ (E = Se, Te, R = Ph; E = Se, R = iPr): Homoleptic Group 12 Complexes and One-electron Oxidation of [HC(PR₂Se)₂]⁻

Jari Konu,† Heikki M. Tuononen‡ and Tristram Chivers†*
Abstract:

Selenium- and tellurium-containing bis(diphenylphosphinoyl)methane monoanions were prepared by oxidation of the anion [HC(PPh₂)₂]⁻ with elemental chalcogens. The selenium-containing iso-propyl derivative was synthesized by generating [H₂C(PPr₂)₂] via a reaction between [H₂C(PCl₂)₂] and four equivalents of iPrMgCl prior to in situ oxidation with selenium followed by deprotonation with LiNᵢPr₂. The solid-state structures of the lithium salts of the monochalcogeno anions TMEDA·Li[HC(PPh₂E)(PPh₂)] [E = Se (Li₇a), E = Te (Li₇b)] and the dichalcogeno anions TMEDA·Li[HC(PR₂Se)₂] [R = Ph (Li₈a), iPr (Li₈c)] revealed five- and six-membered LiEPCP and LiSePCPSₐSe rings, respectively. The homoleptic group 12 complexes {M[HC(PPh₂Se)₂]} [M = Zn (9a); Hg (9b)] were prepared from Li₈a and MCl₂ and shown to have distorted tetrahedral structures; the non-planarity of the carbon center in the PC(H)P unit of the Zn complex 9a is attributed to crystal packing effects. The complexes Li₇a, Li₇b, Li₈a, TMEDA·Li[HC(PPh₂Te)₂] (Li₈b), Li₈c, 9a and 9b were characterized in solution by multinuclear (¹H, ⁷Li, ¹³C, ³¹P, ⁷⁷Se, ¹²⁵Te and ¹⁹⁹Hg) NMR spectroscopy. One-electron oxidation of Li₈a and Li₈c with iodine in a variety of organic solvents produced [H₂C(PR₂Se)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 [HC(PR₂Se)₂]⁺ (R = iPr, Ph).
Introduction

Mono- and dichalcogenoimidodiphosphinate monoanions, [N(PR₂E)(PR₂)]⁻ (1) and [N(PR₂E)₂]⁻ (2) (R = ³Pr, ³Bu, Ph; E = S, Se, 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 [N(PR₂)₂]⁻ prior to oxidation with the elemental chalcogen.⁴

Of particular interest is the recent utilization of the dichalcogenoimidodiphosphinate monoanions 2 (E = S, Se, Te; R = ³Pr, ³Bu) 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 [EPR₂NR₂PE-EPR₂NR₂PE] (3a), formally involving the association of two [EPR₂NR₂PE]⁺ 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 [N(PR₂E)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 [N(PR₂E)₂]⁺; the calculated energy differences between the forms 3a-c are small especially when E = S or Se.⁵,⁶

Furthermore, the formally 6π-electron five-membered cations [N(PR₂E)₂]⁺ (E = S, Se,
Te; R = {^1Pr, ^1Bu} are obtained as iodide salts by two-electron oxidation of the corresponding anions (2). 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.

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. 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). 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. Prior to our study, Le Floch and co-workers had noted that the mild oxidation of Li₂4 with hexachloroethane produces a monomeric form of 5, i.e. [ClC(PPh₂S)₂]Li(OEt₂).²

While the sulfur-containing dianion 4 has attracted considerable interest lately, primarily due to the exciting work of Le Floch et al., 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 \{Ge[(Me₃Si)C(PMe₂)(PMe₂Se)]₂\}_₁² and the diseleno complex \{Cₚ*Rh[HC(PPh₂Se)₂]ClO₄\}_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 (E = Te) or their neutral precursors have been reported.

In this contribution we report the synthesis, spectroscopic and structural characterization of the lithium salts TMEDA·Li[HC(PPh₂E)(PPh₂)] [E = Se (Li₇a); E = Te (Li₇b)] and TMEDA·Li[HC(PPh₂E)₂] [E = Se (Li₈a), Te (Li₈b)]. In addition, we describe a one-step reaction to generate the iso-propyl derivative of the PCP ligand, [H₂C(PPr₂)₂], for the subsequent production of TMEDA·Li[HC(PPr₂Se)₂] (Li₈c). The utility of Li₈a as a metathetical reagent is demonstrated by the preparation of the homoleptic group 12 complexes \{M[HC(PPh₂Se)₂]₂\} [M = 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 [HC(PR₂Se)₂]⁺ (10a, R = Ph; 10c, R = 'Pr) (hydrogen abstraction) compared to that of [N(PR₂Se)₂]⁺ (R = 'Pr, '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 [H₂C(PPh₂)₂] (Aldrich, 97%), [H₂C(PCl₂)₂] (Strem Chemicals, >90%), 'PrMgCl (Aldrich, 2.0 M sol. in THF), TMEDA (Aldrich, 99%), MeLi (Aldrich, 1.6 M sol. in Et₂O), ZnCl₂ (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 Li⁷a, Li⁷b, Li⁸a, Li⁸c, ⁹a and ⁹b are summarized in Table 1 (see also supplementary data). Crystals of TMEDA·Li[HC(PPh₂Se)(PPh₂)] (Li⁷a), TMEDA·Li[HC(PPh₂Te)(PPh₂)] (Li⁷b), TMEDA·Li[HC(PPh₂Se)₂] (Li⁸a), TMEDA·Li[HC(PPr₂Se)₂] (Li⁸c), {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 MoKα 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. 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. Molecular structures were optimized with the hybrid PBE1PBE exchange-correlation functional together with the Ahlrichs' TZVP basis sets. 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.

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, $^2J(^1H, ^3P) = 7.6$ and 12.4 Hz]. $^{13}$C NMR (23 °C): $^\delta$ 147.5 [dd, Ph, $C_{ipso}$, $^1J(^{13}$C, $^3$P) = 10.6 Hz, $^3J(^{13}$C, $^3$P) = 1.6 Hz], 144.6 [dd, Ph, $C_{ipso}$, $^1J(^{13}$C, $^3$P) = 74.7 Hz, $^3J(^{13}$C, $^3$P) = 3.5 Hz], 132.4 [d, Ph, $C_{ortho}$, $^2J(^{13}$C, $^3$P) = 16.5 Hz], 132.2 [d, Ph, $C_{ortho}$, $^2J(^{13}$C, $^3$P) = 10.2 Hz], 129.0 [d, Ph, $C_{para}$, $^4J(^{13}$C, $^3$P) = 2.8 Hz], 127.9 [d, Ph, $C_{meta}$, $^3J(^{13}$C, $^3$P) = 6.6 Hz], 127.5 [d, Ph, $C_{meta}$, $^3J(^{13}$C, $^3$P) = 11.6 Hz], 126.7 [s, Ph, $C_{para}$], 58.7 [s, TMEDA, -CH$_2$], 46.1 [s, TMEDA, -CH$_2$], 20.1 [dd, PCP carbon, $^1J(^{13}$C, $^3$P) = 107.7 Hz, $^1J(^{13}$C, $^3$P) = 20.4 Hz]. $^7$Li NMR (23 °C): $^\delta$ 1.41. $^{31}$P NMR (23 °C): $^\delta$ 33.2 [d, $^2J(^{31}$P, $^{31}$P) = 173.7 Hz, $^1J(^{31}$P, $^{77}$Se) = 556 Hz], -10.9 [d, br, $^2J(^{31}$P, $^{31}$P) = 173.7 Hz]. $^{77}$Se NMR (23 °C): $^\delta$ -203 [dd, $^1J(^{77}$Se, $^{31}$P) = 557 Hz, $^2J(^{77}$Se, $^{31}$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(PPh$_2$Te)(PPh$_2$)] (Li7b).**

A mixture of TMEDA·Li[HC(PPh$_2$Te)(PPh$_2$)] (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 [H$_2$C(PPh$_2$)$_2$] and TMEDA·Li[HC(PPh$_2$Te)$_2$] (Li8b) was not possible due to the extreme moisture-sensitivity of Li7b. $^1$H NMR (d$_8$-THF, 23 °C): $^\delta$ 7.12–7.92 [m, 20H, C$_5$H$_3$], 2.34 [s, 4H, -CH$_2$ of TMEDA], 2.17 [s, 12H, -CH$_3$ of TMEDA], 1.61 [s, br, 1H, -CH of the PCP carbon]. $^{13}$C NMR (23 °C): $^\delta$ 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, -CH$_2$], 46.2 [s, TMEDA, -CH$_3$], 22.0 [s, br, PCP carbon. $^7$Li NMR (23 °C): $^\delta$ 1.01. $^{31}$P NMR (23 °C): $^\delta$ -4.4 [d, $^2J(^{31}$P, $^{31}$P) = 181.9 Hz], -14.2 [d, $^2J(^{31}$P, $^{31}$P) = 181.9 Hz, $^1J(^{31}$P, $^{125}$Te) = 1359 Hz]. $^{125}$Te NMR (23 °C): $^\delta$ -374 [d, br, $^1J(^{125}$Te, $^{31}$P) =
1358 Hz]. X-ray quality crystals of Li7b 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] (Li8a).**

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 Li8a 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. \(^1\)H NMR (d8-THF, 23 °C): δ 7.25-8.01 [m, 20H, C\(_6\)H\(_5\)], 2.32 [s, 4H, -CH\(_2\) of TMEDA], 2.14 [s, 12H, -CH\(_3\) of TMEDA], 1.54 [t, 1H, -CH of the PCP carbon, \(^2\)J\(^{\text{1}H, \text{31P}}\) = 2.2 Hz]. \(^{13}\)C NMR (23 °C): δ 141.5 [dd, Ph, C\(_\text{ipso}\), \(^1\)J\(^{\text{13C, 31P}}\) = 90.7 Hz, \(^3\)J\(^{\text{13C, 31P}}\) = 6.6 Hz], 132.6 [m, Ph, C\(_\text{ortho}\), \(^2\)J\(^{\text{13C, 31P}}\) = 5.5 Hz], 129.7 [s, Ph, C\(_\text{para}\)], 127.8 [m, Ph, C\(_\text{meta}\), \(^3\)J\(^{\text{13C, 31P}}\) = 6.0 Hz], 58.5 [s, TMEDA, -CH\(_2\)], 46.2 [s, TMEDA, -CH\(_3\)], 18.4 [t, PCP carbon, \(^1\)J\(^{\text{13C, 31P}}\) = 100.4 Hz]. \(^7\)Li NMR (23 °C): δ 1.20. \(^{31}\)P NMR (23 °C): δ 25.1 [s, \(^1\)J\(^{\text{31P, 77Se}}\) = 585 Hz, \(^2\)J\(^{\text{31P, 31P}}\) = 30.1 Hz]. \(^{77}\)Se NMR (23 °C): δ -166.2 [d, \(^1\)J\(^{\text{77Se, 31P}}\) = 585 Hz]. X-ray quality crystals of Li8a 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] (Li8b).**

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 \(^{31}\)P NMR spectrum showed a ca. 2:1:1 mixture of TMEDA·Li[HC(PPh2Te)(PPh2)] (Li7b), [H\(_2\)C(PPh2)\(_2\)] and TMEDA·Li[HC(PPh2Te)2] (Li8b). Increased reaction time (up to 24 h) and/or
elevated temperature resulted in decomposition and, eventually, the formation of $[\text{H}_2\text{C(Ph}_2\text{)}_2]$ as the sole product containing the PCP unit ($^{31}\text{P}$ NMR). NMR data for TMEDA·Li[HC(Ph$_2$Te)$_2$] (Li8b): $^{31}$P NMR (d$_8$-THF, 23°C): $\delta$ -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): $\delta$ -245 [d, br, $^1J^{(^{125}\text{Te}, ^{31}\text{P}) = 1380}$ Hz].

**Synthesis of TMEDA·Li[HC(P$i$Pr$_2$Se)$_2$] (Li8c).**

A solution of [H$_2$C(PCl$_2$)$_2$] (0.871 g, 4.00 mmol) in 40 mL of THF was cooled to -80 °C and a solution of $^i$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, [H$_2$C(P$i$Pr$_2$)$_2$], was extracted with ca. 100 mL of Et$_2$O. 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 [H$_2$C(P$i$Pr$_2$)$_2$]): $\delta$ -1.3 in THF, cf. lit. value of 1.3 ppm in CDCl$_3$). 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 [H$_2$C(P$i$Pr$_2$Se)$_2$] was confirmed by $^{31}$P NMR spectroscopy [$\delta$ 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$i$Pr$_2$ (0.450 g, 4.20 mmol, 5% excess) in 20 mL of THF was added to the solution of [H$_2$C(P$i$Pr$_2$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$i$Pr$_2$. 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 C$_{19}$H$_{45}$LiN$_2$P$_2$Se$_2$: C 43.19; H 8.58; N 5.30. Found: C 42.81; H 8.31; N 5.36.**

$^1$H NMR (d$_8$-THF, 23 °C): $\delta$ 2.67 [s, 4H, -CH$_2$ of TMEDA], 2.53 [s, 12H, -CH$_3$ of TMEDA], 2.27 [m,
4H, -CH of \(^{3}Pr\), 1.47 [m, 24H, -CH\(_{3}\) of \(^{3}Pr\)], 0.59 [s, 1H, -CH of the PCP carbon]. \(^{13}\)C NMR (23 °C): \(\delta\) 58.4 [s, TMEDA, -CH\(_{2}\)], 46.3 [s, TMEDA, -CH\(_{3}\)], 32.33 [d, \(^{3}Pr\), -CH, \(^{1}J\)(\(^{13}\)C,\(^{31}\)P) = 55.0 Hz], 17.8 [d, \(^{3}Pr\), -CH\(_{3}\), \(^{2}J\)(\(^{13}\)C,\(^{31}\)P) = 4.1 Hz], 4.0 [t, PCP carbon, \(^{1}J\)(\(^{13}\)C,\(^{31}\)P) = 97.5 Hz]. \(^{7}\)Li NMR (23 °C): \(\delta\) 1.05. \(^{31}\)P NMR (23 °C): \(\delta\) 52.5 [s, \(^{1}J\)(\(^{31}\)P,\(^{77}\)Se) = 563 Hz, \(^{2}J\)(\(^{31}\)P,\(^{31}\)P) = 13.1 Hz]. \(^{77}\)Se NMR (23 °C): \(\delta\) -355.2 [d, \(^{1}J\)(\(^{77}\)Se,\(^{31}\)P) = 563 Hz]. X-ray quality crystals of Li\(^{8}\)c were obtained from Et\(_{2}\)O solution at 5 °C in 12 h.

**Synthesis of \{Zn[HC(PPh\(_{2}\)Se)\(_{2}\)]\}(9a).**

A solution of ZnCl\(_{2}\) (0.034 g, 0.25 mmol) in 15 mL of THF was cooled to -80 °C and a solution of TMEDA·Li[HC(PPh\(_{2}\)Se)\(_{2}\)] (Li\(^{8}\)a) (0.332 g, 0.50 mmol) in 20 mL of THF was added via cannula. The reaction mixture was stirred for \(\frac{1}{2}\) h at -80 °C and 2 h at 23 °C. The solvent was evaporated under vacuum and the product was washed with cold Et\(_{2}\)O (0 °C) to remove H\(_{2}\)C(PPh\(_{2}\)Se)\(_{2}\) 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 C\(_{50}\)H\(_{42}\)P\(_{4}\)Se\(_{4}\)Zn: C 52.31; H 3.69. Found: C 52.42; H 3.83. \(^{1}\)H NMR (d\(_{8}\)-THF, 23 °C): \(\delta\) 7.26-7.87 [m, 20H, C\(_{6}\)H\(_{5}\)], 1.72 [s, 1H, -CH of the PCP carbon]. \(^{13}\)C NMR (23 °C): \(\delta\) 137.0 [d, Ph, C\(_{ipso}\), \(^{1}J\)(\(^{13}\)C,\(^{31}\)P) = 89.9 Hz], 132.7 [m, Ph, C\(_{ortho}\), \(^{2}J\)(\(^{13}\)C,\(^{31}\)P) = 5.5 Hz], 131.1 [s, Ph, C\(_{para}\)], 128.5 [m, Ph, C\(_{meta}\), \(^{3}J\)(\(^{13}\)C,\(^{31}\)P) = 6.5 Hz], 15.5 [t, PCP carbon, \(^{1}J\)(\(^{13}\)C,\(^{31}\)P) = 88.0 Hz]. \(^{31}\)P NMR (23 °C): \(\delta\) 25.4 [s, \(^{1}J\)(\(^{31}\)P,\(^{77}\)Se) = 502 Hz, \(^{2}J\)(\(^{31}\)P,\(^{31}\)P) = 22.3 Hz]. \(^{77}\)Se NMR (23 °C): \(\delta\) -124.2 [d, \(^{1}J\)(\(^{77}\)Se,\(^{31}\)P) 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 $\{\text{Hg[HC(PPh}_2\text{Se)}_2]\}_2$ (9b).

A solution of HgCl$_2$ (0.081 g, 0.30 mmol) in 15 mL of THF was cooled to -80 °C and a solution of TMEDA·Li[HC(PPh$_2$Se)$_2$] (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 C$_{50}$H$_{42}$P$_4$Se$_4$Hg: C 46.80; H 3.30. Found: C 47.10; H 3.49.

$^1$H NMR (d$_8$-THF, 23 °C): $\delta$ 7.30-7.86 [m, 20H, C$_6$H$_5$], 1.76 [s, 1H, -C$H$ of the PCP carbon]. $^{13}$C NMR (23 °C): $\delta$ 137.4 [d, Ph, C$_{ipso}$, $^1J$($^{13}$C,$^{31}$P) = 89.8 Hz], 132.7 [m, Ph, C$_{ortho}$, $^2J$($^{13}$C,$^{31}$P) = 5.6 Hz], 131.2 [s, Ph, C$_{para}$], 128.6 [m, Ph, C$_{meta}$, $^3J$($^{13}$C,$^{31}$P) = 6.3 Hz], 16.1 [t, PCP carbon, $^1J$($^{13}$C,$^{31}$P) = 89.6 Hz]. $^{31}$P NMR (23 °C): $\delta$ 26.0 [s, $^1J$($^{31}$P,$^{77}$Se) = 510 Hz, $^2J$($^{31}$P,$^{31}$P) = 20.5 Hz, $^2J$($^{31}$P,$^{199}$Hg) = 109.2 Hz]. $^{77}$Se NMR (23 °C): $\delta$ -82.3 [d, $^1J$($^{77}$Se,$^{31}$P) 510 Hz]. $^{199}$Hg NMR (23 °C): $\delta$ -793.2 (s, br). X-ray quality crystals were obtained by layering Et$_2$O on top of a THF solution of 9b for 4 h at +5 °C.

Oxidation of TMEDA·Li[HC(PPh$_2$Se)$_2$] (Li8a) and TMEDA·Li[HC(P$i$Pr$_2$Se)$_2$] (Li8c) with I$_2$.

A solution of TMEDA·Li[HC(PPh$_2$Se)$_2$] (Li8a) (0.066 g, 0.10 mmol) in 30 mL of THF was cooled to -80 °C and a solution of I$_2$ (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 [H$_2$C(PPh$_2$Se)$_2$]; $^1$H NMR (d$_8$-toluene, 23 °C): $\delta$ 6.92-7.87 [m, 20H, C$_6$H$_5$], 4.20 [t, 2H, -C$H$ of the PCP carbon, $^2J$($^1$H,$^{31}$P) = 13.2 Hz]. $^{31}$P NMR (23 °C): $\delta$ 26.3 [s, $^1J$($^{31}$P,$^{77}$Se) = 763 Hz, $^2J$($^{31}$P,$^{31}$P) = 18.6 Hz].

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The one-electron oxidation of TMEDA·Li[HC(PPr₂Se₂)] (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(PPr₂Se₂)] as the sole product after 1 h at 23 °C; [δ 56.8 with ¹J(³¹P,⁷⁷Se) = 726 Hz and ²J(³¹P,³¹P) = 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(PPh₂E₂)] [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(diphenylphosphino)ethylene, [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(PR₂Te₂)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 TMEDA-Li[HC(PPh₂)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 ³¹P NMR spectra of these lithium derivatives (d₈-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(³¹P,³¹P) coupling constants show unusually high values of ca. 175-180 Hz, cf. 50-85 Hz in the neutral P(III)CH₂P(V) systems [H₂C(PPh₂E)(PPh₂)] (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 ⁷⁷Se and ¹²⁵Te satellites are observable in the ³¹P NMR resonances at 33.2 (Li7a) and -14.2 ppm (Li7b). The magnitude of the coupling constants of ¹J(³¹P,⁷⁷Se) = 556 Hz and ¹J(³¹P,¹²⁵Te) = 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(³¹P,⁷⁷Se) = 763 Hz in
[H₂C(PPh₂Se)₂]²⁻ and ¹J₁(³¹P,¹²⁵Te) = 1654 Hz in [N(PPr₂Te)(PPr₂H)]⁵⁻. Furthermore, the two notably different ¹J₁(¹³C,³¹P) coupling constants of 108 and 20 Hz obtained for the PCP carbon from the ¹³C NMR spectrum of Li₇a indicates a substantial inequality in the P-C bond lengths. Interestingly, the selenium-bound ³¹P(Se) chemical shift in Li₇a is markedly downfield from the value of -3.7 ppm observed for the anion [HC(PPh₂)]⁻ whereas the ³¹P(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 ³¹P NMR spectrum of the reaction solution of Li₇b after 2½ hours shows two minor signals (ca. 3%) attributed to [H₂C(PPh₂)₂] (δ -21.4) and TMEDA·Li[HC(PPh₂Te)] (Li₈b, δ -27.0, vide infra); after prolonged standing only the former by-product is observed in the ³¹P NMR spectrum. A similar disproportionation of the related P(III)/P(V) system, Li[N(PPr₂Te)(PPr₂)], to give the symmetrical P(III)/P(III) and P(V)/P(V) compounds, [HN(PPr₂)₂] and Li[N(PPr₂Te)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 ¹J₁(¹³C,³¹P) coupling constants could not be obtained from the ¹³C NMR spectrum and only a very broad doublet is observed in the ¹²⁵Te NMR spectrum, whereas the ⁷⁷Se NMR spectrum of Li₇a displays a well-resolved doublet of doublets due to the ¹J₁(⁷⁷Se,³¹P) and ²J₁(⁷⁷Se,³¹P) couplings.

The oxidation of TMEDA·Li[HC(PPh₂)] with two equivalents of elemental selenium in toluene requires moderate heating (55 °C) to complete the formation of Li₈a (Scheme 1). The ³¹P NMR spectrum of Li₈a (d₈-THF, 23 °C) exhibits a singlet at 25.1 ppm with ⁷⁷Se satellites showing ¹J₁(⁷⁷Se,³¹P) and ²J₁(³¹P,³¹P) 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$^7$a has likely been replaced by a P-Se bond in Li$^8$a. The $^{77}\text{Se}$ NMR spectrum of Li$^8$a exhibits a doublet at -166 ppm, *ca.* 35 ppm downfield from the signal observed for Li$^7$a, and the $^{1}J(^{13}\text{C},^{31}\text{P})$ coupling constant of 100 Hz, obtained from the PCP carbon resonance at 18.4 ppm in the $^{13}\text{C}$ NMR spectrum of Li$^8$a, is close to one of the two inequivalent couplings resolved for Li$^7$a. Taken together, these NMR data suggest formation of the expected LiSePCPSe six-membered ring with equivalent P(V) atoms for Li$^8$a.

The reaction between elemental tellurium and TMEDA·Li[HC(PPh$_2$)$_2$] in a 2:1 molar ratio is more complicated than the corresponding reaction with selenium. After 3 hours at 23 °C the $^{31}\text{P}$ NMR spectrum of the reaction mixture shows resonances attributed to Li$^7$b (doublets at -4.4 and -14.2 ppm) and [H$_2$C(PPh$_2$)$_2$] (δ -21.4), in addition to a singlet at -27.0 ppm. The last signal exhibits $^{125}\text{Te}$ satellites with the $^{1}J(^{31}\text{P},^{125}\text{Te})$ and $^{2}J(^{31}\text{P},^{31}\text{P})$ coupling constants of 1376 and 40.3 Hz, respectively. The former coupling is somewhat bigger than that obtained for the asymmetric monotelluro compound Li$^7$b, and the latter coupling is in the same range as that observed for the diseleno anion in Li$^8$a. In addition, a broad doublet is resolved in the $^{125}\text{Te}$ NMR spectrum of the reaction mixture at -245 ppm, *ca.* 130 ppm downfield from that of Li$^7$b, with a $^{1}J(^{31}\text{P},^{125}\text{Te})$ coupling constant of 1380 Hz. Comparison of these NMR data with those of the monotelluro compound Li$^7$b, and the selenium congeners Li$^7$a and Li$^8$a, is consistent with the formation of ditelluro anion in Li$^8$b. However, longer reaction times or even moderate heating leads to decomposition to yield neutral [H$_2$C(PPh$_2$)$_2$]; consequently, we have not been able to isolate a pure sample of Li$^8$b.

**Synthesis and Spectroscopic Characterization of TMEDA·Li[HC(P^3Pr$_2$Se)$_2$] (Li$^8$c).** While the parent PCP backbone in 7 and 8 as the phenyl derivative, [H$_2$C(PPh$_2$)$_2$], 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, \([\text{H}_2\text{C(PCI}_2\text{)}_2]\), 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 \(^{31}\text{P} \text{NMR spectroscopy}^{21}\) prior to \textit{in situ} reaction with 2 equivalents of elemental selenium (Eq. 2) followed by \textit{(in situ)} deprotonation with Li\(^i\text{Pr}_2\) in the presence of TMEDA (Eq. 3). This three-step process affords analytically pure TMEDA·Li[HC(P\(^i\text{Pr}_2\text{Se})_2]\) (Li\(^8\text{c}\)) in excellent yield (84%, calculated from \([\text{H}_2\text{C(PCI}_2\text{)}_2]\)).

\[
\begin{align*}
\text{[H}_2\text{C(PCI}_2\text{)}_2] \ + \ 4 \text{ } ^i\text{PrMgCl} & \rightarrow \text{[H}_2\text{C(P}^{i}\text{Pr}_2\text{)}_2] \ + \ 4 \text{ MgCl}_2 \\
\text{[H}_2\text{C(P}^{i}\text{Pr}_2\text{)}_2] \ + \ 2 \text{ Se} & \rightarrow \text{[H}_2\text{C(P}^{i}\text{Pr}_2\text{Se})_2] \\
\text{[H}_2\text{C(P}^{i}\text{Pr}_2\text{Se})_2] \ + \ \text{LiN}^{i}\text{Pr}_2 \ + \ \text{TMEDA} & \rightarrow \text{TMEDA·Li[HC(P}^{i}\text{Pr}_2\text{Se})_2] \ + \ \text{HN}^{i}\text{Pr}_2
\end{align*}
\]

\text{(Li\(^8\text{c}\))}

The \(^{31}\text{P} \text{NMR spectrum of Li}^{8}\text{c}\) 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 Li\(^8\text{a}\). The triplet resolved at 4.0 ppm for the PCP carbon in the \(^{13}\text{C} \text{NMR spectrum of Li}^{8}\text{c}\) exhibits \(^1J(^{13}\text{C},^{31}\text{P})\) coupling constant of 97.5 Hz, \textit{cf.} 100.4 Hz in Li\(^8\text{a}\), and a singlet is observed at 0.59 ppm for the corresponding hydrogen in the \(^1\text{H} \text{NMR spectrum. In both of these spectra the typical signal patterns are also seen for the } ^i\text{Pr and TMEDA groups. In addition, a doublet is found at -355.2 ppm in the } ^{77}\text{Se NMR spectrum of Li}^{8}\text{c}\) with the \(^1J(^{77}\text{Se},^{31}\text{P})\) of 563 Hz, which is \textit{ca.} 160 Hz smaller than that in the neutral precursor, \([\text{H}_2\text{C(P}^{i}\text{Pr}_2\text{Se})_2]\) (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), 'Pr (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). 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), 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 $^1J(^{13}C, ^{31}P)$ 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 monotelluroimidodiphosphinate monoanions 1 after metallation of the P-H unit in the neutral [N(P'Pr₂Te)(P'Pr₂H)] (Scheme 2).
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 Li8a and MCl2 (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 HgCl2 in toluene at -80 °C proceeded cleanly to produce \( \{\text{Hg}[\text{HC(PPh}_2\text{Se)}_2]_2\} \) (9b) in good yield, whereas the synthesis of the zinc congeners, \( \{\text{Zn}[\text{HC(PPh}_2\text{Se)}_2]_2\} \) (9a), afforded also a significant amount of the neutral \( \text{H}_2\text{C(PPh}_2\text{Se)}_2 \) (\(^{31}\text{P}\) NMR) regardless of the reaction conditions or the source of ZnCl2.

The \(^1\text{H}\) 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 \(^1J(\text{C},^{31}\text{P})\) of ca. 90 Hz is resolved for the corresponding carbon in the \(^{13}\text{C}\) 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 \(^1J(\text{C},^{31}\text{P})\) coupling constant ca. 45 Hz larger than the value observed for the only structurally characterized complex of the \([\text{HC(PPh}_2\text{Se)}_2]^-[\}\) anion, \(\{\text{Cp}^*\text{Rh}[\text{HC(PPh}_2\text{Se)}_2]\text{ClO}_4\}\).\(^{13}\) Together with the absence of \(^{199}\text{Hg}\) satellites for the PCP carbon resonance in the \(^{13}\text{C}\) 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 \(^1J(\text{C},^{31}\text{P})\) is consistent with somewhat shorter P-C bond lengths than those in the rhodium complex (vide infra). The \(^{31}\text{P}\) NMR spectra of 9a and 9b display a singlet with \(^{77}\text{Se}\) satellites at 25.4 and 26.0 ppm, respectively. The \(^2J(\text{P},^{31}\text{P})\) and \(^1J(\text{P},^{77}\text{Se})\) coupling constants are somewhat smaller than those in Li8a 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 \(^{199}\text{Hg}\) 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, \(\{\text{Hg}[\text{H}_2\text{C(PPh}_2\text{Se)}_2]\text{ClO}_4\}_2\).\(^{31}\) 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 ($\Sigma \angle$C1 352°, 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, {M[N(PR$_2$Se)$_2$]}$_2$ (M = Zn, R = iPr, Ph;$_{30d}$ M = Hg, R = iPr,$_{30c}$ Ph$_{32}$). 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 [H$_2$C(PPh$_2$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 $^1J$(P,$^{77}$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 \{ZnI₂[H₂C(PPh₂Se)₂]\} \(^{33}\) and \{HgX₂[H₂C(PPh₂Se)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 \(^1J(\text{¹³C, ³¹P})\), 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 \{Cp⁺Rh[HC(PPh₂Se)₂]ClO₄\}. \(^{13}\) 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, \{M[N(PR₂Se)₂]₂\} (M = Zn, R = 'Pr, Ph; \(^{30d}\) M = Hg, R = 'Pr, \(^{30e}\) Ph),\(^{32}\) 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(PiPr₂Se)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, [N(PR₂E)₂]₂ (E = Se, Te; R = 'Pr, '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 [H₂C(PPh₂Se)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 Li⁸a, the reaction of the iso-propyl derivative Li⁸c 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 'Pr and 'Bu substituents were utilized.⁵ ⁶ In the case of Li⁸c, 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 Li⁸a, NMR spectroscopy showed the formation of [H₂C(PPr₂Se)₂] as the final product (Scheme 3).

**Scheme 3.** One-electron oxidation of Li⁸a and Li⁸c.

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 'Pr-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, [N(PR₂E)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, [N(PR₂E)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 –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 ⁷⁷Se and ¹³C 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.⁵⁵

Conclusions

Synthetic routes to the heavy chalcogen-centered anionic ligands, [HC(PPh₂E)(PPh₂)]⁻ and [HC(PPh₂E)₂]⁻ (E = Se, Te), have been developed. The selenium-containing monoanions [HC(PPh₂Se)(PPh₂)]⁻ (7a) and [HC(PPh₂Se)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, M[HC(PPh₂Se)₂]₂ (M = Zn, Hg). By contrast, the tellurium
congeners Li$^7\text{b}$ and Li$^8\text{b}$ are thermally unstable. Consequently, although the solid-state structure of the monotelluro anion Li$^7\text{b}$ was determined, its use as a reagent is limited to in situ reactions.

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

Acknowledgments

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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.

References


(3) Ritch, J. S.; Chivers, T. *Dalton Trans.* **2008**, *957*.


(13) Valderrama, M.; Contreras, R.; Bascunan, M. Polyhedron 1994, 13, 1101.


(28) Bond orders were calculated by the Pauling equation \( N = 10^{(D-R)/0.71} \), where \( R \) is the observed bond length (Å). The single bond length \( D \) is estimated from the sums of appropriate covalent radii (Å):\(^{27}\) Li-P 2.35, Li-Se 2.48, Li-Te 2.66, Se-P 2.27, Te-P 2.45.


(35) A referee has pointed out that the magnitude of $^{31}$P hfccs is markedly dependent on ring torsion angles in certain heterocyclic P(V) radicals.\textsuperscript{36} In the current case, however, it seems unlikely that the discrepancy between the calculated and experimental $^{31}$P hfccs can be attributed to a conformational change, i.e. bond rotation, since the calculated values for 10a and 10b differ by only a few Gauss despite their significantly different conformations.

<table>
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<tr>
<th>Li7a</th>
<th>Li7b</th>
<th>Li8a</th>
<th>Li8c</th>
<th>9a</th>
<th>9b</th>
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<tbody>
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<td>C(<em>{31})H(</em>{37})Li(_2)N(_2)P(_2)Te</td>
<td>C(<em>{31})H(</em>{37})Li(_2)N(_2)P(_2)Se (_2)</td>
<td>C(<em>{19})H(</em>{43})Li(_2)N(_2)P(_2)Se (_2)</td>
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<td>P2(_1)/c</td>
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<td>P-1</td>
<td>C2/c</td>
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<tr>
<td>c, Å</td>
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<td>reflns [I&gt;2σ(I)]</td>
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<td>0.996</td>
<td>0.996</td>
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$^a\lambda$ (MoKα) = 0.71073 Å. $^b R_1 = \sum |F_o| - |F_c|/\sum |F_o|$. $^c wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$. 
Table 2. Selected bond lengths (Å) and angles (°) in Li7\textsuperscript{a} and Li7\textsuperscript{b} [calculated bond orders in square brackets].\textsuperscript{28}

<table>
<thead>
<tr>
<th></th>
<th>Li7\textsuperscript{a}</th>
<th>Li7\textsuperscript{b}</th>
<th>Li7\textsuperscript{a}</th>
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<td>E1-P1</td>
<td>2.1591(6) [1.43]</td>
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<td>E1···E1\textsuperscript{a}</td>
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\textsuperscript{a} E = Se, \textsuperscript{b} E = Te. Symmetry operation for the atoms marked with a single quote (‘): \textsuperscript{c} -x, 1-y, -z; \textsuperscript{d} 1-x, 1-y, 1-z.
Table 3. Selected bond lengths (Å) and angles (°) in Li₈a and Li₈c.

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

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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(PPh₂Se₂)] (Li8a) and (b) TMEDA·Li[HC(PPr₂Se₂)] (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(PPh₂Se₂)]₂] (9a) and (b) [Hg[HC(PPh₂Se₂)]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(PR₂Se₂)]⁺; (a) R = Ph (10a), and (b) R = ‘Pr (10c).
Figure 1.
Figure 2.
Figure 3.
Figure 4.