

Cite this: DOI: 10.1039/c2dt12361d

www.rsc.org/dalton

PCP-bridged chalcogen-centred anions: coordination chemistry and carbon-based reactivity

Tristram Chivers,*^a Jari Konu*^b and Ramalingam Thirumoorthi^a

Received 6th December 2011, Accepted 18th January 2012

DOI: 10.1039/c2dt12361d

Since the discovery of the stabilising influence of thiophosphinoyl groups in methanediides by Le Floch *et al.* (*Angew. Chem. Int. Ed.*, 2004, **43**, 6382), numerous transition metal, lanthanide and actinide complexes of bis(thiophosphinoyl) carbene ligands have been investigated with an emphasis on the electronic structure and reactivity of the metal–carbon bonds. This Perspective begins by discussing main group (s- and p-block) complexes of this ligand and draws attention to differences compared to their d and f-block analogues. Investigations targeting the heavy chalcogen analogues of the Le Floch ligand have revealed an unusual carbon-based reactivity that led to the discovery of novel multidentate chalcogen-centred ligands as both monomers and, upon oxidation, dimers linked by dichalcogenido functionalities. Studies of main group and coinage metal complexes have established the flexibility and redox-activity of these novel anionic ligands.

1. Introduction

The discovery of the chalcogen-centred PNP-bridged ligands of the type $[N(PR_2E)_2]^-$ (**1**, E = O, S, Se; R = alkyl, aryl) in the 1960s¹ paved the way for extensive investigations of the coordination chemistry of these monoanions.² In the past decade, renewed interest in this class of metal complexes has been stimulated through their application as single-source molecular precursors for semiconducting metal selenides in the form of thin films or quantum dots by the group of O'Brien.³ In the early 2000s, the development of a synthetic route to the first ditelluro PNP-

bridged anions (**1**, E = Te; R = Ph,^{4a} ⁱPr,^{4b} ^tBu^{4c}) facilitated investigations of their metal complexes as sources of binary metal tellurides,^{5a} *e.g.* Sb₂Te₃,^{5b} PbTe^{5c} and CdTe,^{5d} which are of interest for applications in the electronics industry.

Although the *in situ* generation of the PCP-bridged anions $[HC(PR_2E)_2]^-$ (**2**, E = S, Se; R = Ph), which are isoelectronic with **1** (Fig. 1), was employed 40 years ago to prepare homoleptic Fe(II), Co(II) and Ni(II) complexes,⁶ studies of the coordination chemistry of these dichalcogeno ligands have been limited. A few transition metal examples have been generated by deprotonation of complexes with neutral ligands $[H_2C(PPh_2E)_2]$ (E = S, Se) with sodium hydride.⁷ In these complexes the involvement of the carbon atom of ligand **2** in a C,E or E,C,E coordination mode is frequently observed. By contrast, N-coordination is observed only rarely for metal complexes of **1**, notably the lanthanides.⁸

^aDepartment of Chemistry, The University of Calgary, Calgary, Alberta, Canada, T2N 1N4. E-mail: chivers@ucalgary.ca

^bDepartment of Chemistry, University of Jyväskylä, P. O. Box 35, FI-40014 Jyväskylä, Finland. E-mail: jari.a.konu@jyu.fi



Tristram Chivers

interests are in the area of the chemistry of the main group elements. He is the author of the book "A Guide to Chalcogen–Nitrogen Chemistry" and co-authored "Inorganic and Rings and Polymers of the p-Block Elements: From Fundamentals to Applications" with Ian Manners.

Tristram Chivers received his B.Sc., Ph.D. and D.Sc. degrees from the University of Durham, U.K. He has been a faculty member at the University of Calgary, Canada, since 1969 and currently holds the titles of Faculty Professor and Professor Emeritus. His research



Jari Konu

interests are in the general area of main group chemistry, especially chalcogen compounds.

Jari Konu received his M.Sc., Lic. Phil. and Ph.D. degrees in inorganic chemistry from the University of Oulu, Finland, under the supervision of Prof. R. S. Laitinen. He was a Postdoctoral Fellow and Research Associate with Prof. T. Chivers at the Univer-

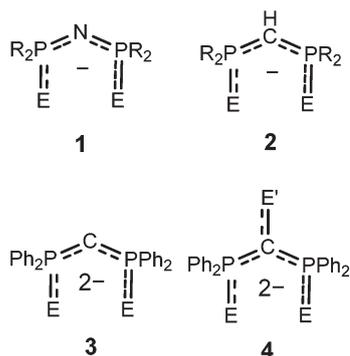


Fig. 1 The anionic ligands 1, 2, 3 and 4.

The PCP-bridged dianion $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ (**3**, E = S) is also iso-electronic with **1**. The first metal derivative of this sulfur-centred ligand was a dinuclear Pt(II) complex obtained in 1989 by Dixon *et al.* via the double metallation of the neutral ligand $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$.⁹ The development of a synthetic route to the dilithium derivative of **3** (E = S) by Le Floch and co-workers in 2004¹⁰ opened the door for extensive studies of the coordination chemistry of this PCP-bridged dianion via metathetical reactions with metal halides. The initial focus was on transition metal, lanthanide and, more recently, actinide complexes and this work has been summarized as part of two recent reviews.^{11,12} The primary interest in these complexes, all of which involve S,C,S-coordination to the metal centre, is the electronic structure and reactivity of the metal–carbon bond. DFT calculations indicate a highly polar approximately single bond for both early and late transition metals with the carbon lone pair being stabilised by negative hyperconjugation into the σ^* P–C and P–S antibonding orbitals.^{11,12} By contrast, the metal–carbon bonds in lanthanide and actinide complexes exhibit significant multiple bond character. The investigation of the structures and reactivity of these metal complexes of **3** (E = S), and the related imino ligand (E = NSiMe₃),¹³ have revealed an interesting dichotomy with respect to their description as either Fischer carbenes or Schrock alkylidenes. The presence of heteroatom substituents implies that they

could be classified as the former; on the other hand, the nucleophilic reactivity of the carbon centres is more in keeping with the latter. Consequently, it has been pointed out by two groups independently that these complexes obscure the distinction between Fischer carbenes or Schrock alkylidenes.^{12,14}

This Perspective will commence with a description of salient aspects of recent investigations of complexes of **3** (E = S) with s- and p-block metals and metalloids. In addition to drawing attention to the differences in the structure and bonding between these main group complexes and their transition metal, lanthanide and actinide counterparts, this discussion will provide a backdrop for the examination of heavy chalcogen ligands of the type **2** and **3** that follows. In our investigations of the chalcogen-centred PNP-bridged anions **1**, we observed significant differences between the heavier (Se and Te) and lighter (S) chalcogens in both their coordination chemistry and redox behaviour.^{15,16} For example, the relatively weak P–Te bonds facilitate metal-insertion reactions (intramolecular oxidative addition) to give new metal–tellurium ring systems^{17a,b} and the large Te donor sites can lead to unique structures involving bridging Te-centred ligands.^{17c} In this context, we will consider the challenges involved in the synthesis of alkali metal derivatives of heavy chalcogen-centred PCP-bridged ligands of the type **2** and **3** (E = Se, Te), which are potentially important reagents for the generation of other metal complexes via metathesis. The subsequent section highlights the carbon-centred reactivity of dichalcogeno PCP-bridged anions, demonstrated most notably by the selenium–proton exchange that is observed in reactions of **2** (E = Se, R = Ph) with main group metal halides. This transformation generates the all-selenium derivative of a novel class of trichalcogeno PCP-bridged dianions of the type **4** (E = E' = Se). In the final sections, we present the synthesis of the related ligands **4** (E = S, E' = S or Se), which, upon oxidation, engender the dimeric dichalcogenides $[(\text{SPh}_2\text{P})_2\text{CEEC}(\text{PPh}_2\text{S}_2)]^{2-}$ (E = S, Se), a versatile new class of multidentate chalcogen-centred ligand as illustrated by their coordination complexes with main group and coinage metals.

2. Main group complexes of PCP-bridged sulfur-centred ligands

2.1 Synthesis

Two approaches have been used for the synthesis of main group (s- and p-block) complexes of **3** (E = S): (a) metallation (dealkylation or deamination) of the neutral ligand $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ and (b) metathesis via reactions of either $\text{Li}[\text{HC}(\text{PPh}_2\text{S})_2]$ (**5**) or $\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2]$ (**6**) and metal halides. Method (a) is successful for the generation of derivatives of more electropositive metals. Thus, the monolithiated reagent **5** is obtained by treatment of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ with ⁿBuLi in THF at 0 °C,^{18,19} while the dilithiated derivative (**6**) requires the use of two equivalents of MeLi.¹⁰ Metallation of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ is also effected by ⁿBu₂Mg in THF at 60 °C to give the homoleptic magnesium complex $[\text{MgC}(\text{PPh}_2\text{S})_2(\text{THF})_2]$ (**7**).²⁰ The deamination approach is successful for the synthesis of the homoleptic group 14 dimers $[\text{M}\{\mu^2\text{-C}(\text{PPh}_2\text{S})_2\}]_2$ (**8a**, M = Sn; **8b**, M = Pb) from $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ and $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ in toluene.^{18,21} The unsolvated potassium reagent $\{\text{K}[\text{HC}$



Ramalingam Thirumoorthi

Ramalingam Thirumoorthi received his B.Sc. and M.Sc. degrees from Madurai Kamaraj University, India, and completed his Ph.D. degree under the supervision of Prof. V. Chandrasekhar at IIT Kanpur, India, in 2009. Prior to joining the group of Prof. T. Chivers at the University of Calgary, Canada, in 2010 he was a Post-doctoral Research Associate at the University of Massachusetts, U.S.A. His research interests focus on the chemistry of group 14, 15 and 16 elements.

$(\text{PPh}_2\text{S})_2\}_\infty$ is readily prepared by treatment of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ with $\text{K}[\text{N}(\text{SiMe}_3)_2]$ in THF and toluene.^{22a}

The monolithiated reagent **5** has been employed in the preparation of the heteroleptic, divalent group 14 complexes $[\text{MCl}\{\text{HC}(\text{PPh}_2\text{S})_2\}]$ (**9a**, M = Ge; **9b**, M = Sn).¹⁸ However, the metathesis of **5** with group 13 trihalides is accompanied by dehydrochlorination to give complexes of the dianion **3** (E = S, R = Ph), viz. $[\text{MCl}\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**10a**, M = Al; **10b**, M = Ga; **10c**, M = In).²⁰ The analogous group 15 derivatives $[\text{MCl}\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**11a**, M = Sb; **11b**, M = Bi) are best prepared from the dilithiated reagent **6** and MCl_3 ,²³ although the bismuth complex **11b** may also be obtained from **5** and BiCl_3 by the dehydrochlorination route.^{22b} The reagent **6** has also been used to synthesise the homoleptic germanium(IV) complex $[\text{Ge}\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**12a**) from GeCl_4 ²⁴ and the heteroleptic tellurium(IV) complexes $[\text{TeX}_2\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**13a**, X = Cl; **13b**, X = Br; **13c**, X = I) from the corresponding tellurium tetrahalide.²⁵ The homoleptic tin(IV) analogue **12b** is obtained by treatment of the magnesium reagent **7** with SnCl_4 .²⁶ Complexes **12a** and **12b** represent the first examples of 2-germa- and 2-stanna-allenes, respectively.

2.2 Structure and bonding

The structures of the main group metal complexes of the anions $[\text{HC}(\text{PPh}_2\text{S})_2]^-$ and $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ illustrate the versatility of these chalcogen-centred PCP-bridged ligands as depicted in Fig. 2. The monoanionic ligand in $\text{Li}[\text{HC}(\text{PPh}_2\text{S})_2](\text{THF})(\text{Et}_2\text{O})$ (**5**) is *S,S'*-chelated to a bis-solvated Li centre.²⁰ The unsolvated potassium derivative $[\text{K}[\text{HC}(\text{PPh}_2\text{S})_2]]_\infty$ has a polymeric ladder structure in which monomeric units are associated by weak $\text{K}\cdots\text{S}$ interactions to form 4-membered K_2S_2 rings,^{22a} cf. the PNP-bridged analogue $[\text{K}[\text{N}(\text{PPh}_2\text{S})_2]]_\infty$.²⁷ Two dimeric structures of $\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2]$ with different degrees of solvation of the Li centres have been structurally characterised.¹⁹ The monosolvated complex $\{\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2](\text{OEt}_2)\}_2$ (**6**) exhibits both 3- and 4-coordinate Li centres; the former involve *S,S'*-chelated Li atoms solvated by an Et_2O molecule, whereas the latter consist of Li atoms that bridge two carbon atoms and are also bonded to two S atoms. The homoleptic magnesium complex $[\text{MgC}(\text{PPh}_2\text{S})_2(\text{THF})_2]$ (**7**) and the heteroleptic group 13 derivatives $[\text{MCl}\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**10a**, M = Al; **10b**, M = Ga; **10c**, M = In) adopt similar dimeric structures in which two metal methanediide monomers are linked head-to-tail *via* the sulfur atoms.²⁰ By contrast, the group 15 analogues $[\text{MCl}\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**11a**, M = Sb; **11b**, M = Bi) display *S,C,S*-coordination of the tridentate ligand to the metal and dimerise through weak $\text{M}\cdots\text{S}$ interactions.²³ The tellurium(IV) complexes $[\text{TeX}_2\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**13a**, X = Cl; **13b**, X = Br; **13c**, X = I) adopt a similar *S,C,S*-coordination mode, but in this case dimerisation occurs *via* the halide bridges.²⁵

In the monomeric group 14 complexes $[\text{MCl}\{\text{HC}(\text{PPh}_2\text{S})_2\}]$ (**9a**, M = Ge; **9b**, M = Sn) the monoanion is *C,S*-coordinated to the divalent metal centre.¹⁸ Similarly, the two ligands are *C,S*-bonded to the metal atom in the homoleptic germanium(IV) complex $[\text{Ge}\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**12a**) and one of the thiophosphinoyl groups of each ligand is pendant.²⁴ By contrast, the metal centre in **12b** is hexacoordinate with all four sulfur atoms bound

to tin (*S,C,S*-bonding), although variable temperature NMR studies indicate an equilibrium between the four- and six-coordinated complexes in solution.²⁶ The dianions in the dimeric complexes $[\text{M}\{\mu^2\text{-C}(\text{PPh}_2\text{S})_2\}]_2$ bridge two metal(II) centres with two of the sulfur donor atoms of both ligands coordinated to the metal in the case of $\text{Pb}(\text{II})$ (**8b** in Fig. 2); in the $\text{Sn}(\text{II})$ analogue, **8a**, only one sulfur of each ligand is coordinated to the metal (not shown in Fig. 2).¹⁸

In addition to the different coordination modes observed for ligand **3** (E = S) in main group element complexes, a few general comments about their structural parameters are warranted. The complexes in which the carbon atom of the PCP-bridge is three-coordinate exhibit approximately planar geometry [**10a–c** (350.4–352.4°), **11a,b** (359.3–359.5°), **12a** (358.3°), **12b** (354.7°), **13a–c** (359.7–359.8°)], while the dimeric complexes **6** and **8a,b** have distorted tetrahedral environments, as expected for the four-coordinate carbon atom. The P–C and P–S bond lengths are significantly shortened and lengthened, respectively, in all complexes compared to the reported values for the neutral ligand $\text{H}_2\text{C}(\text{Ph}_2\text{PS})_2$ ²⁸ indicating delocalisation in these complexes.²⁹ A comparison of the metal–carbon bond lengths for these main group complexes with the sum of the appropriate carbon and metal (or metalloid) covalent radii and with M–C single bonds in related complexes reveals a significant shortening (by 5–6% for **11a,b** and **13a–c**). The change in the electronegativity of the halide substituent in the tellurium(IV) complexes **13a–c** has a small, but significant, effect on the Te–C bond length with values of 2.024(3), 2.030(6) and 2.045(8) Å for X = Cl, Br and I, respectively.²⁵ More importantly, the metalloid–sulfur distances in the *S,C,S*-bonded group 15 and group 16 complexes are substantially longer than the sum of the covalent radii (12–13% for **11a,b** and *ca.* 10% for **13a–c**). The significance of these structural parameters is discussed below in the light of the bonding insights provided by theoretical calculations.

The NBO analysis of the dilithium derivative **6** showed that the C–Li and S–Li interactions are essentially electrostatic in nature with two lone pairs occupying approximately sp^2 and pure p orbitals on carbon and three lone pairs on each sulphur atom.¹⁹ The nature of the Mg–C bonding in the dimer **7** has not been addressed.²⁰ An understanding of the nature of the metal–ligand bonding and, in particular, the degree of metal–carbon multiple bonding in p-block metal complexes of dianion **3** (E = S) is currently being developed. DFT calculations and a topological analysis of the electron densities in the homoleptic *C,S*-bonded germanium(IV) complex **12** led to the conclusion that “the Ge–C bonds are polar and covalent and their bond nature is between a single and double bond”.²⁴ On the other hand, a DFT analysis of the electronic structures of the *S,C,S*-bonded group 15 derivatives $[\text{MCl}\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**11a**, M = Sb; **11b**, M = Bi) revealed a polar, *single* bond and three-centre two-electron S–M–S bonding for the metal–ligand interaction (Fig. 3a).²³ The latter calculations also reveal a negligible mixing of the orbitals that are predisposed for π -bonding on the carbon and the group 15 centres (see Fig. 3b). The simultaneous presence of one hard and one soft lone pair in the M–C functionality has intriguing implications for the reactivity of these complexes towards Lewis acids. A similar bonding description, *i.e.* a polar, *single* bond and three-centre two-electron S–M–S bonding,

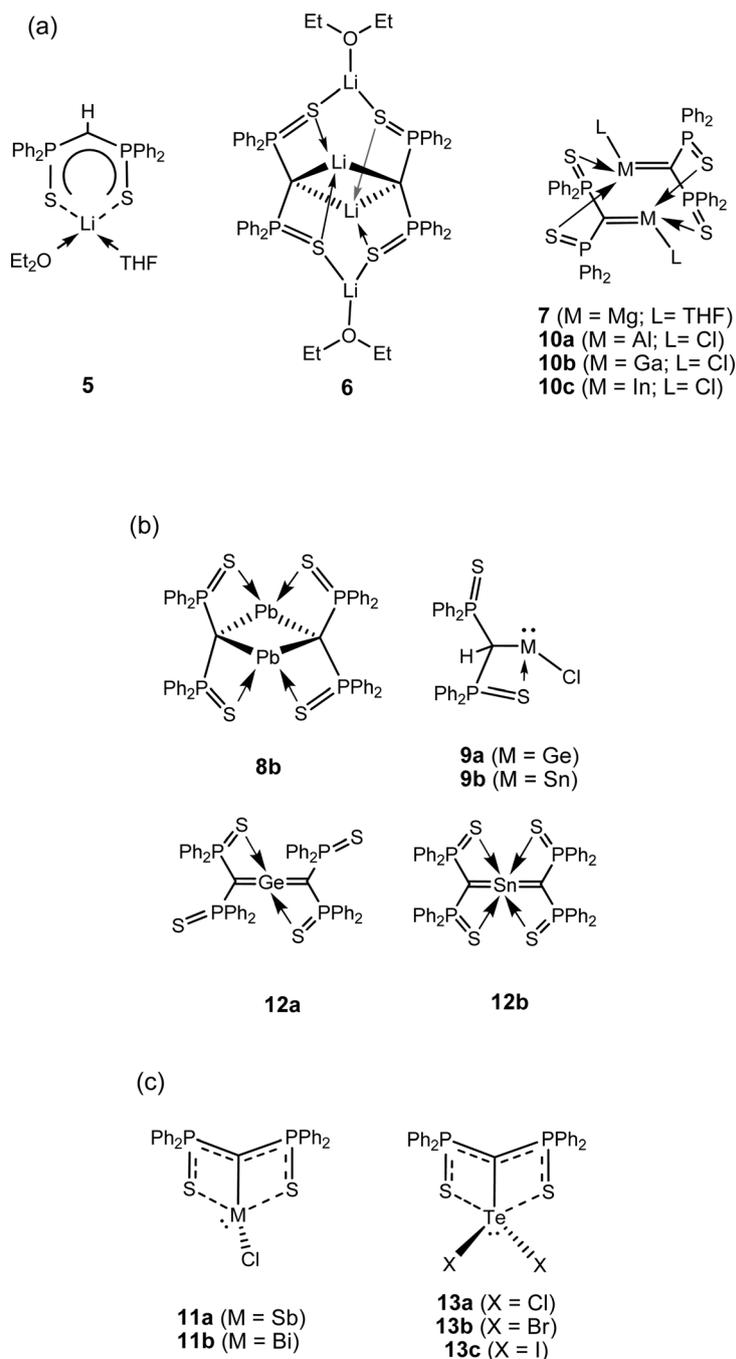


Fig. 2 The structures of s- and p-block metal complexes of $[\text{HC}(\text{PPh}_2\text{S})_2]^-$ and $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$; (a) s-block and group 13, (b) group 14, (c) group 15 and 16.

applies to the tellurium(IV) complexes $[\text{TeX}_2\{\text{C}(\text{PPh}_2\text{S})_2\}]_2$ (**13a**, X = Cl; **13b**, X = Br; **13c**, X = I).²⁵ A change in the halide substituent has no significant effect on the M–C or M–S bond orders; however, the calculated atomic charges indicate a more polar Te–C bond for **13a**, which may account for the shorter Te–C bond length in this derivative.²⁵

In summary, the structures and bonding in main group metal and metalloid complexes of the Le Floch ligand **3** (E = S, R = Ph) differ significantly from those of analogous transition metal, lanthanide and actinide complexes. In contrast to the

monomeric complexes formed by the latter, dimeric structures involving P = S donor centres are observed for homoleptic complexes of electron-deficient main group metals, e.g. **6**, **7**, **8a,b** and **10a–c**. On the other hand, heteroleptic complexes of electron-rich main group metals or metalloids form monomeric structures with M–C single bonds and three-centre two-electron S–M–S bonding arrangements, e.g. **11a,b**, **13a–c**. Since the bonding analysis of group 15 and 16 complexes, **11a,b** and **13a–c**, reveals the simultaneous presence of hard and soft lone pairs on the carbon and main group metal centres, respectively

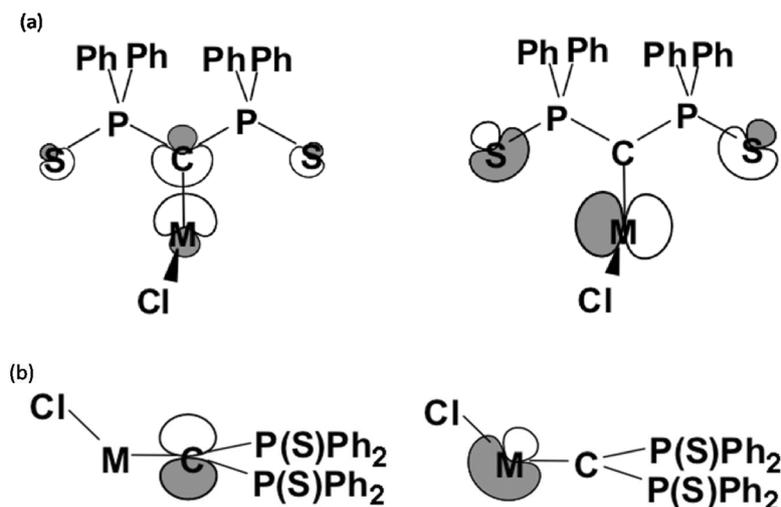


Fig. 3 A schematic representation of (a) the M–L bonding interactions in **11a** (M = Sb) and **11b** (M = Bi) and (b) the orbitals available for the π_{C-M} -interaction.

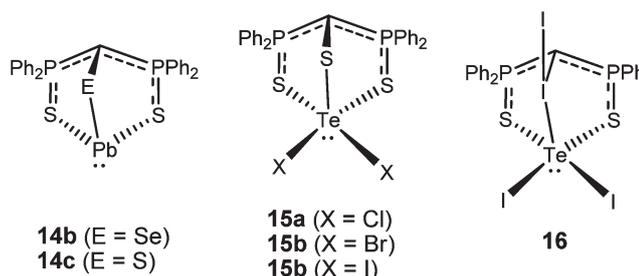


Fig. 4 Compounds **14b,c**, **15a–c** and **16**.

(Fig. 3), detailed investigations of the reactions of these methanediides that focus on the reactivity of the M–C functionality with electrophilic reagents should be revealing.

2.3 Reactions

Preliminary reports of the reactivity of p-block metal complexes of dianion **3** (E = S) have been limited to M–C bond insertion reactions. Leung and co-workers described the facile insertion of chalcogens into the Pb–C bond of **8b** at an ambient temperature in toluene to give the monomeric lead(II) complexes Pb[(E)C(PPh₂S)₂] (**14b**, E = Se; **14c**, E = S) (Fig. 4), which incorporate the trichalcogeno PCP-bridged dianions [(E')C(PPh₂E)₂]^{2–} (**4**, E = S, E' = S, Se) (see Section 5).¹⁸ The isolation of small amounts of the complexes [TeBr₂{SC(PPh₂S)₂}]₂ (**15b**) and [TeI₂{(I₂)C(PPh₂S)₂}]₂ (**16**) (see Fig. 4), from the metathesis of **6** with TeBr₄ and TeI₄, respectively,²⁵ suggests that the Te–C bond in the complexes [TeX₂{C(PPh₂S)₂}]₂ (**13b**, X = Br; **13c**, X = I) is susceptible to *in situ* insertion reactions with S or molecular iodine. However, attempts to prepare **15b** and **16** by direct insertion of sulfur or I₂ into the Te–C bond of **13b** and **13c**, respectively, generated a complicated mixture of products. The complete series [TeX₂{SC(PPh₂S)₂}]₂ (**15a**, X = Cl; **15b**, X = Br; **15c**, X = I) can, however, be synthesised by the metathesis

of the trichalcogeno dianions [(E')C(PPh₂E)₂]^{2–} (**4**, E = S, E' = S, Se) with the appropriate tellurium tetrahalide (Section 5.1).²⁵

The I₂-insertion product **16** is especially intriguing; it is a rare example of a structurally characterised organoiodine compound with a hypervalent I–I bond.³⁰ The central iodine atom in **16** features a T-shaped geometry with an almost linear Te–I–I unit. The I–I bond distance of 2.883(1) Å is substantially shorter than that of *o*-nitrodiphenyl iodonium iodide³⁰ and only *ca.* 6% longer than the interatomic distance in I₂ in the solid state.³¹ The calculated bond orders for the Te–I–I unit are typical for a three-centre interaction and the hypervalent iodine centre carries a significant positive charge.²⁵ The C–I bond length of 2.177(1) Å in **16** is in the middle of the range (2.14–2.21 Å) reported for C(sp³)–I bonds³² and close to the value of 2.147(3) Å found for the dimeric lithium complex of the anion [IC(PPh₂S)₂][–] (see **20**, in Scheme 3).³³ The sp³ character of this carbon atom is evinced by a prominent lobe in the electron localization function.²⁵

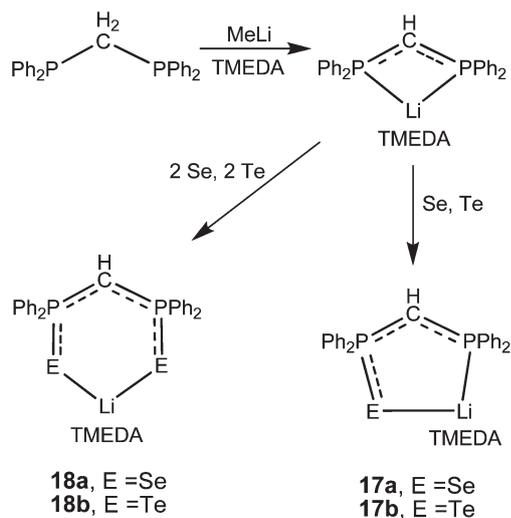
3. PCP-bridged heavy chalcogen-centred ligands

The synthesis of heavy chalcogen derivatives of anions **2** and **3** presents challenges as a result of (a) the greater lability of the P–E bonds (E = Se, Te) compared to P–S and (b) the relatively low oxidizing power of Te. In order to circumvent P–Se bond cleavage, which was first noted in the preparation of the PCP-bridged monoseleno reagent Li[SePPh₂C(H)PPh₂] (**17a**),³⁴ we have employed the metallation-first approach for preparations of **17a** and the diseleno derivative **18a** (Scheme 1).³⁵ Very recently, however, we have found that deprotonation of H₂C(PPh₂Se)₂ by K[N(SiMe₃)₂] occurs without P–Se bond cleavage to give the potassium analogue of **18a** as the unsolvated polymer {K[HC(PPh₂Se)₂]}_∞.^{22a}

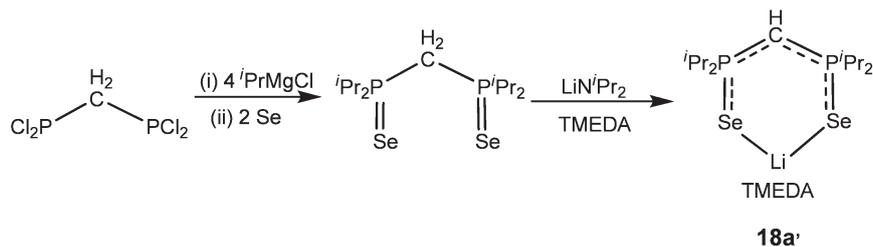
The low reactivity of H₂C(PPh₂)₂ towards elemental tellurium also necessitates the use of this method for the synthesis of the monotelluride Li[TePPh₂C(H)PPh₂] (**17b**), which was used as an *in situ* reagent to prepare a homoleptic Hg(II) complex characterised by ³¹P and ¹⁹⁹Hg NMR.³⁴ More recently, **17b** was isolated as a yellow powder in 82% yield with 97% purity.³⁵ However,

this monotelluride is thermally unstable owing to disproportionation to $\text{H}_2\text{C}(\text{PPh}_2)_2$ and the corresponding ditelluro PCP-bridged species $\text{Li}[\text{HC}(\text{PPh}_2\text{Te})_2]$ (**18b**), which has been characterised by only ^{31}P and ^{125}Te NMR.³⁵ Nevertheless, it was possible to obtain an X-ray crystal structure of **17b**·(TMEDA), which forms a centrosymmetric dimer occasioned by a weak $\text{Te}\cdots\text{Te}$ contact [3.514(1) Å].³⁵ The related PNP-bridged monotelluride $\text{Li}[\text{TeP}^i\text{Pr}_2\text{NP}^i\text{Pr}_2]$ also undergoes disproportionation, but it has been employed as an *in situ* reagent to prepare homoleptic complexes of group 10, 11 and 12 metals.³⁶

In the application of metal complexes of the PNP-bridged anions of the type **1** (E = Se, Te) as molecular precursors for thin films of nanocrystals to binary metal chalcogenides,^{3,5} isopropyl derivatives are preferred over their phenyl analogues because of their higher volatility. The synthesis of isopropyl derivatives of the PCP-bridged monoanions requires the use of the commercially available tetrachloro compound $\text{H}_2\text{C}(\text{PCl}_2)_2$ in a three-step process that produces the monoanionic diseleno ligand $\text{Li}[\text{HC}(\text{P}^i\text{Pr}_2\text{Se})_2]$ (**18a'**) in excellent yield (Scheme 2). The use of LiN^iPr_2 for the deprotonation step avoids P–Se cleavage in this case.³⁵ This protocol can likely be expanded to the synthesis of other alkyl derivatives (R = Me, ^tBu etc.) as well as to the ditelluro analogue $\text{Li}[\text{HC}(\text{P}^i\text{Pr}_2\text{Te})_2]$ (**18b'**), which is expected to have a higher thermal stability than the phenyl derivative **18b**, on the basis of our observations for the isoelectronic PNP-bridged ditelluro systems **1** (E = Te; R = Ph, ^iPr , ^tBu).⁴



Scheme 1 The synthesis of phenyl derivatives of PCP-bridged heavy chalcogen-centred anions.



Scheme 2 The synthesis of the isopropyl derivative of the PCP-bridged selenium-centred anion.

The solid-state structures of $\text{TMEDA}\cdot\text{Li}[\text{HC}(\text{PR}_2\text{Se})_2]$ (R = Ph, **18a**; R = ^iPr , **18a'**) exhibit Se,Se' -coordination towards the four-coordinate Li centre,³⁵ cf. the dithio analogue **5**.²⁰ By contrast, the unsolvated potassium analogue $\{\text{K}[\text{HC}(\text{PPh}_2\text{Se})_2]\}_\infty$ forms a one-dimensional polymer in which the K^+ ions are Se,Se' -chelated by the anion and coordinated to one Se atom of a neighbouring anion. The coordination sphere of the K^+ ions is supplemented by η^3 - and η^6 -interactions with Ph groups (Fig. 5).^{22a} The monochalcogeno derivatives, $\text{TMEDA}\cdot\text{Li}[\text{EPPH}_2\text{C}(\text{H})\text{PPh}_2]$ (**17a**, E = Se; **17b**, E = Te), form centrosymmetric dimers with weak chalcogen–chalcogen intermolecular contacts that are stronger for Te than for Se (3.641(1) Å, E = Se; 3.514(1) Å, E = Te).³⁵

To date, neither the Se or Te analogues of the Le Floch dianion **3** (E = S) have been synthesized owing to the competition with the P–E (E = Se, Te) bond cleavage by RLi or R_2Mg reagents in metallation (deprotonation) reactions.^{34,35} Nevertheless, investigations of the reactions of the monoanion **2** (E = Se, R = Ph), which have received little attention in the case of the thio analogue, have revealed some very interesting chemistry which is discussed in Section 4.3.³⁷

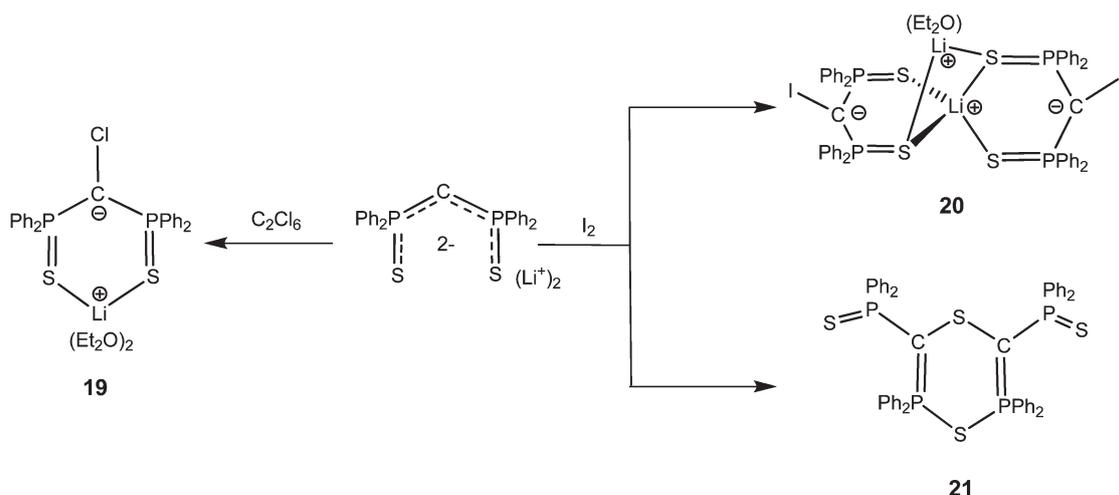
4. Carbon-centred reactivity of PCP-bridged dichalcogeno ligands

4.1 Formation of stable carbenoids

The behaviour of the sulfur-centred dianion **3** (E = S) upon oxidation provides a compelling illustration of the novel carbon-centred reactivity that may be expected for PCP-bridged systems. Le Floch and co-workers demonstrated that oxidation of this dianion with C_2Cl_6 produces the remarkably stable carbenoid **19** (Scheme 3).³⁸ Subsequently, Konu and Chivers found that the use of I_2 as a mild oxidising agent generates a dimeric form of this carbenoid that incorporates the LiI by-product (**20**) together with an unsaturated six-membered $\text{C}_2\text{P}_2\text{S}_2$ ring (**21**) (Scheme 3).³³ The novel heterocycle **21** is formally comprised of two molecules of the carbene, $:\text{C}(\text{PPh}_2\text{S})_2$, one of which has undergone a P → C sulfur-transfer process.³³

4.2 Hydrogen abstraction

The behaviour of the PCP-bridged monoanions **2** (E = Se; R = Ph, ^iPr) upon oxidation provides a striking distinction compared with that of the related PNP-bridged systems. In contrast to the chalcogen-centred dimerization process observed in the one-electron oxidation of the latter anions **1** (E = S, Se, Te; R = ^iPr ,



Scheme 3 Formation of stable carbenoids upon mild oxidation of $\text{Li}_2[\text{C}(\text{PPh}_2\text{S})_2]$.

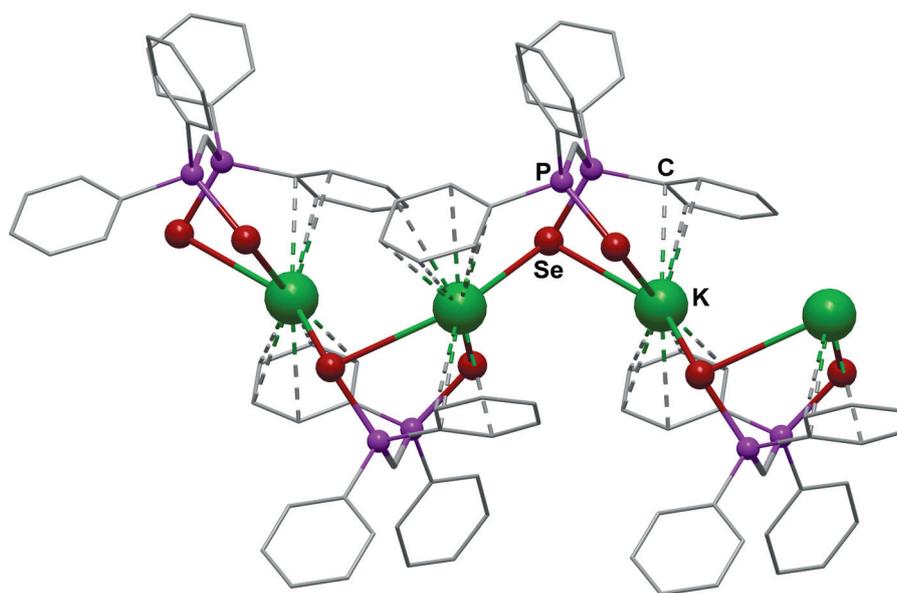


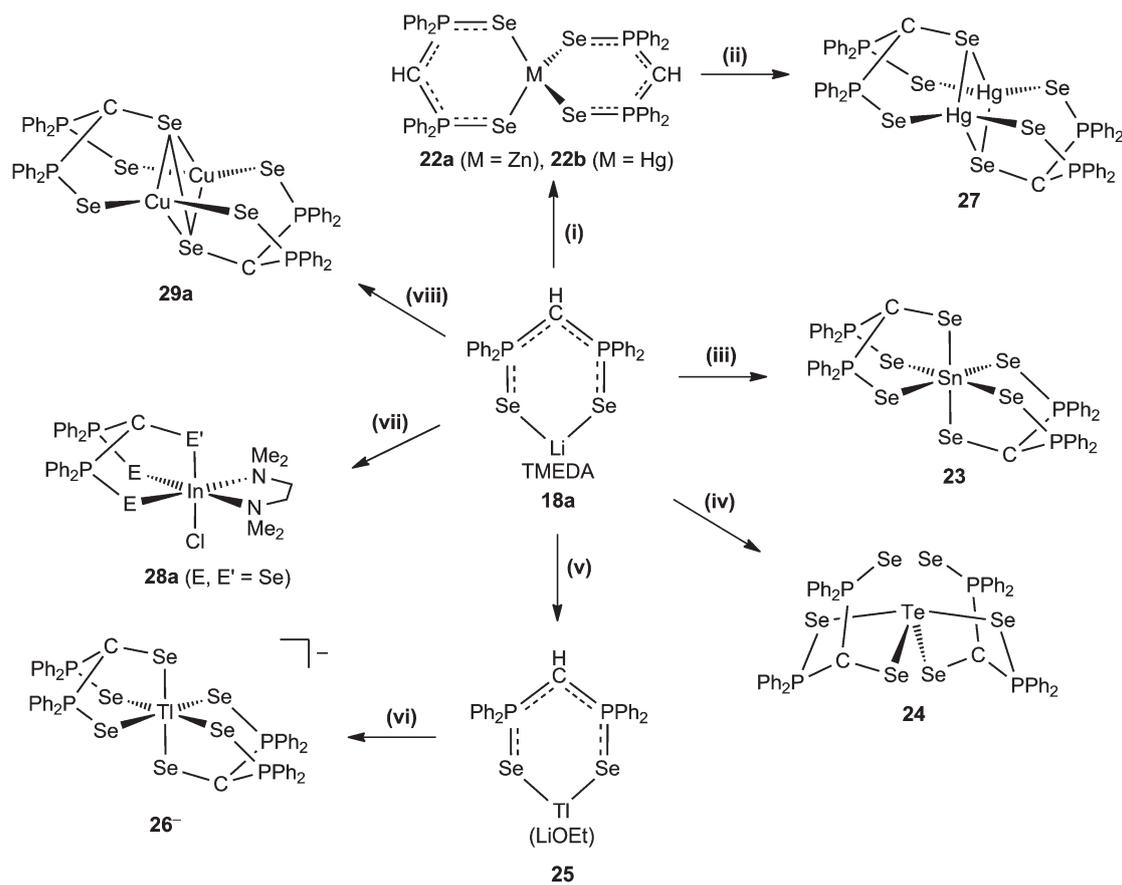
Fig. 5 The structure of the one-dimensional polymer $\{\text{K}[\text{HC}(\text{PPh}_2\text{Se})_2]\}_\infty$. H atoms on the Ph substituents have been omitted for clarity.

'Bu)³⁹ and related mixed chalcogen species,⁴⁰ the one-electron oxidation of the PCP-bridged analogues **2** (E = Se; R = Ph, ⁱPr) with I_2 produces the neutral compounds $[\text{H}_2\text{C}(\text{PR}_2\text{Se})_2]$, presumably *via* hydrogen abstraction by the intermediate radicals $[\text{HC}(\text{PR}_2\text{Se})_2]$ from the solvent.³⁵ This carbon-centred reactivity is attributed to the different spatial morphologies of the SOMOs of the isovalent neutral radicals, $[\text{N}(\text{PR}_2\text{Te})_2]$ and $[\text{HC}(\text{PR}_2\text{Se})_2]$. The SOMO in the PNP-bridged radical is almost entirely localised on the chalcogen centres,^{39a} whereas the SOMOs of the PCP-bridged species have a large contribution from the p-orbital on carbon.³⁵

4.3 Selenium–proton exchange at the carbon centre

The most far-reaching manifestation of the carbon-centred reactivity of PCP-bridged diseleno ligands is observed in the reactions of the monoanion **2** (E = Se, R = Ph) with a variety of main group metal halides. In the initial study of the coordination

chemistry of this diseleno ligand the metathetical reactions of the lithium reagent **18a** with MCl_2 (M = Zn, Hg) proceeded in a predictable manner to produce homoleptic group 12 complexes, $\{\text{M}[\text{HC}(\text{PPh}_2\text{Se})_2]_2\}$ (M = Zn (**22a**); M = Hg (**22b**), Scheme 4).³⁵ In distinct contrast, the analogous reactions of **18a** with group 14 and 16 dihalides MCl_2 (M = Sn, Te) resulted in the formation of the novel *triseleno* PCP-bridged dianion, $[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$, and the neutral monoselenide, $[(\text{H}_2\text{C}(\text{PPh}_2)\text{Se})]$ (identified by ³¹P NMR), through a *selenium–proton exchange process* at the PCP-carbon of the diseleno monoanions $[\text{HC}(\text{PPh}_2\text{Se})_2]^-$ (Scheme 4).⁴¹ This intriguing transformation also involves a concomitant redox disproportionation at the metal centre $[\text{M}(\text{II}) \rightarrow \text{M}(\text{IV}) + \text{M}(\text{0})]$ to afford homoleptic $\text{M}(\text{IV})$ complexes, $\{\text{M}[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]_2\}$ (M = Sn (**23**), Te (**24**)).⁴¹ In a comparable conversion, the homoleptic thallium(I) complex, $\{\text{EtOLi}\cdot\text{Tl}[\text{HC}(\text{PPh}_2\text{Se})_2]\}$ (**25**), obtained from the reaction between TlOEt and **17a** in a 1 : 1 molar ratio, forms a dinuclear, mixed valent $\text{Tl}(\text{I})\text{–Tl}(\text{III})$ complex, $\text{Tl}\{\text{Tl}[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]_2\}$



Scheme 4 Selenium–proton exchange reactions to afford triseleno dianion, $[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$, in the metathesis of **18a** with metal halides: (i) $+\text{MCl}_2$ ($\text{M} = \text{Zn}, \text{Hg}$),³⁵ (ii) 65°C ,⁴¹ (iii) $+\text{SnCl}_4$,⁴¹ (iv) $+\text{TMTU}\cdot\text{TeCl}_4$,⁴¹ (v) $+\text{TIOEt}$,⁴² (vi) 60°C ,⁴² (vii) $+\text{InCl}_3$,⁴² (viii) $+\text{CuCl}_2$,⁴³ (i–viii) $-\text{[H}_2\text{C}(\text{PPh}_2)(\text{PPh}_2\text{Se})]$. Only the anion is shown for **26** (see Fig. 6 for the polymeric structure).

(**26**), upon a prolonged reaction time or by moderate heating (Scheme 4 and Fig. 6).⁴² The change in the oxidation state of the metal centre is not, however, necessary for the selenium–proton exchange between diseleno monoanions, $[\text{HC}(\text{PPh}_2\text{Se})_2]^-$, to occur. Mild thermolysis of the homoleptic mercury(II) complex **22b** generates a dinuclear Hg(II)–Hg(II) complex of the triseleno dianion, $\{\text{Hg}_2[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]_2\}$ (**27**),⁴¹ and the reaction between **18a** and InCl_3 in a 2 : 1 molar ratio produces the heteroleptic indium(III) compound, $\{(\text{TMEDA})\text{ClIn}[(\text{E}')\text{C}(\text{PPh}_2\text{E})_2]\}$ (**28a**; $\text{E}, \text{E}' = \text{Se}$), with N,N' -chelated TMEDA completing the octahedral coordination for the indium centre.⁴²

The metathesis of **18a** with CuCl_2 reveals an interesting feature of the chemistry of the triseleno ligand $[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$. In addition to $\text{Se}-\text{H}^+$ exchange, reduction of the metal centre occurs to give the dinuclear Cu(I)–Cu(I) complex, $\{\text{Cu}_2-\eta^2:\eta^2-[(\text{SePh}_2\text{P})_2\text{CSeSeC}(\text{PPh}_2\text{Se})_2]\}$ (**29a**, Scheme 4), comprised of two radical anions, $[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]^-$ connected by a relatively short Se–Se bond of 2.683(2) Å.⁴³ Similar Cu(I)–Cu(I) complexes (**29b** and **29c**, Scheme 7) of the related dichalcogenide dianions, $[(\text{SPh}_2\text{P})_2\text{CE}'\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ ($\text{E}' = \text{S}$ or Se) are discussed in Sections 5 and 6.

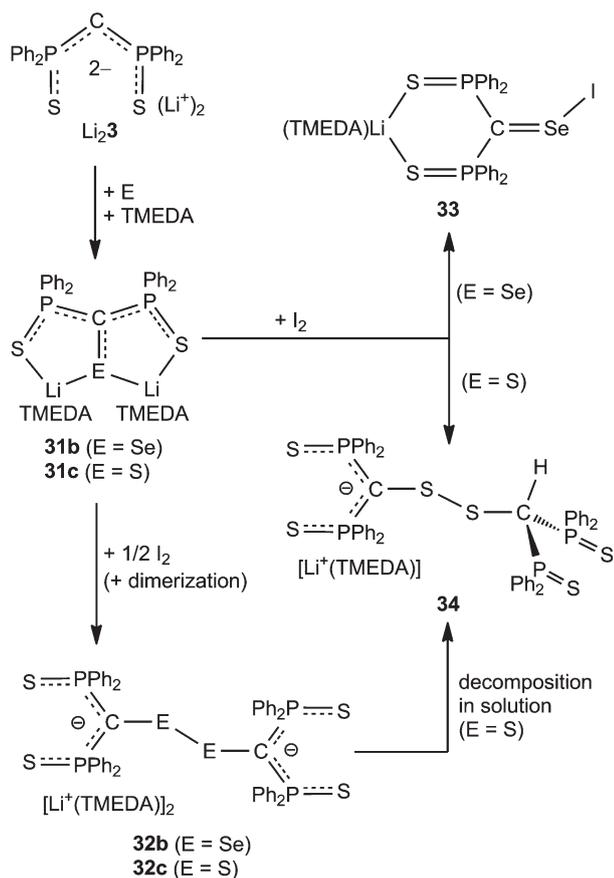
The selenium–proton exchange manifested in the reactions of $[\text{HC}(\text{PPh}_2\text{Se})_2]^-$ with metal halides is in marked contrast to the dehydrochlorination process observed in the metathesis of the dithio analogue $[\text{HC}(\text{PPh}_2\text{S})_2]^-$ with group 13 trihalides and

BiCl_3 , which produces complexes of the dianion $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ (Section 2.1).^{20,22b} Although the mechanism of the conversion to the diseleno monoanion $[\text{HC}(\text{PPh}_2\text{Se})_2]^-$ to afford the triseleno dianion $[(\text{Se})\text{C}(\text{PPh}_2\text{Se})_2]^{2-}$ is not fully understood, the disparity in the behaviour of the dithio and diseleno congeners **5** and **18a** can likely be attributed to the greater lability of a P–Se linkage compared to the P–S bond (Section 3).^{34,35}

5. PCP-bridged trichalcogeno-centred anions

5.1 Synthesis and structures

Concurrent with the serendipitous discovery by Konu and Chivers of the PCP-bridged triseleno dianion **4** ($\text{E}, \text{E}' = \text{Se}$) formed through the mechanistically obscure *selenium–proton exchange* process,⁴¹ Leung *et al.* reported the synthesis of monomeric lead(II) complexes of the related trichalcogeno dianions, $\{\text{Pb}[(\text{E})\text{C}(\text{PPh}_2\text{S})_2]\}$ [$\text{E} = \text{Se}$ (**14b**), S (**14c**)] (Fig. 4), *via chalcogen insertion* into the Pb–C bond of the dimer $\{\text{Pb}[\mu^2-\text{C}(\text{PPh}_2\text{S})_2]_2\}$ (**8b**).¹⁸ The apparent versatility of the novel trichalcogeno-centred dianions, $[(\text{E}')\text{C}(\text{PPh}_2\text{E})_2]^{2-}$ ($\text{E}, \text{E}' = \text{S}, \text{Se}$), in the formation of a variety of mono- and binuclear metal complexes (Scheme 4), prompted the search for a direct synthesis of alkali metal derivatives that could be utilized to explore the coordination chemistry of these intriguing tridentate ligands



Scheme 5 The synthesis and redox behaviour of PCP-bridged trichalcogeno-centred dianions.

via metathetical reactions with halides of main group elements, transition metals and lanthanides.

In view of the unavailability of $[C(PPh_2Se)_2]^{2-}$, **3** ($E = Se$) (Section 3),³⁵ the dithio analogue, $[C(PPh_2S)_2]^{2-}$ (**3**, $E = S$) was selected as an easily accessible reagent for reactions with chalcogens. Indeed, *chalcogen insertion* reactions with the dilithium salt **6** in the presence of TMEDA readily produce the desired complexes $[Li(TMEDA)]_2[(E)C(PPh_2S)_2]$ (**31b**, $E = Se$; **31c**, $E = S$) as orange-red or red solids in excellent yields (Scheme 5).⁴⁴ The solid-state structure of **31b** reveals a monomeric compound with both $[Li^+(TMEDA)]$ cations *S,Se*-chelated by the dianionic ligand.⁴⁴

The *metathetical reactions* of the tridentate dianions **31b** and **31c** with $InCl_3$ in a 1 : 1 molar ratio generate the octahedral indium(III) complexes $\{(TMEDA)ClIn[(E')C(PPh_2E)_2]\}$ (**28b**, $E = S$, $E' = Se$; **28c**, $E, E' = S$), respectively, *cf.* the triseleno analogue **28a** ($E, E' = Se$, Scheme 4).⁴² Similarly, the reactions between TeX_4 ($X = Cl, Br, I$) and **31c** proceed *via* metathesis to give the tellurium(IV) complexes, $\{TeX_2[(S)C(PPh_2S)_2]\}_2$ (**15a**, $X = Cl$; **15b**, $X = Br$; **15c**, $X = I$), which, in the case of **15b**, was first observed as a minor product from the reaction of **6** with $TeBr_4$ (Section 2.2 and Fig. 4).²⁵ The reactions of **31b** and **31c** with metal halides may also involve interesting redox transformations as manifested by the reduction of $CuCl_2$ to form the dinuclear $Cu(I)-Cu(I)$ complexes, $\{Cu_2-\eta^2:\eta^2-[(EPh_2P)_2CE'E'C-$

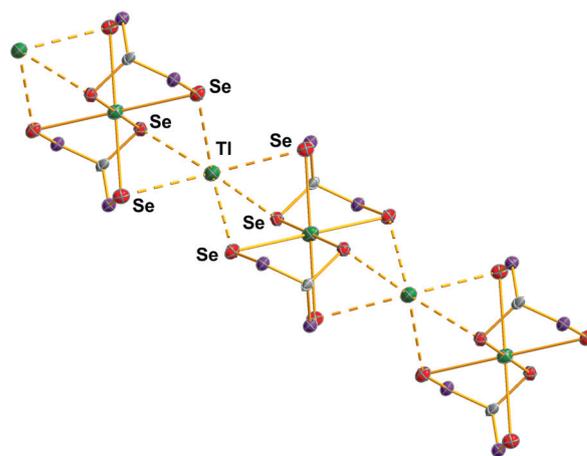


Fig. 6 A polymeric strand of the mixed-valent thallium complex **26**. Colour scheme for unlabelled atoms: P, purple; C, gray.

$(PPh_2E)_2\}$ (**29b**, $E = S$, $E' = Se$; **29c**, $E = E' = S$, Scheme 7), *cf.* the all-selenium derivative **29a** (Scheme 4).^{43,45}

The flexibility of the tridentate PCP-bridged ligands, $[(E')C(PPh_2E)_2]^{2-}$ ($E, E' = S, Se$), is evident from the variety of molecular architectures established for the existing metal complexes (see Scheme 4). The tin(IV) compound **23** assumes a distorted octahedral structure, while the stereochemical activity of the lone pair on the tellurium(IV) centre in **24** imposes a see-saw geometry in which one of the $Se(P)$ atoms in each ligand is only weakly coordinated to the central Te atom.⁴¹ In the monomeric lead(II) complexes **14b** and **14c**, the influence of the lone pair induces a trigonal pyramidal geometry for the metal centre.¹⁸ The distorted tetrahedral metal centres in the dinuclear $Hg(II)-Hg(II)$ complex are connected by two tridentate ligands in which the carbon-bound selenium is three-coordinate, while the $Se(P)$ atoms remain two-coordinate.⁴¹

The most structurally interesting example of the versatile coordination behaviour of the triseleno dianion $[(Se)C(PPh_2Se)_2]^{2-}$ is the mixed-valent $[Tl(I)-Tl(III)]$ complex **26** in which the octahedral anions $\{Tl[(Se)C(PPh_2Se)_2]_2\}^-$, *cf.* the iso-valent $Sn(IV)$ complex **23**, are connected to the $Tl(I)$ cations *via* weak $Tl \cdots Se$ interactions to give a one-dimensional polymer (Fig. 6).⁴²

In general, the bond lengths involving phosphorus ($P-C$, $P-S$ or $P-Se$) in metal complexes of $[(E')C(PPh_2E)_2]^{2-}$ ($E, E' = S, Se$) are remarkably invariant and somewhat shorter than the respective single-bond values, thus indicating electron delocalization in the EPCPE unit. The geometry of the PCP carbon atom is quite elastic with the sum of bond angles commonly in the range $336-341^\circ$, but with the exception of *ca.* 354° in the dinuclear mercury(II) and lithium(I) complexes, **27** and **31b**, respectively. In general, the $M-E(C)$ bonds are significantly shorter than the $M-E(P)$ contacts (by up to 0.40 \AA in the $Tl(I)-Tl(III)$ complex **26**).⁴² However, DFT calculations for the all-sulfur dianion $[(S)C(PPh_2S)_2]^{2-}$ place slightly more of the negative charge on the $S(P)$ atoms compared to $S(C)$ (-0.41 vs. -0.34) and a charge of -0.25 on the carbon atom.²⁵ In the case of the tellurium(IV) complex **15b**, calculations show that the charge on the inserted sulfur atom is close to zero and the $C-S$ bond has a substantial double bond character with the π electron pair

strongly polarised towards carbon.²⁵ We note that the C–E bond lengths (E = S, Se) in complexes of $[(E')C(PPh_2E)_2]^{2-}$ (E, E' = S, Se) show significant variations, e.g. $d(C-Se)$ ranges from 1.890(5) Å in **24** to 1.973(7) Å in **28a**, indicating significant reorganization of the electron density of these dianions upon complexation with a metal fragment.

5.2 Redox behaviour and proton abstraction

Le Floch *et al.* have reported the isolation and structural characterisation of alkali metal salts of the alkene radical anion $[Ph_2C=C(PPh_2S)_2]^-$ stabilised by the electron-accepting phosphine sulfide substituents.⁴⁶ Since thioketyl radical anions $[R_2C=S]^-$ (e.g. R = ^tBu, Me) have been characterised only in solution,⁴⁷ the oxidation of the dilithium derivatives **31b** and **31c** was investigated to evaluate the stabilising effect of the PPh₂S substituents on the radical anions $[(E)C(PPh_2S)_2]^-$ and neutral chalcogenocarbonyls $[(E)C(PPh_2S)_2]$ (E = Se, S).⁴⁴

The one-electron oxidation of **31b** and **31c** with I₂ generates the $[Li^+(TMEDA)]$ derivatives of dimers of the radical anions, $\{[Li^+(TMEDA)]_2[(SPh_2P)_2CEEC(PPh_2S)_2]\}$ (**32b**, E = Se; **32c**, E = S), joined by slightly elongated (by *ca.* 8%) chalcogen–chalcogen bonds as orange and yellow powders, respectively, in excellent yields (Scheme 5).⁴⁴ DFT-level electronic structures of the dichalcogenide dianions, **32b** and **32c**, and the putative paramagnetic monoanions, $[(E)C(PPh_2S)_2]^-$ (E = Se, S), reveal that the net chalcogen–chalcogen bonding interaction is solely due to a somewhat poor overlap of the SOMOs of the monoanionic radicals, which themselves are comprised of an antibonding combination of p-orbitals on the C=E bond (Fig. 7). The notably small calculated binding energies of **32b** and **32c** (90 and 72 kJ mol⁻¹, respectively) are in accordance with the elongated chalcogen–chalcogen bonds observed in the solid-state structures.⁴⁴ Although the formation of a persistent paramagnetic species in the solutions of **32b** and **32c** is evident from the EPR spectra, the radical anions $[(E)C(PPh_2S)_2]^-$ (E = Se, S) could not be identified with certainty.⁴⁴

The two-electron oxidation of the selenium-containing dianion **31b** with I₂ produces the dark red LiI adduct of the neutral selone $[(Se)C(PPh_2S)_2]$ (**33**, Scheme 5).⁴⁴ This selenocarbonyl exhibits a significant shortening of the C=Se bond to 1.815(4) Å, compared to 1.885(3) Å for the diselenide **32b** and 1.970(3) Å for the dianionic precursor **31b**, despite the relatively strong Se–I contact of 2.722(1) Å, *cf.* values in the range 2.56–2.73 Å for the charge-transfer complexes of selones with I₂ or IBr.⁴⁸ The Se–I interaction in neutral selone **33** appears to provide crucial stability, since attempts to remove LiI from this adduct, e.g. with 12-crown-4, resulted in decomposition.⁴⁴

In contrast to the facile formation of the neutral selone **33** as the LiI adduct, the treatment of the all-sulfur dianion **31c** with iodine in a variety of solvents generates primarily protonated species **34**, which was also observed as a part of the decomposition process of the dimeric dianion **32c** (Scheme 5).⁴⁴ The diamagnetic compound **34** is formally constructed from the radical anion $[(S)C(PPh_2S)_2]^-$ and the neutral radical $[H(S)C(PPh_2S)_2]$ linked by an S–S bond. In this context we note that the HOMO of the dimeric dianion **32c** displays a significant contribution from the p-orbitals of the backbone carbon atoms (Fig. 7)

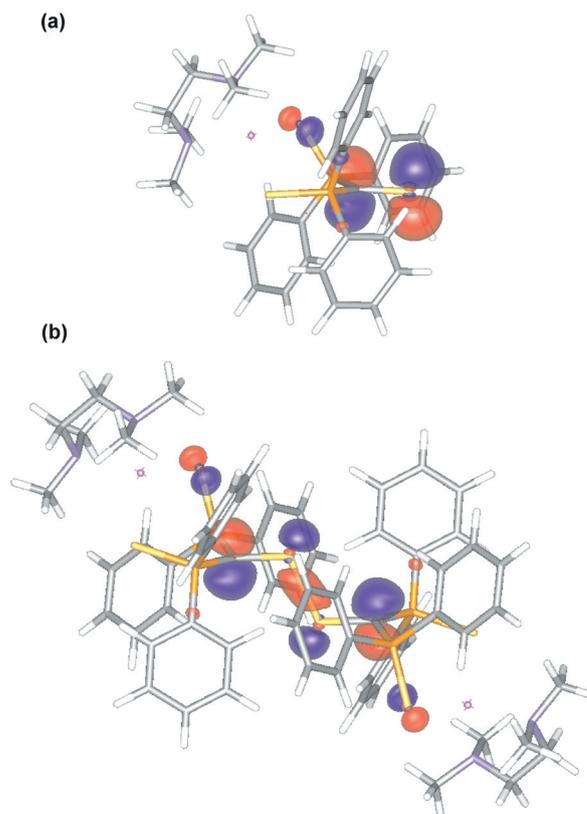


Fig. 7 The frontier MOs of $[Li(TMEDA)]^+$ salts of (a) the monoanion radical $[(S)C(PPh_2S)_2]^-$ (SOMO) and (b) the corresponding disulfide **32c** (HOMO).

thereby contributing to the apparent tendency for proton abstraction.

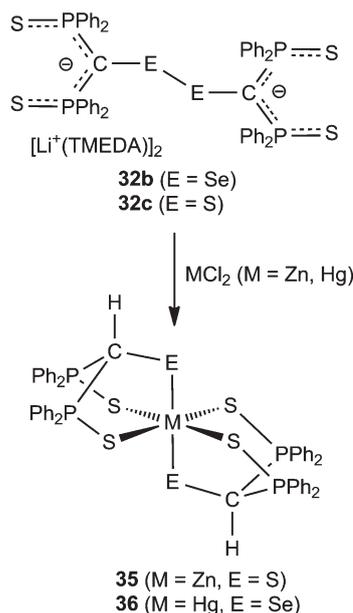
Another example of the proclivity of the dimeric system **32b,c** to undergo proton abstraction is provided by their metathetical reactions with group 12 dihalides, which produce the octahedral complexes $\{M[H(E)C(PPh_2S)_2]_2\}$ (**35**, M = Zn, E = S; **36**, M = Hg, E = Se) (Scheme 6).⁴⁹ The tridentate, monoanionic ligands $[H(E)C(PPh_2S)_2]^-$ coordinated to the metal centres in **35** and **36** are reminiscent of the neutral radical $[H(S)C(PPh_2S)_2]$ that forms the right-hand side of disulfide **34** (Scheme 5).

6. Coinage metal complexes of dichalcogenide dianions

6.1 Chalcogen–chalcogen bond stretching

The analogous mixed-chalcogen and all-sulfur derivatives, $\{Cu_2-\eta^2:\eta^2-[(SPh_2P)_2CEEC(PPh_2S)_2]\}$ (**29b**, E = Se; **29c**, E = S), are readily produced by the treatment of either **31** with CuCl₂ or **32** with CuCl (Scheme 7).^{43,45} Similarly, the reactions of dichalcogenides **32b** and **32c** with two equivalents of AgOSO₂CF₃ generate the dinuclear silver(i) congeners, $\{Ag_2-\eta^2:\eta^2-[(SPh_2P)_2CEEC(PPh_2S)_2]\}$ (**37b**, E = Se; **37c**, E = S), in good yields (Scheme 7).⁴⁵

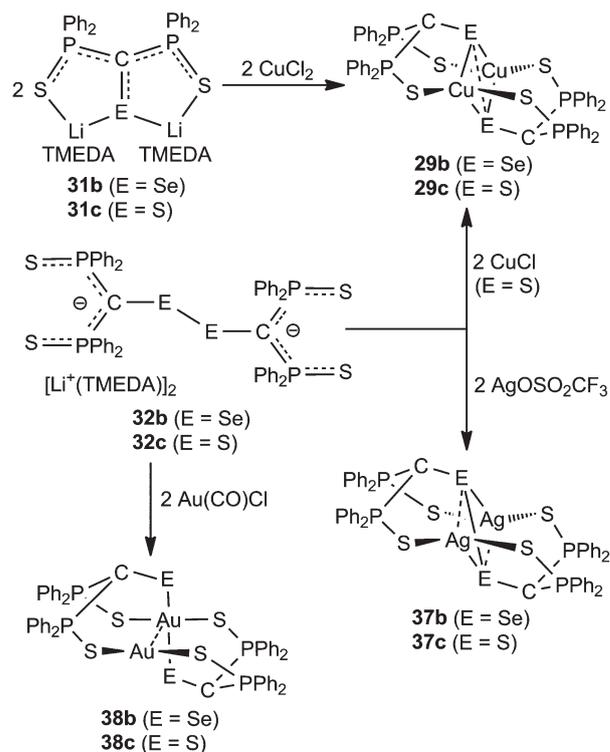
The overall geometry of the coinage metal M(i)–M(i) complexes **29a–c** and **37b,c** (M = Cu, Ag, respectively) resembles that of the dinuclear mercury(ii) complex **27** (Scheme 4) with the



Scheme 6 The reactions of dichalcogenides **32b** and **32c** with group 12 halides.

dimeric arrangement and distorted tetrahedral metal centres. As a result of the central (C)E–E(C) (E = S, Se) contact in the dianionic dichalcogenides, however, the two metal centres in **29a–c** and **37b,c** are well separated (by *ca.* 4.5 Å), whereas the Hg(II)···Hg(II) distance in **27** is only 3.105(1) Å. The η^2 -Se₂ bonding mode adopted by the copper(I) centres in the selenium derivatives **29a** and **29b** is the first example of this bonding arrangement for transition metal complexes of the generic diselenide ligands, RSe–SeR,⁴³ for which oxidative addition (insertion of the metal into the Se–Se bond) is more commonly observed.⁵⁰

Intriguingly, the solid-state structures of the dinuclear copper (I) complexes **29a–c** reveal significantly elongated chalcogen–chalcogen contacts in the central (C)E–E(C) unit (E = S, Se).⁴⁵ In the all-sulfur system **29c**, the S–S distances of 2.540(4) and 2.720(3) Å in the two discrete molecules in the crystal lattice are *ca.* 0.32 and 0.50 Å longer, respectively, than those in the dilithium derivative **32c**, while the corresponding Se–Se contacts of *ca.* 2.61–2.69 Å in **29a** and **29b** exhibit a slightly less pronounced elongation of *ca.* 0.15 Å compared to the dilithium derivative **32b**. The former contacts are in the same range as the weak transannular S···S interactions observed in unsaturated eight-membered S–N rings, *e.g.* 2.60 Å in S₄N₄,⁵¹ and values in the range 2.43–2.55 Å for the bicyclic compounds 1,5-R₄P₂N₄S₂ (R = alkyl, aryl)⁵² for which Breher has suggested a diradical character.^{53,54} Thus, the pronounced chalcogen–chalcogen bond stretching of 15% (Se–Se) to 32% (S–S) in **29a–c** compared to the typical E–E (E = Se, S) single bond lengths of 2.34 and 2.06 Å, respectively, suggests the onset of bond cleavage and the creation of diradical character for the dinuclear Cu(I)–Cu(I) complexes. Theoretical calculations at the DFT and MP2 levels support the presence of moderate diradical character for the dinuclear Cu(I)–Cu(I) complexes **29a–c**, which is chalcogen-dependent (*i.e.* higher for sulfur, as can also be inferred from the solid-state structures).⁴⁵ While the selenium-containing Ag(I)–Ag(I) complex **37b** is structurally similar to the copper(I) derivatives **29a–c**, the much weaker and markedly asymmetrical

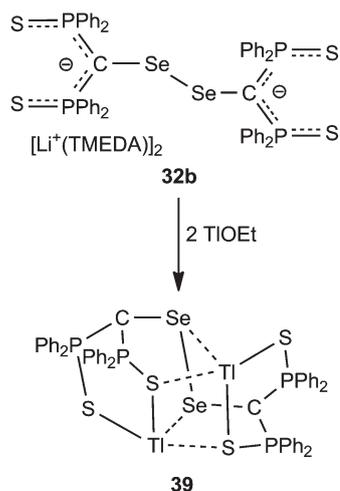


Scheme 7 The synthesis of coinage metal complexes of the dichalcogenides **32b** and **32c**.

Ag··· η^2 -Se₂ contacts result in a normal chalcogen–chalcogen single-bond length $d[(\text{C})\text{Se}–\text{Se}(\text{C})] = 2.510(2)$ Å,⁴⁵ *cf.* $d(\text{Se}–\text{Se})$ of 2.508(1) Å for the dilithium precursor **32b**.⁴⁴ This structural difference may also account for the fluxional behaviour (and possible isomerism) observed in solution by variable temperature ³¹P NMR studies of the all-sulfur congener **37c**, which is not exhibited by the Cu(I)–Cu(I) complexes **29a–c**.⁴⁵

6.2 Redox behaviour

In contrast to the facile formation of the dinuclear Cu(I)–Cu(I) and Ag(I)–Ag(I) complexes of the dimeric dianions by the metathesis of dilithium precursors **32b,c** with M(I) halides, the analogous reactions with the gold(I) reagent Au(CO)Cl involve a redox process in which the dianionic dichalcogenide ligands are reduced to the corresponding monomeric dianions [(E)C(PPh₂S)₂]^{2–} (E = Se, S) with the concomitant oxidation of one of the gold centres to produce the mixed-valent Au(I)–Au(III) complexes, {Au[(E)C(PPh₂S)₂]₂}₂ (**38b**, E = Se; **38c**, E = S; Scheme 7).⁴⁵ While the gold(I) and gold(III) centres in **38b** and **38c** assume typical linear (two-coordinate) and square-planar (four-coordinate) geometries, respectively,⁵⁵ the significant deviation from linearity of *ca.* 25° in the S–Au(I)–S angle in both compounds is indicative of a relatively strong Au(I)···Au(III) interaction.⁴⁵ Consistently, the Au(I)···Au(III) separations of *ca.* 3.12 Å lie at the low end of the normal range reported for Au(I)···Au(III) interactions,⁵⁶ although shorter contacts have been observed in compounds where the supporting ligands bring the



Scheme 8 The synthesis of the dinuclear Tl(I)–Tl(I) complex **39**.

two metal centres into close proximity owing to steric hindrance.⁵⁷

In contrast to the redox process observed with Au(CO)Cl, the metathesis of the dilithium derivative **32b** with TIOEt generates a dinuclear Tl(I)–Tl(I) complex, {Tl₂[(SPh₂P)₂CSeSeC(PPh₂S)₂]} (**39**, Scheme 8), in which the dimeric ligand remains intact.⁴² The solid-state structure of **39** is, however, quite distinct from those of the dilithium precursor **32b** and the dinuclear coinage metal M(I)–M(I) complexes **29a–c** and **37b,c** (M = Cu and Ag, respectively). Each Tl(I) centre in **39** is S,S'-chelated by one-half of the dimeric dianion and S₃Se-chelated by the other half to afford a polycyclic arrangement. Consequently, the metal centres in **39** are drawn towards the opposite half of the dianionic ligand through Tl⋯E contacts (E = S, Se) resulting in four-coordinate thallium(I) atoms.

7. Conclusions

Recent studies demonstrate that the Le Floch ligand **3** (E = S) forms dimeric complexes with electron-deficient metals, whereas electron-rich group 15 and 16 metalloids adopt monomeric, S,C, S-bonded structures with three-centre two-electron S–M–S bonds in heteroleptic complexes. The M–C linkage in the latter is a polar single bond and incorporates one hard and one soft lone pair (on C and M, respectively). The implications of this bonding arrangement for the reactivity of these complexes await investigation. The synthesis of Se or Te analogues of the Le Floch ligand, either as the dianion **3** (E = Se, Te) with s-block metal cations or in complexes with p-, d- or f-block metals, represents a significant challenge. However, the recent discovery of the monodeprotonation of H₂C(PPh₂Se)₂ by K[N(SiMe₃)₂] without P–Se bond cleavage is a promising step towards this goal.^{22a}

The diseleno PCP-bridged monoanion **2** (E = Se, R = Ph) undergoes a novel selenium–proton exchange in reaction with main group and coinage metal halides that spawns the triseleno PCP-bridged dianion **4** (E = E' = Se; R = Ph). A direct synthesis of this new class of trichalcogeno-centred ligand has been developed and studies of the redox behaviour have generated the

intriguing dianionic dichalcogenides **32b,c**. The versatility of these new multidentate, chalcogen-centred ligands is clearly illustrated in their behaviour towards group 11 and 13 metals, which includes the formation of binuclear complexes with diradical character (chalcogen–chalcogen bond stretching) as well as redox processes involving chalcogen–chalcogen bond cleavage. Future studies of the coordination chemistry of monomeric ligands of the type similar to **4** and the corresponding dimers **32b,c**, especially with metals that readily assume different oxidation states, are likely to be rewarding. Stable complexes of the radical anions [(E)C(PPh₂S)₂]^{•−} (E = Se, S) represent an interesting and realistic target.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada and the Academy of Finland for continuing financial support. We also acknowledge the insightful contributions to this work from Dr. H. M. Tuononen (University of Jyväskylä) and Prof. I. Vargas-Baca (McMaster University, Canada) through their theoretical calculations.

References

- 1 A. Schmidpeter and R. Böhm, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 704.
- 2 For reviews, see: (a) T. Q. Ly and J. D. Woollins, *Coord. Chem. Rev.*, 1998, **176**, 451; (b) C. Silvestru and J. E. Drake, *Coord. Chem. Rev.*, 2001, **223**, 117; (c) I. Haiduc, in *Comprehensive Coordination Chemistry II*, ed. A. B. P. Lever, Elsevier Pergamon, Amsterdam, Oxford, 2004, vol. 1, pp. 323–347.
- 3 For selected examples, see: (a) M. Afzaal, D. Crouch, M. A. Malik, M. Motevalli, P. O'Brien and J.-H. Park, *J. Mater. Chem.*, 2003, **13**, 639; (b) M. Afzaal, K. Ellwood, N. L. Pickett, P. O'Brien, J. Raftery and J. Waters, *J. Mater. Chem.*, 2004, **14**, 1310; (c) J. Waters, D. J. Crouch, J. Raftery and P. O'Brien, *Chem. Mater.*, 2004, **16**, 3289; (d) D. J. Crouch, P. O'Brien, M. A. Malik, P. J. Skabara and S. P. Wright, *Chem. Commun.*, 2003, 1454.
- 4 (a) G. Briand, T. Chivers and M. Parvez, *Angew. Chem., Int. Ed.*, 2002, **41**, 3468; (b) T. Chivers, D. J. Eisler and J. S. Ritch, *Dalton Trans.*, 2005, 2675; (c) J. S. Ritch, T. Chivers, D. J. Eisler and H. M. Tuononen, *Chem.–Eur. J.*, 2007, **13**, 4643.
- 5 For a review, see: (a) J. S. Ritch, M. Afzaal, T. Chivers and P. O'Brien, *Chem. Soc. Rev.*, 2007, **36**, 1622; (b) S. S. Garje, D. J. Eisler, J. S. Ritch, M. Afzaal, P. O'Brien and T. Chivers, *J. Am. Chem. Soc.*, 2006, **128**, 3120; (c) J. S. Ritch, T. Chivers, K. Ahmad, M. Afzaal and P. O'Brien, *Inorg. Chem.*, 2010, **49**, 1198; (d) K. Ahmad, M. Afzaal, J. S. Ritch, T. Chivers and P. O'Brien, *J. Am. Chem. Soc.*, 2010, **132**, 5964.
- 6 (a) A. Davison and D. L. Reger, *Inorg. Chem.*, 1971, **10**, 1967; (b) In this Perspective the generic term "PCP-bridged chalcogen-centred anions" refers collectively to dichalcogeno anions of the type **2** (methanides) and **3** (methanediides) as well as the trichalcogeno dianions **4**; it is not intended to indicate the distribution of negative charge in these anions.
- 7 For examples, see: (a) A. Laguna, M. Laguna, A. Rojo and M. N. Fraile, *J. Organomet. Chem.*, 1986, **315**, 269; (b) J. Browning, G. W. Bushnell, K. R. Dixon and R. W. Hiltz, *J. Organomet. Chem.*, 1992, **434**, 241; (c) R. Contreras, M. Valderrama and S. Yañez, *Transition Met. Chem.*, 1993, **18**, 73; (d) M. Valderrama, R. Contreras, M. Bascunan and D. Boys, *Polyhedron*, 1994, **13**, 1101; (e) S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *Z. Naturforsch.*, 2007, **62B**, 407.
- 8 For examples see: (a) C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 2000, **39**, 1222; (b) C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 2000, **39**, 1216; (c) C. G. Pernin and J. A. Ibers, *Inorg. Chem.*, 1999, **38**, 5478.
- 9 J. Browning, K. R. Dixon and R. W. Hiltz, *Organometallics*, 1989, **8**, 552.

- 10 T. Cantat, N. Mézailles, L. Ricard, Y. Jean and P. Le Floch, *Angew. Chem., Int. Ed.*, 2004, **43**, 6382.
- 11 T. Cantat, N. Mézailles, A. Auffrant and P. Le Floch, *Dalton Trans.*, 2008, 1957.
- 12 (a) S. T. Liddle, D. P. Mills and A. J. Wooles, *Chem. Soc. Rev.*, 2011, **40**, 2164; (b) S. T. Liddle, D. P. Mills and A. J. Wooles, *Organomet. Chem.*, 2010, **36**, 29.
- 13 T. K. Panda and P. W. Roesky, *Chem. Soc. Rev.*, 2009, **38**, 2782.
- 14 D. J. Mindiola and J. Scott, *Nat. Chem.*, 2011, **3**, 15.
- 15 T. Chivers, J. Ritch, S. D. Robertson, J. Konu and H. M. Tuononen, *Acc. Chem. Res.*, 2010, **43**, 1053.
- 16 For a comparison of the redox behaviour of PNP- and PCP-bridged selenium and tellurium-centred ligands, see: T. Chivers and J. Konu, in *Selenium and Tellurium Chemistry: From Small Molecules to Biomolecules and Materials*, ed. J. D. Woollins and R. S. Laitinen, Springer-Verlag, Berlin, 2011, ch. 4, pp. 79–102.
- 17 (a) M. C. Copey and T. Chivers, *Chem. Commun.*, 2005, 4938; (b) D. J. Eisler, S. D. Robertson and T. Chivers, *Can. J. Chem.*, 2009, **87**, 39; (c) J. S. Ritch and T. Chivers, *Inorg. Chem.*, 2009, **48**, 3857.
- 18 W.-P. Leung, C.-L. Wan, K.-W. Kan and T. C. W. Mak, *Organometallics*, 2010, **29**, 814.
- 19 The monoanion is also formed as a white solid from the reaction of $[\text{H}_2\text{C}(\text{PPh}_2\text{S})_2]$ with MeLi in Et₂O in the presence of two equivalents of TMEDA: T. Cantat, L. Ricard, Le Floch and N. Mézailles, *Organometallics*, 2006, **25**, 4965.
- 20 W.-P. Leung, C.-L. Wan and T. C. W. Mak, *Organometallics*, 2010, **29**, 1622.
- 21 Deamination has also been employed for the synthesis of Sn(II) complexes of the imino-thio ligands $[\text{CH}(\text{Ph}_2\text{PNSiMe}_3)(\text{Ph}_2\text{PS})]^-$ and $[\text{C}(\text{Ph}_2\text{PNSiMe}_3)(\text{Ph}_2\text{PS})]^{2-}$: J. Guo, K.-C. Lau, H.-W. Xi, K. H. Lim and C.-W. So, *Chem. Commun.*, 2010, **46**, 1929.
- 22 (a) R. Thirumoorathi and T. Chivers, *Eur. J. Inorg. Chem.*, submitted; (b) R. Thirumoorathi and T. Chivers, unpublished observations.
- 23 R. Thirumoorathi, T. Chivers and I. Vargas-Baca, *Dalton Trans.*, 2011, **40**, 8086.
- 24 C. Foo, K.-C. Lau, Y.-F. Yang and C.-W. So, *Chem. Commun.*, 2009, 6816.
- 25 R. Thirumoorathi, T. Chivers and I. Vargas-Baca, *Organometallics*, 2012, **31**, 627.
- 26 W.-P. Leung, Y.-C. Chan and T. C. W. Mak, *Inorg. Chem.*, 2011, **50**, 10517.
- 27 A. M. Z. Slawin, J. Ward, D. J. Williams and J. D. Woollins, *J. Chem. Soc., Chem. Commun.*, 1994, 421.
- 28 C. J. Carmalt, A. H. Cowley, A. Decken, Y. G. Lawson and N. C. Norman, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, **C52**, 931.
- 29 Alternatively, these structural trends can be attributed to the contributions of dipolar resonance forms, as discussed in the review by Liddle *et al.*^{12a}.
- 30 The other example is *o*-nitrodiphenyliodonium iodide with $d(\text{I}-\text{I}) = 3.1802(2) \text{ \AA}$, $d(\text{Cax}-\text{I}) = 2.175(3) \text{ \AA}$, $d(\text{Ceq}-\text{I}) 2.109(3) \text{ \AA}$ and $\angle \text{I}-\text{I}-\text{Cax} = 176.83(8)^\circ$: V. A. Nikiforov, V. S. Karavan, S. A. Miltsov, S. I. Selivanov, E. Kolehmainen, E. Wegelius and M. Nissinen, *ARKIVOC*, 2003, **4**, 191. The original structure was reported as the salt $[\text{2-NO}_2\text{C}_6\text{H}_4-\text{I}-\text{C}_6\text{H}_5] + \text{I}^-$, neglecting the I–I interaction. In ref. 25, revised distances and bond angles were obtained from the data deposited at the Cambridge Crystallographic Data Centre, reference code enigen.
- 31 F. V. Bolhuis, P. B. Koster and T. Migchelsen, *Acta Crystallogr.*, 1967, **23**, 90.
- 32 J. Trotter in *The Chemistry of the Carbon–Halogen Bond*, Part 1, ed. S. Patai, John Wiley & Sons Ltd., 1973, pp. 49–62.
- 33 J. Konu and T. Chivers, *Chem. Commun.*, 2008, 4995.
- 34 M. Lusser and P. Peringer, *Inorg. Chim. Acta*, 1987, **127**, 151.
- 35 J. Konu, H. M. Tuononen and T. Chivers, *Inorg. Chem.*, 2009, **48**, 11788.
- 36 (a) J. S. Ritch and T. Chivers, *Dalton Trans.*, 2008, 957; (b) S. D. Robertson, T. Chivers, J. Akhtar, M. Afzaal and P. O'Brien, *Dalton Trans.*, 2008, 7004; (c) J. S. Ritch and T. Chivers, *Inorg. Chem.*, 2009, **48**, 3857; (d) S. D. Robertson, J. S. Ritch and T. Chivers, *Dalton Trans.*, 2009, 8582.
- 37 Recently, 1 : 1 adducts of the neutral ligand $[\text{H}_2\text{C}(\text{PPh}_2\text{Se})_2]$ with TeX_2 (X = I, Br) have been structurally characterised and shown to embody a square planar *cis*-Se₂TeI₂ arrangement: (a) C. G. Hrib, P. G. Jones, W.-W. du Mont, V. Lippolis and F. A. Devillanova, *Eur. J. Inorg. Chem.*, 2006, 1294; (b) W. Levason, G. Reid, M. Victor and W. Zhang, *Polyhedron*, 2009, **28**, 4010.
- 38 T. Cantat, X. F. Jacques, L. Ricard, X. F. Le Goff, N. Mézailles and P. Le Floch, *Angew. Chem., Int. Ed.*, 2007, **46**, 5947.
- 39 (a) T. Chivers, D. J. Eisler, J. S. Ritch and H. M. Tuononen, *Angew. Chem., Int. Ed.*, 2005, **44**, 4953; (b) J. S. Ritch, T. Chivers, D. J. Eisler and H. M. Tuononen, *Chem.–Eur. J.*, 2007, **13**, 4643.
- 40 (a) S. D. Robertson, T. Chivers and H. M. Tuononen, *Inorg. Chem.*, 2008, **47**, 10634; (b) S. D. Robertson, T. Chivers and H. M. Tuononen, *Inorg. Chem.*, 2009, **48**, 6755.
- 41 J. Konu and T. Chivers, *Chem. Commun.*, 2010, **46**, 1431.
- 42 M. Risto, T. Chivers and J. Konu, *Dalton Trans.*, 2011, **40**, 8238.
- 43 M. Risto, J. Konu and T. Chivers, *Inorg. Chem.*, 2011, **50**, 406.
- 44 J. Konu, T. Chivers and H. M. Tuononen, *Chem.–Eur. J.*, 2010, **16**, 12977.
- 45 J. Konu, T. Chivers and H. M. Tuononen, *Chem.–Eur. J.*, 2011, **17**, 11844.
- 46 T. Cantat, F. Biaso, A. Momin, L. Ricard, M. Geoffroy, N. Mézailles and P. Le Floch, *Chem. Commun.*, 2008, 874.
- 47 (a) C.-P. Klages and J. Voss, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 726; (b) D. Helling, C.-P. Klages and J. Voss, *J. Phys. Chem.*, 1980, **84**, 3638; (c) A. G. Davies and A. G. Neville, *J. Chem. Soc., Perkin Trans. 2*, 1992, **2**, 171.
- 48 These Se–I bonds are described as “strong” in the literature. F. Cristiani, F. Demartin, F. A. Devillanova, F. Isaia, V. Lippolis and G. Verani, *Inorg. Chem.*, 1994, **33**, 6315.
- 49 J. Konu and T. Chivers, unpublished observations.
- 50 R. Oilunkaniemi, R. S. Laitinen and M. Ahlgren, *J. Organomet. Chem.*, 2001, **623**, 168.
- 51 M. L. Delucia and P. Coppens, *Inorg. Chem.*, 1978, **17**, 2336.
- 52 T. Chivers, R. W. Hilts, P. Jin, Z. Chen and X. Lu, *Inorg. Chem.*, 2010, **49**, 3810 and references therein.
- 53 F. Breher, *Coord. Chem. Rev.*, 2007, **251**, 1007.
- 54 Recent high-level computations have revealed a significant diradical component of the bonding in S₄N₄ and 1,5-R₄P₂N₄S₂: J. Moilanen and H. M. Tuononen, private communication.
- 55 H. Schmidbaur and K. C. Dash, *Adv. Inorg. Chem.*, 1982, **25**, 239.
- 56 (a) M. J. Calhorda, F. Canales, M. C. Gimeno, J. Jimenez, P. G. Jones, A. Laguna and L. F. Veiros, *Organometallics*, 1997, **16**, 3837; (b) S. Canales, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna and F. Mendizabal, *Organometallics*, 2001, **20**, 4812; (c) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931; (d) M. C. Gimeno and A. Laguna, *Chem. Soc. Rev.*, 2008, **37**, 1952.
- 57 (a) R. G. Raptis, L. C. Porter, R. J. Emrich, H. H. Murray and J. P. Fackler Jr., *Inorg. Chem.*, 1990, **29**, 4408; (b) H. Schmidbaur, C. Hartmann, G. Reber and G. Muller, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1146; (c) K. Ortner, L. Hilditch, Y. Zheng, J. R. Dilworth and U. Abram, *Inorg. Chem.*, 2000, **39**, 2801.