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PAPER

Homoleptic, heteroleptic and mixed-valent thallium and indium complexes of multidentate chalcogen-centred PCP-bridged ligands†

Maarit Risto,[a] Tristram Chivers*[a] and Jari Konu[a,b]

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The metathetical reaction of [Li(TMEDA)][HC(PPh$_2$Se)$_2$] ([Li(TMEDA)]**1**) with TlOEt in a 1 : 1 molar ratio afforded a homoleptic Tl(I) complex as an adduct with LiOEt, Tl[HC(PPh$_2$Se)$_2$]·LiOEt (**7**), which undergoes selenium–proton exchange upon mild heating (60 °C) to give the mixed-valent Tl(I)/Tl(III) complex {[Tl][Tl{(Se)C(PPh$_2$Se)$_2$}$_2$]}$_\infty$ (**8**). Treatment of TlOEt with [Li(TMEDA)]$_2$[(SPh$_2$P)$_2$CE′E′C(PPh$_2$S)$_2$] (**3b**, E′ = S; **3c**, E′ = Se) in a 2 : 1 molar ratio produced the binuclear Tl(I)/Tl(I) complexes Tl$_2$[(SPh$_2$P)$_2$CE′E′C(PPh$_2$S)$_2$] (**9b**, E′ = S; **9c**, E′ = Se), respectively. Selenium–proton exchange also occurred upon addition of [Li(TMEDA)]**1** to InCl$_3$ to yield the heteroleptic complex (TMEDA)InCl[(Se)C(PPh$_2$Se)$_2$] (**10a**). Other examples of this class of In(III) complex, (TMEDA)InCl[(E′)C(PPh$_2$E)$_2$] (**10b**, E = E′ = S; **10c**, E = S, E′ = Se) were obtained *via* metathesis of InCl$_3$ with [Li(TMEDA)]$_2$[(E′)C(PPh$_2$E)$_2$] (**2b**, E = E′ = S; **2c**, E = S, E′ = Se, respectively). All new compounds have been characterized in solution by ^{1}H and ^{31}P NMR spectroscopy and the solid-state structures have been determined for **8**, **9c** and **10a–c** by single-crystal X-ray crystallography. Complex **8** is comprised of Tl$^+$ ions that are weakly coordinated to octahedral [Tl{(Se)C(PPh$_2$Se)$_2$}$_2$]$^-$ anions to give a one-dimensional polymer. The complex **9c** is comprised of two four-coordinate Tl$^+$ ions that are each *S*,*S*′,*S*″,*Se* bonded to the hexadentate [(SPh$_2$P)$_2$CSeSeC(PPh$_2$S)$_2$]$^{2-}$ ligand in which *d*(Se–Se) = 2.531(2) Å. The six-coordinate In(III) centres in the distorted octahedral complexes **10a–c** are connected to a tridentate [(E′)C(PPh$_2$E)$_2$]$^{2-}$ dianion, a chloride ion and a neutral bidentate TMEDA ligand.

Introduction

Our recent development of a synthesis of the TMEDA-solvated lithium derivative of the PCP-bridged monoanion [HC(PPh$_2$Se)$_2$]$^-$ (**1**)[1] has paved the way for a comparison of the coordination behaviour of this selenium-centred ligand with that of the well-studied PNP-bridged analogue.[2,3] Metathetical reactions of **1** with group 12 dihalides MCl$_2$ proceed in the expected manner to give homoleptic complexes M[HC(PPh$_2$Se)$_2$]$_2$ (M = Zn, Hg) that exhibit *Se*,*Se*′ chelation,[1] *cf.* M[N(PPh$_2$Se)$_2$]$_2$.[4,5] In distinct contrast to this normal behaviour, however, the reactions of **1** with certain main group dihalides MCl$_2$ generate the triseleno PCP-bridged dianion [(Se)C(PPh$_2$Se)$_2$]$^{2-}$ (**2a**) in homoleptic complexes with M(IV) (M = Sn,Te) *via* a carbon-centred proton–selenium exchange combined with redox disproportionation of the metal centre.[6] Interestingly, mild thermolysis of the mononuclear Hg(II) derivative of **1**, Hg[HC(PPh$_2$Se)$_2$]$_2$, also promotes proton–selenium exchange to give a binuclear Hg(II)/Hg(II) complex of **2a**.[6]

In order to circumvent the mechanistically obscure proton–selenium exchange process[7] for the production of the novel class of trichalcogeno ligands of the type **2**, we have prepared the dianions **2b** and **2c** as TMEDA-solvated Li$^+$ derivatives, by the treatment of Li$_2$[C(PPh$_2$S)$_2$][8] with sulfur or selenium, respectively.[9] The all-selenium derivative cannot be obtained *via* this route because of the unavailability of Li$_2$[C(PPh$_2$Se)$_2$] owing to cleavage of P–Se bonds by RLi reagents.[1] One-electron oxidation of the dianions **2b** and **2c** with I$_2$ produces the dimeric dianions [(SPh$_2$P)$_2$CE′E′C(PPh$_2$S)$_2$]$^{2-}$ (**3b**, E′ = S; **3c**, E′ = Se) with elongated central chalcogen–chalcogen bonds as *S*,*S*′-chelated, TMEDA-solvated Li$^+$ derivatives.[9]

The potential versatility of the multidentate chalcogen-centred ligands **1–3** has been established through investigations of their behaviour towards coinage metals.[10,11] Intriguing binuclear Cu(I)/Cu(I) complexes of the type **4** are formed by (a) treatment of monoanion **1** with CuCl *via* the proton–selenium exchange process (**4a**), (b) the redox reaction of monomeric dianion **2c** with CuCl$_2$ (**4c**), or (c) metathesis of dimeric dianions **3b** and **3c** with CuCl (**4b** and **4c**).[10,11] The η^2-Se$_2$ motif observed in the complexes **4a** and **4c** is a novel bonding arrangement for RSe–SeR ligands.[12] Coordination of the two copper centres to the central E–E bond results in a (further) elongation of this bond compared to the

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[a] *Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4. E-mail: chivers@ucalgary.ca; Fax: +1 403 289 9488; Tel: +1 403 220 5741*

[b] *Current address: Department of Chemistry, University of Jyväskylä, P.O. Box 35, FI-40014, Jyväskylä, Finland*

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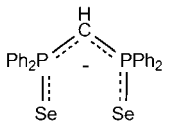

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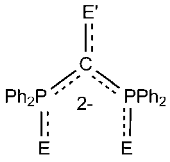
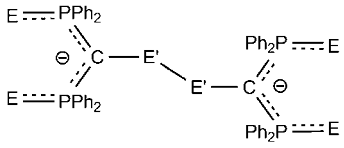
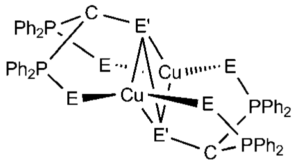


2a (E = E′ = Se)
2b (E = E′ = S)
2c (E= S; E′ = Se)

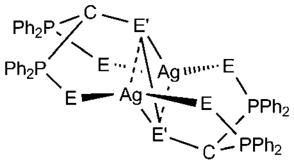


3a (E = E′ = Se)
3b (E = E′ = S)
3c (E = S, E′ = Se)

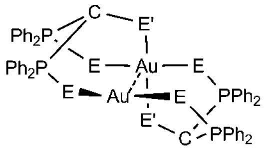
distance in the corresponding bis-*E*,*E*′-chelated Li$^+$ derivatives. This bond-stretching is especially pronounced in the all-sulfur system **4b** for which DFT calculations indicate some diradicaloid character.[11,13] Silver (I) forms a binuclear Ag(I)/Ag(I) complex **5c** with the dimeric dianion **3c** that is structurally similar to the Cu(I) complex **4c**.[12] By contrast, the treatment of **3b** or **3c** with Au(CO)Cl produces the mixed-valent Au(I)/Au(III) complexes **6b** and **6c**, respectively, in which the central chalcogen–chalcogen bond has been cleaved and the ligands are the tridentate dianions $[(E')C(PPh_2S)_2]^{2-}$ (**2b**, E′ = S; **2c**, E′ = Se).[11]



4a (E = E′ = Se)
4b (E = E′ = S)
4c (E= S; E′ = Se)



5b (E = E′ = S)
5c (E= S; E′ = Se)



6b (E = E′ = S)
6c (E= S; E′ = Se)

In this context we were motivated to investigate the co-ordination and redox chemistry of ligands of the type **1–3** towards heavy group 13 metals for which both +1 and +3 oxidation states are readily available. The reaction of **1** with Tl(I) reagents was also of interest in view of our recent studies of the first Tl(I) complexes of dichalcogeno PNP-bridged ligands $[N(PPh_2E)_2]^-$ (E = S, Se, Te), which form coordination polymers.[14] In this contribution we describe the reactions of TlOEt with (a) the diseleno monoanion **1** and (b) the dimeric dianions **3b** and **3c**. The former affords the mononuclear Tl(I) complex, $Tl[HC(PPh_2Se)_2]\cdot LiOEt$ (**7**), as an intermediate, which undergoes a selenium–proton exchange to give a mixed-valent Tl(I)/Tl(III) complex $\{[Tl][Tl\{(Se)C(PPh_2Se)_2\}_2]\}_\infty$ (**8**). The latter reaction generates the binuclear Tl(I)/Tl(I) complexes $Tl_2[(SPh_2P)_2CE'E'C(PPh_2S)_2]$ (**9b**, E′ = S; **9c**, E′ = Se). Selenium–proton exchange also occurs upon treatment of **1** with $InCl_3$ to yield the heteroleptic complex $(TMEDA)InCl[(Se)C(PPh_2Se)_2]$ (**10a**). Other examples of this class of In(III) complex, $(TMEDA)InCl[(E')C(PPh_2E)_2]$ (**10b**, E = E′ = S; **10c**, E = S, E′ = Se) can be obtained *via* metathesis of **2b** or **2c** with $InCl_3$, respectively. All new compounds have been characterized in solution by ^{1}H and ^{31}P NMR spectroscopy and the solid-state structures of **8**, **9c** and **10a–c** have been determined by single-crystal X-ray crystallography.

Experimental

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 $[H_2C(PPh_2)_2]$ (Aldrich, 97%), TMEDA (Aldrich, 99%), MeLi (Aldrich, 1.6 M sol. in Et_2O), $InCl_3$ (Aldrich, 98%) and TlOEt (Aldrich, 98%) were used as received. $[Li(TMEDA)][HC(PPh_2Se)_2]$,[1] $[Li(TMEDA)]_2[(E')C(PPh_2S)_2]$ (E′ = S, Se)[9] and $[Li(TMEDA)]_2[(SPh_2P)_2CE'E'C(PPh_2S)_2]$ (E′ = S, Se)[9] were prepared according to literature methods. The solvents *n*-hexane, toluene, Et_2O and THF were dried by distillation over Na/benzophenone and CH_2Cl_2 over CaH_2 under an argon atmosphere prior to use. Elemental analyses were performed by Analytical Services, Department of Chemistry, University of Calgary.

Spectroscopic methods

The ^{1}H, ^{7}Li and ^{31}P NMR spectra were obtained in CD_2Cl_2 or d_8-THF on a Bruker DRX 400 spectrometer operating at 399.46, 155.53 and 161.71 MHz, respectively. The ^{1}H spectra are referenced to the solvent signal and the chemical shifts are reported relative to $(CH_3)_4Si$. The ^{7}Li and ^{31}P NMR spectra are referenced externally, and the chemical shifts are reported relative to a 1.0 M solution of LiCl in D_2O and to an 85% solution of H_3PO_4. The ^{13}C and ^{77}Se NMR spectra could not be obtained owing to the limited solubility of the complexes in NMR solvents.

X-ray crystallography

Crystallographic data for **8**, **9c**·$(CH_2Cl_2)_7$ and **10a–c** are summarized in Table 1. Crystals of all compounds were coated with Paratone 8277 oil and mounted on a glass fibre. Diffraction data were collected on a Nonius Kappa CCD diffractometer using monochromated Mo-Kα radiation (λ = 0.71073 Å) at −100 °C. The data sets were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied to the net intensities. The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97.[15,16] After full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions (C–H = 0.95 Å for –CH, 0.99 Å for –CH_2 and 0.98 Å for –CH_3 hydrogens). The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the corresponding carbon for –CH and –CH_2 hydrogens, and 1.5 times for –CH_3 hydrogens. In the final refinement the hydrogen atoms were riding on their respective carbon atoms.

Table 1 Crystallographic data for $\{[\mathrm{Tl}][\mathrm{Tl}\{(\mathrm{Se})\mathrm{C}(\mathrm{PPh_2Se})_2\}_2]\}_\infty$ (**8**), $\mathrm{Tl_2[(SPh_2P)_2CSeSeC(PPh_2S)_2]\cdot(CH_2Cl_2)_7}$ (**9c**$\cdot(\mathrm{CH_2Cl_2})_7$) and $\mathrm{(TMEDA)InCl[(Se)C(PPh_2Se)_2]}$ (**10a**), $\mathrm{(TMEDA)InCl[(S)C(PPh_2S)_2]}$ (**10b**) and $\mathrm{(TMEDA)InCl[(Se)C(PPh_2S)_2]}$ (**10c**)[a]

	8	**9c**$\cdot(\mathrm{CH_2Cl_2})_7$	**10a**	**10b**	**10c**
Emp. formula	$\mathrm{C_{50}H_{40}P_4Se_6Tl_2}$	$\mathrm{C_{107}H_{94}Cl_{14}P_8S_8Se_4Tl_4}$	$\mathrm{C_{31}H_{36}ClInN_2P_4Se_3}$	$\mathrm{C_{31}H_{36}ClInN_2P_4S_3}$	$\mathrm{C_{31}H_{36}ClInN_2P_4S_2Se}$
Formula weight	1647.20	3513.68	885.71	745.01	791.91
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	27.544(6)	15.101(3)	17.311(4)	17.380(4)	17.180(3)
b/Å	12.641(3)	18.743(4)	16.969(3)	16.863(3)	16.748(3)
c/Å	16.371(3)	22.487(5)	11.992(2)	11.805(2)	12.007(2)
α (°)	90.00	90.00	90.00	90.00	90.00
β (°)	118.85(3)	105.79(3)	107.99(3)	108.59(3)	108.28(3)
γ (°)	90.00	90.00	90.00	90.00	90.00
V/Å^3	4992.2(17)	6124(2)	3350.4(12)	3279.2(11)	3280.4(11)
Z	4	2	4	4	4
T/°C	−100	−100	−100	−100	−100
ρ_c/g cm^{-3}	2.192	1.905	1.756	1.509	1.603
μ(Mo-Kα)/mm^{-1}	10.985	7.026	4.164	1.115	2.161
Crystal size/mm	0.26 × 0.12 × 0.04	0.16 × 0.10 × 0.10	0.36 × 0.28 × 0.20	0.20 × 0.18 × 0.16	0.16 × 0.16 × 0.12
F(000)	3064	3364	1736	1520	1592
Θ range, deg.	2.04–25.03	2.62–25.03	2.15–25.03	2.71–25.02	2.73–25.03
Reflns collected	8291	20524	11454	5759	9574
Unique reflns	4374	10721	5888	5759	5751
R_{int}	0.0469	0.0624	0.0391	0.0000	0.0343
Reflns [$I > 2\sigma(I)$]	3688	8053	4984	4625	5137
R_1 [$I > 2\sigma(I)$][b]	0.0502	0.0625	0.0524	0.0663	0.0756
wR_2 (all data)[c]	0.1672	0.1280	0.1160	0.1344	0.1667
GOF on F^2	1.130	1.096	1.116	1.132	1.341
Completeness	0.995	0.991	0.996	0.995	0.991

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

Two of the phenyl groups in compounds **10a–c** were disordered. The disorder was taken into account by refining the site occupation factors of each disordered pair and constraining their sums to unity. A chlorine atom in one of the solvating $\mathrm{CH_2Cl_2}$ molecules in **9c**$\cdot(\mathrm{CH_2Cl_2})_7$ was disordered over two sites; this was included in the refinement using partial site occupancy factors.

Synthesis of $\mathrm{Tl[HC(PPh_2Se)_2]\cdot LiOEt}$ (7)

A solution of TlOEt (0.100 g, 0.40 mmol) in toluene (5 mL) was added to a suspension of [Li(TMEDA)]**1** (0.266 g, 0.40 mmol) in toluene (30 mL) at −80 °C. The reaction mixture was stirred for 15 min at −80 °C and 2 h at 23 °C. The resulting powder was allowed to settle and the solution was decanted *via* cannula. The product was washed with toluene (40 mL) affording $\mathrm{Tl[HC(PPh_2Se)_2]\cdot LiOEt}$ (**7**) as a pale brown powder (0.241 g, 75%). Elemental analysis calcd (%) for $\mathrm{C_{27}H_{26}LiOP_2Se_2Tl}$: C, 40.65; H, 3.29; found: C, 40.40; H, 2.95. ^{1}H NMR (d_8-THF, 23 °C): δ 7.88–7.09 [m, 20H, $\mathrm{C_6}H_5$], 4.14 [qr, 2H, –CH_2 of LiOEt], 2.59 [s, 1H, –CH of the PCP carbon], 1.24 [t, 3H, –CH_3 of LiOEt]; ^{7}Li NMR (d_8-THF, 23 °C): δ 0.01; ^{31}P{^{1}H} NMR (d_8-THF, 23 °C): δ 22.7 [s, $^1J(^{31}\mathrm{P},^{77}\mathrm{Se})$ = 584 Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ = 26 Hz].

Synthesis of $\{[\mathrm{Tl}][\mathrm{Tl}\{(\mathrm{Se})\mathrm{C}(\mathrm{PPh_2Se})_2\}_2]\}_\infty$ (8)

Method A. A solution of TlOEt (0.188 g, 0.75 mmol) in toluene (5 mL) was added to a mixture of [Li(TMEDA)]**1** (0.500 g, 0.75 mmol) and elemental selenium (0.030 g, 0.38 mmol) in toluene (30 mL) by using cannula. The reaction mixture was stirred at 60 °C for 3 days. The resulting dark powder was allowed to settle and the solution was decanted *via* cannula. The powder was washed with toluene (20 mL) and dissolved in 80 mL of warm (40 °C) THF. The solution was filtered through a PTFE-disk and the solvent was evaporated under vacuum. The product was washed with *n*-hexane (60 mL) to afford $\{[\mathrm{Tl}][\mathrm{Tl}\{(\mathrm{Se})\mathrm{C}(\mathrm{PPh_2Se})_2\}_2]\}_\infty$ (**8**) as a dark purple powder (0.229 g, 74%). Elemental analysis calcd (%) for $\mathrm{C_{50}H_{40}P_4Se_6Tl_2}$: C, 36.46; H, 2.45; found: C, 36.90; H, 2.55. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 23 °C): δ 8.20–6.87 [m, 40H, $\mathrm{C_6}H_5$]; ^{31}P{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 23 °C): δ 52.4 [s, $^1J(^{31}\mathrm{P},^{77}\mathrm{Se})$ = 533 Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ = 45 Hz]. X-ray quality crystals of **8** were obtained by layering *n*-hexane onto the $\mathrm{CH_2Cl_2}$ solution of **7** after 24 h at room temperature.

Method B. A mixture of $\mathrm{Tl[HC(PPh_2Se)_2]\cdot LiOEt}$ (**7**) (0.284 g, 0.36 mmol) and elemental selenium (0.015 g, 0.19 mmol) in toluene (30 mL) was stirred at 60 °C for 3 days resulting in a dark grayish solid and a purple solution. The powder was allowed to settle and the solution was decanted *via* a cannula. The powder was washed with toluene (20 mL) and dissolved in 80 mL of warm (40 °C) THF. The solution was filtered through a PTFE-disk and the solvent was evaporated under vacuum. The product was washed with hexane (60 mL) to afford $\{[\mathrm{Tl}][\mathrm{Tl}\{(\mathrm{Se})\mathrm{C}(\mathrm{PPh_2Se})_2\}_2]\}_\infty$ (**8**) as a dark purple powder (0.132 g, 90%), The identity of the product was confirmed by both ^{31}P NMR spectroscopy and X-ray crystallography (unit cell measurement after recrystallization from $\mathrm{CH_2Cl_2}$/*n*-hexane mixture).

Synthesis of $\mathrm{Tl_2[(SPh_2P)_2CSSC(PPh_2S)_2]}$ (9b)

A solution of TlOEt (0.080 g, 0.32 mmol) in toluene (5 mL) was added to a suspension of $[\mathrm{Li(TMEDA)}]_2$**3b** (0.193 g, 0.16 mmol) in toluene (20 mL) at −80 °C. The reaction mixture was stirred for

15 min at −80 °C and 2 h at 23 °C. The solvent was removed by evaporation and the product was washed with Et_2O (2 × 30 mL) affording $Tl_2[(SPh_2P)_2CSSC(PPh_2S)_2]$ (**9b**) as an orange-red powder (0.174 g, 79%). Elemental analysis calcd (%) for $C_{50}H_{40}P_4S_6Tl_2$: C, 43.97; H, 2.95; found: C, 44.01; H, 3.02. ^1H NMR (CD_2Cl_2, 23 °C): δ 8.15–6.98 [m, 40H, C_6H_5]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 23 °C): δ 48.2 [s (br), $\Delta w_{\frac{1}{2}} \approx 250$ Hz]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C): δ 63.9 [s (br)], 57.7 [s (br)], 49.7 [s (br)], 46.6 [s (br)], 40.1 [s (br)].

Synthesis of $Tl_2[(SPh_2P)_2CSeSeC(PPh_2S)_2]$ (9c)

A solution of TlOEt (0.161 g, 0.65 mmol) in toluene (5 mL) was added to a suspension of $[Li(TMEDA)]_2$**3c** (0.419 g, 0.32 mmol) in toluene (20 mL) at −80 °C. The reaction mixture was stirred for 15 min at −80 °C and 2 h at 23 °C. The resulting dark red powder was allowed to settle and the solution was decanted *via* cannula. The product was washed with Et_2O (30 mL) and *n*-hexane (30 mL) affording $Tl_2[(SPh_2P)_2CSeSeC(PPh_2S)_2]$ (**9c**) as a dark red powder (0.362 g, 77%). Elemental analysis calcd (%) for $C_{50}H_{40}P_4S_4Se_2Tl_2$: C, 41.14; H, 2.76; found: C, 41.68; H, 2.86. ^1H NMR (CD_2Cl_2, 23 °C): δ 8.12–6.88 [m, 40H, C_6H_5]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 23 °C): δ 47.3 [s (br) $\Delta w_{\frac{1}{2}} \approx 950$ Hz]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 50.4 [d, $^2J(^{31}P,^{31}P) = 55$ Hz], 49.2 [d, $^2J(^{31}P,^{31}P) = 59$ Hz], *ca.* 41.2 [two overlapping doublets]. X-ray quality crystals were obtained by layering *n*-hexane onto the CH_2Cl_2 solution of **9c** after 24 h at 5 °C.

Synthesis of $(TMEDA)InCl[(Se)C(PPh_2Se)_2]$ (10a)

A mixture of [Li(TMEDA)]**1** (0.337 g, 0.51 mmol) and $InCl_3$ (0.056 g, 0.25 mmol) powders was cooled to −80 °C and cold toluene (50 mL) was added *via* cannula. The reaction mixture was stirred for 15 min at −80 °C and 4 h at 50 °C. The resulting powder was allowed to settle and the solution was decanted *via* cannula. The product was washed with toluene (25 mL) affording $(TMEDA)InCl[(Se)C(PPh_2Se)_2]$ (**10a**) as a pale-yellow powder (0.157 g, 70%). Elemental analysis calcd (%) for $C_{31}H_{36}ClInN_2P_2Se_3$: C, 42.04; H, 4.10; N, 3.16; found: C, 41.98; H, 4.19; N, 3.07. ^1H NMR (CD_2Cl_2, 23 °C): δ 8.24–6.81 [m, 20H, C_6H_5], 2.87 [s, 6H, $-CH_3$ of TMEDA], 2.79 [s (br), 2H, $-CH_2$ of TMEDA], 2.45 [s (br), 2H, $-CH_2$ of TMEDA], 2.32 [s, 6H, $-CH_3$ of TMEDA]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 23 °C): δ 50.2 [s, $^1J(^{31}P,^{77}Se) = 512$ Hz, $^2J(^{31}P,^{31}P) = 29$ Hz]. X-ray quality crystals of **10a** were obtained from the undisturbed reaction solution after 24 h at 23 °C.

Synthesis of $(TMEDA)InCl[(S)C(PPh_2S)_2]$ (10b)

A solution of $[Li(TMEDA)]_2$**2b** (0.60 mmol, prepared *in situ* from 0.269 g of $[H_2C(PPh_2S)_2]$, 0.75 mL of MeLi, 0.139 g of TMEDA and 0.019 g of sulfur)[9] in toluene (20 mL) was added to a suspension of $InCl_3$ (0.133 g, 0.60 mmol) in toluene (10 mL) at −80 °C. The reaction mixture was stirred for 15 min at −80 °C and $1\frac{1}{2}$ h at 23 °C. The resulting powder was allowed to settle and the solution was decanted *via* cannula. The product was washed with *n*-hexane (20 mL) affording $(TMEDA)InCl[(S)C(PPh_2S)_2]$ (**10b**) as a pale-yellow powder (0.315 g, 70%). Elemental analysis calcd (%) for $C_{31}H_{36}ClInN_2P_2S_3$: C, 49.97; H, 4.87; N 3.76; found: C, 49.08; H, 4.87; N, 3.67. ^1H NMR (CD_2Cl_2, 23 °C): δ 8.20–6.82 [m, 20H, C_6H_5], 2.81 [s, 6H, $-CH_3$ of TMEDA], 2.74 [s (br), 2H, $-CH_2$ of TMEDA], 2.43 [s (br), 2H, $-CH_2$ of TMEDA], 2.26 [s, 6H, $-CH_3$ of TMEDA]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 23 °C): δ 48.0. X-ray quality crystals were obtained by layering Et_2O onto the CH_2Cl_2 solution of **10b** after 24 h at −20 °C.

Synthesis of $(TMEDA)InCl[(Se)C(PPh_2S)_2]$ (10c)

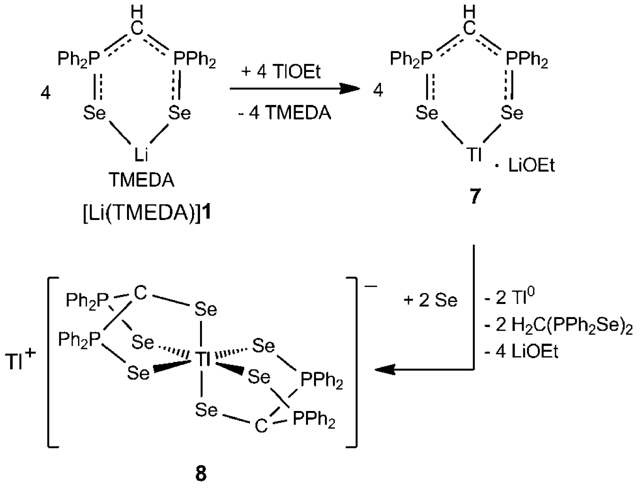
A solution of $[Li(TMEDA)]_2$**2c** (0.60 mmol, prepared *in situ* from 0.269 g of $[H_2C(PPh_2S)_2]$, 0.75 mL of MeLi, 0.139 g of TMEDA and 0.047 g of selenium)[9] in toluene (20 mL) was added to a suspension of $InCl_3$ (0.133 g, 0.60 mmol) in toluene (10 mL) at −80 °C. The reaction mixture was stirred for 15 min at −80 °C and $1\frac{1}{2}$ h at 23 °C. The resulting powder was allowed to settle and the solution was decanted *via* cannula. The product was washed with *n*-hexane (20 mL) affording $(TMEDA)InCl[(Se)C(PPh_2S)_2]$ (**10c**) as a pale-yellow powder (0.380 g, 80%). Elemental analysis calcd (%) for $C_{31}H_{36}ClInN_2P_2S_2Se$: C, 47.02; H, 4.58; N, 3.54; found: C, 45.92; H, 4.61; N, 3.37. ^1H NMR (CD_2Cl_2, 23 °C): δ 8.20–6.83 [m, 20H, C_6H_5], 2.86 [s, 6H, $-CH_3$ of TMEDA], 2.80 [s (br), 2H, $-CH_2$ of TMEDA], 2.45 [s (br), 2H, $-CH_2$ of TMEDA], 2.34 [s, 6H, $-CH_3$ of TMEDA]; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 23 °C): δ 48.4. X-ray quality crystals were obtained by layering Et_2O onto the CH_2Cl_2 solution of **10c** after 24 h at 5 °C.

Results and discussion

Synthesis and spectroscopic characterization of $Tl[HC(PPh_2Se)_2]\cdot LiOEt$ (7) and $\{[Tl][Tl\{(Se)C(PPh_2Se)_2\}_2]\}_\infty$ (8): crystal structure of 8

The reaction between [Li(TMEDA)]**1** and TlOEt in a 1 : 1 molar ratio in toluene at −80 °C produced a very insoluble pale brown powder upon warming up to room temperature. The $^{31}P\{^1H\}$ NMR spectrum of this powder exhibited a single resonance at δ 22.7 with ^{77}Se satellites [$^1J(^{31}P,^{77}Se) = 584$ Hz, $^2J(^{31}P,^{31}P) = 26$ Hz]. These coupling constants are virtually equal with those in [Li(TMEDA)]**1**,[1] indicating negligible change in the geometry of the ligand **1**. The ^1H NMR spectrum displayed a singlet for the hydrogen in the PC(H)P unit and the typical signal patterns for both phenyl and ethoxide groups. In addition, the ^7Li NMR spectrum showed the presence of Li^+ cation with a singlet at 0.01 ppm. Collectively, the NMR data indicated the formation of an LiOEt adduct of the homoleptic thallium(I) complex, $Tl[HC(PPh_2Se)_2]\cdot LiOEt$ (**7**). An elemental (C, H) analysis of the powder was also consistent with the formation of **7**. However, despite repeated attempts, crystals of sufficient quality for an accurate single crystal X-ray structural determination could not be obtained.[17]

After a prolonged reaction time or upon moderate heating (60 °C), the singlet for **7** in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture was gradually replaced by two mutually coupled doublets indicating the formation of the monoselenide $[H_2C(PPh_2)(PPh_2Se)]$,[18] while the colour of the solid turned from pale brown to dark gray. The consumption of **7** was observed to be faster and the yield of the dark solid higher when elemental selenium was added to the reaction mixture (Method A in Experimental section). The by-product in that case is the neutral diselenide $[H_2C(PPh_2Se)_2]$[18] (Scheme 1).



Scheme 1

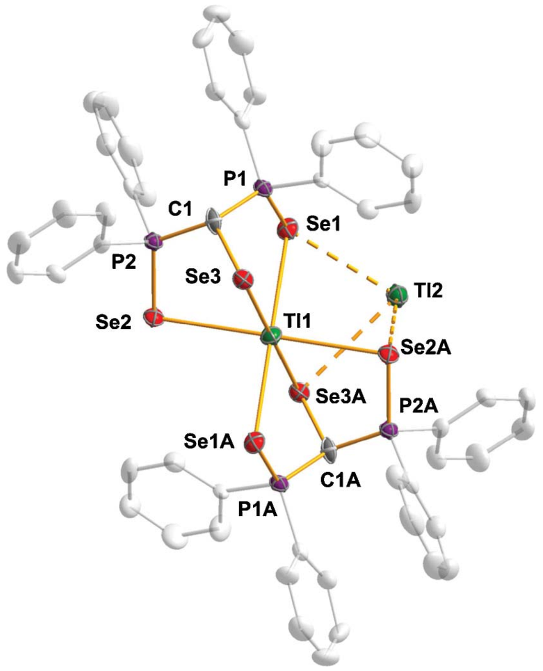


Fig. 1 Molecular structure of $\{[Tl][Tl\{(Se)C(PPh_2Se)_2\}_2]\}_\infty$ (**8**) with atomic numbering scheme. Thermal ellipsoids have been drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Symmetry operation: (A) $2 - x, -y, 1 - z$.

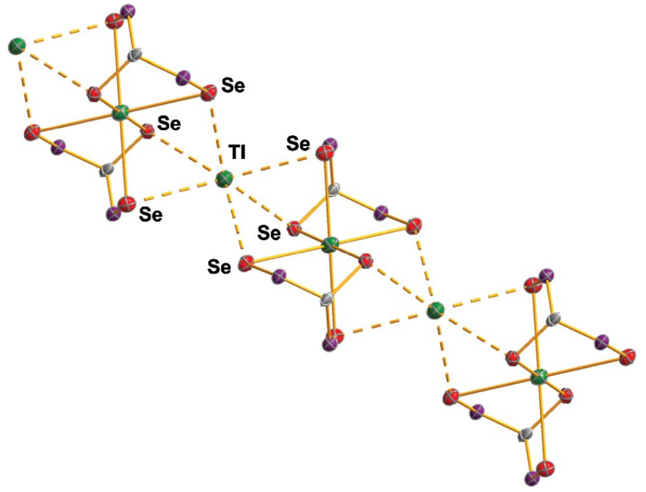


Fig. 2 Polymeric strand of $\{[Tl][Tl\{(Se)C(PPh_2Se)_2\}_2]\}_\infty$ (**8**). Thermal ellipsoids have been drawn at 50% probability level. Phenyl groups have been omitted for clarity. (Green: Tl; red: Se; purple: P; gray: C).

After work-up, a dark purple powder was isolated for which the $^{31}P\{^1H\}$ NMR spectrum displayed a singlet at δ 52.4 with ^{77}Se satellites [$^1J(^{31}P,^{77}Se)$ = 533 Hz, $^2J(^{31}P,^{31}P)$ = 45 Hz]. The ^1H NMR spectrum of this product showed only the presence of phenyl groups and no signal for the PC(H)P hydrogen was observed. Taken together, the NMR data suggested the formation of the dianionic triseleno ligand $[(Se)C(PPh_2Se)_2]^{2-}$ (**2a**) *via* a Se–H^+ exchange process, *cf.* the production of the Sn(IV), Te(IV) and Hg(II) complexes $\{M_n[(Se)C(PPh_2Se)_2]_2\}$ ($n = 1$, M = Sn, Te; $n = 2$, M = Hg).[6]

The same dark purple solid was also obtained in good yield by heating a toluene solution of the isolated complex **7** at 60 °C for 3 days (Method B in Experimental Section), thus confirming that **7** is an intermediate in the formation of this new product.

An X-ray structural determination of one of the crystals obtained by recrystallization of the dark purple powder from a CH_2Cl_2–hexane mixture revealed a mixed-valent Tl(I)/Tl(III) salt $\{[Tl][Tl\{(Se)C(PPh_2Se)_2\}_2]\}_\infty$ (**8**), which is comprised of centrosymmetric $[Tl\{(Se)C(PPh_2Se)_2\}_2]^-$ anions ($[Tl(\mathbf{2a})_2]^-$) and weakly associated thallous Tl^+ counter cations arranged in a one-dimensional polymer. The structure of **8** with the atomic numbering scheme is shown in Fig. 1, and selected bond parameters are presented in Table 2. In the anion $[Tl(\mathbf{2a})_2]^-$, the Tl(III) centre is coordinated to two tridentate, facially bound triseleno ligands $[(Se)C(PPh_2Se)_2]^{2-}$ (**2a**), to give a slightly distorted octahedral geometry with Tl(III)–Se distances of 2.674(2), 3.051(2) and 3.128(2) Å (Fig. 1). The significantly shorter (by *ca.* 0.4 Å) Tl–Se(C) bond (2.674(2) Å) compared to the Tl–Se(P) contacts (3.051(2) and 3.128(2) Å) is likely due to the localization of the negative charge in the dianion on the Se(C) atom. A less pronounced disparity between Sn–Se(C) and Sn–Se(P) bond lengths of *ca.* 0.17 Å is observed in the neutral tin(IV) complex, $\{Sn[(Se)C(PPh_2Se)_2]_2\}$ ($Sn(\mathbf{2a})_2$).[6] The $[Tl(\mathbf{2a})_2]^-$ anions are weakly associated with Tl(I) cations by relatively long Tl(I)–Se interactions (3.335(2)–3.481(2) Å) to form continuous chains (Fig. 2). The geometry at the Tl(I) ions is a distorted trigonal prism.

There are scant data available in the literature describing Tl(III)–Se bonds. Examples are restricted to compounds containing thallium(III) selenide or mixed thallium(I/III) selenide ions, *e.g.* $(Et_4N)_3[Tl_3Se_3(Se_4)_3]$ (d(Tl(III)–Se) = 2.585(5)–2.686(6) Å),[19] $(Ph_4P)_4[Tl_4Se_{16}]$ (d(Tl(III)–Se = 2.584(7)–2.8022(8) Å),[20] (2,2,2-crypt-K)$_3[Tl^{III}(Tl^I)_4Se_5]$ (d(Tl(III)–Se) = 2.543(4)–2.766(3) Å).[21] While the Tl(III)–Se(C) distance in **8** is similar to those observed in thallium selenides, the Tl(III)–Se(P) bonds are significantly elongated when compared with Tl(III)–Se distances in binary anions.

Structural data for compounds with Tl(I)–Se bonds are better established than those of the Tl(III) analogues including some Tl(I) complexes of selenium-containing ligands in addition to binary thallium(I) selenide anions. Consequently, the Tl(I)–Se distances in the octahedrally coordinated Tl(I) centre in **8** can be compared

Table 2 Selected bond lengths (Å) and bond angles (deg) in $\{[Tl][Tl\{(Se)C(PPh_2Se)_2\}_2]\}_\infty$ (**8**)

Tl1–Se1	3.128(2)	P1–Se1	2.169(3)
Tl1–Se2	3.051(2)	P2–Se2	2.172(3)
Tl1–Se3	2.674(2)	C1–P1	1.766(10)
Tl2–Se1	3.335(2)	C1–P2	1.789(11)
Tl2–Se2	3.481(2)	C1–Se3	1.899(11)
Tl2–Se3	3.460(2)		
Se1–Tl1–Se2	83.41(3)	Se2–Tl1–Se2^a	180.0(4)
Se1–Tl1–Se3	89.11(3)	Se3–Tl1–Se3^a	180.0
Se1–Tl1–Se2^a	96.59(3)	Se1–P1–C1	115.1(4)
Se1–Tl1–Se3^a	90.89(3)	Se2–P2–C1	118.0(4)
Se1–Tl1–Se1^a	180.0	P1–C1–Se3	110.9(5)
Se2–Tl1–Se3	81.28(3)	P2–C1–Se3	110.1(6)
Se2–Tl1–Se3^a	98.72(3)	P1–C1–P2	118.5(6)

Symmetry operation:^{a} $2 - x, -y, 1 - z$.

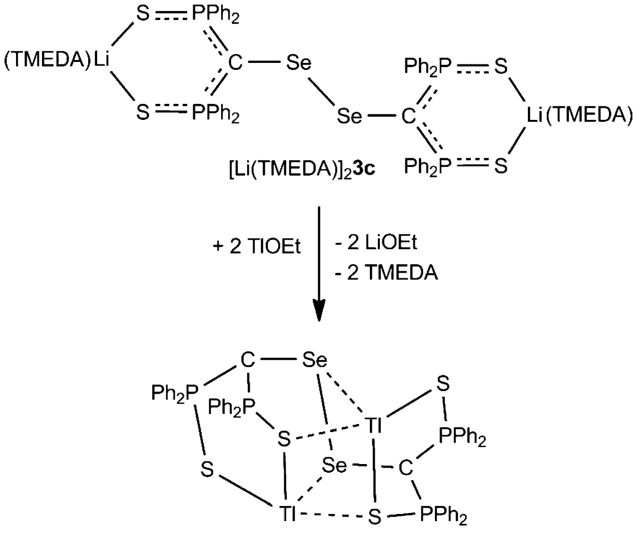
with those seen in $\{Tl[(SeP^iPr_2)_2N]\}_\infty$ (d(Tl(I)–Se = 3.051(1)–3.647(2) Å),[14] as well as in $[Tl\{MeSe(CH_2)_nSeMe\}]PF_6$ (n = 2, 3) (d(Tl(I)–Se = 3.2769(8)–3.5058(8) Å).[22] The latter three complexes form coordination polymers featuring highly coordinated thallium(I) centres. In comparison, the Tl(I)–Se distances for tri- and tetra-coordinated Tl(I) ions in $[Tl^{III}(Tl^I)_4Se_5]^{3-}$ (d(Tl(I)–Se) = 2.814(4)–3.039(4) Å)[21] and $[Tl_2(Se_2C{=}C(CN)_2)_2]^{2-}$ (d(Tl(I)–Se = 3.108(4)–3.162(4) Å),[23] respectively, are significantly shorter than the related contacts in **8**. This variation in Tl(I)–Se distances with Tl(I) coordination number is expected and consistent with the bond valence concept.[24,25]

The geometrical arrangement of the metal centre and ligands in the $[Tl(\mathbf{2a})_2]^-$ anion is similar to that observed in the neutral, octahedral Sn(IV) complex $Sn(\mathbf{2a})_2$.[6] However, the P–C bond lengths of 1.766(10) and 1.789(11) Å in $[Tl(\mathbf{2a})_2]^-$ are *ca.* 0.03 Å longer, and the C–Se distance of 1.899(4) Å is 0.03 Å shorter than the corresponding bonds in the tin(IV) complex. A similar disparity is evident between the P–C and C–Se bond lengths in $[Tl(\mathbf{2a})_2]^-$ and those found in the tellurium and mercury complexes of the dianion **2a**, $\{M_n[SeC(PPh_2Se)_2]_2\}$ (n = 1, M = Te $[Te(\mathbf{2a})_2]$; n = 2, M = Hg $[Hg_2(\mathbf{2a})_2]$).[6] The coordination environment of the PCP carbon in the monoanion of **8** deviates significantly from planarity ($\sum\angle C = 340°$), *cf*. $\sum\angle C$ = 341° and 342° in $Sn(\mathbf{2a})_2$ and $Te(\mathbf{2a})_2$, respectively.[6]

The production of **8** *via* the intermediate **7** formally involves the generation of the dianion $[(Se)C(PPh_2Se)_2]^{2-}$ (**2a**) from the monoanionic $[HC(PPh_2Se)_2]^-$ ligand in **7** with concomitant redox disproportionation of Tl(I) into Tl(III) and, presumably, thallium metal, *cf*. the formation of the M(IV) complexes $Sn(\mathbf{2a})_2$ and $Te(\mathbf{2a})_2$ from $[HC(PPh_2Se)_2]^-$ and MCl_2 (M = Sn, Te).[6] The mechanism of the Tl(I)→Tl(III) oxidation is not currently understood, however a related precedent involves the formation of tetrahedral Tl(III) complexes *via* an internal redox process in thallium(I)-polyselenide systems.[19,26]

Synthesis and spectroscopic characterization of $Tl_2[(SPh_2P)_2CE'E'C(PPh_2S)_2]$ (9b, E′ = S; 9c, E′ = Se): crystal structure of 9c

The metathetical reaction of $[Li(TMEDA)]_2$**3c** with TlOEt in a 1 : 2 molar ratio at −80 °C proceeded cleanly to afford the dinuclear Tl(I)/Tl(I) complex $Tl_2[(SPh_2P)_2CSeSeC(PPh_2S)_2]$ (**9c**) in good yield (Scheme 2).



9c

Scheme 2

The identity of **9c** was established in the solid state by single crystal X-ray structural determination. As illustrated in Fig. 3, the molecular structure of **9c** displays a dinuclear, polycyclic arrangement in which each Tl centre is *S*,*S′*-chelated by one-half of the dimeric ligand and *S*,*Se*-chelated by the other half. Thus, in contrast to the TMEDA-solvated dilithio precursor $[Li(TMEDA)]_2$**3c** (Scheme 2), the metal centres in **9c** are drawn towards the opposite half of the dianionic ligand through Tl···E (E = S, Se) contacts resulting in the polycyclic geometry and four-coordinate Tl(I) atoms. By comparison with the formation of the mixed-valent Au(I)/Au(III) complexes **6b** and **6c** from reactions of $[Li(TMEDA)]_2$**3b** and $[Li(TMEDA)]_2$**3c** with Au(CO)Cl,[11] the dimeric (dichalcogenide) ligand remains intact in the reactions of these precursors with TlOEt and no redox process is observed. The complex **9c** also differs structurally from the previously reported

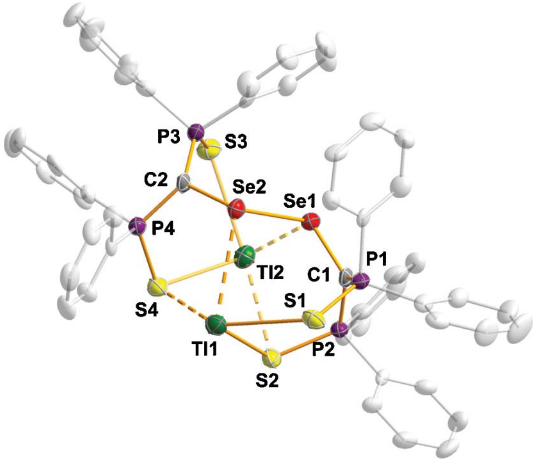


Fig. 3 Molecular structure of $Tl_2[(SPh_2P)_2CSeSeC(PPh_2S)_2]\cdot(CH_2Cl_2)_7$ ($\mathbf{9c}\cdot(CH_2Cl_2)_7$) with atomic numbering scheme. Thermal ellipsoids have been drawn at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. The solid Tl–S bonds indicate *S*,*S′*-chelation of each terminus of the dimeric dianion **3**, and the dashed Tl---E (E = S, Se) contacts are used for interactions to the opposite end of the ligand.

Table 3 Selected bond lengths (Å) and bond angles (deg) in $Tl_2[(SPh_2P)_2CSeSeC(PPh_2S)_2]\cdot(CH_2Cl_2)_7$ (**9c**·$(CH_2Cl_2)_7$)

Tl1–S1	3.128(3)	P1–C1	1.757(11)
Tl1–S2	2.999(3)	P2–C1	1.755(11)
Tl1–S4	3.289(4)	P3–C2	1.741(11)
Tl1–Se2	3.203(2)	S4–P4	2.003(4)
Tl2–S2	3.380(4)	S1–P1	1.993(4)
Tl2–S3	3.070(3)	S2–P2	2.005(4)
Tl2–S4	2.953(3)	S3–P3	1.991(4)
Tl2–Se1	3.221(2)	Se2–C2	1.888(10)
Se1–Se2	2.531(2)	P4–C2	1.765(11)
Se1–C1	1.882(10)		
S1–Tl1–S2	90.77(8)	S3–P3–C2	115.5(4)
S1–Tl1–Se2	81.32(6)	S4–P4–C2	117.6(4)
S2–Tl1–Se2	97.93(6)	P1–C1–Se1	116.3(6)
S3–Tl2–S4	90.03(8)	P2–C1–Se1	114.6(5)
S3–Tl2–Se1	83.27(6)	P3–C2–Se2	117.9(6)
S4–Tl2–Se1	96.48(7)	P4–C1–Se2	114.1(5)
S1–P1–C1	116.5(4)	P1–C1–P2	123.8(6)
S2–P2–C1	117.4(4)	P3–C2–P4	121.5(6)

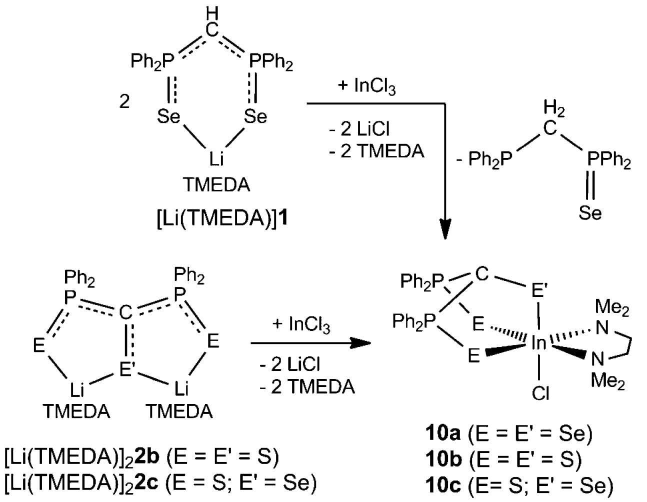
dinuclear coinage metal complexes **4a–c** and **5c** in which two metal centres are *E*,*E*′-chelated by one chalcogen atom in each terminus of the dianionic ligand and η^2-bonded to the central chalcogen–chalcogen linkage.[10,11] However, the average P–C, P–S and C–Se bond lengths of *ca.* 1.75, 2.00, 1.88 Å (Table 3), respectively, in **9c** as well as the bond angles involving these atoms are comparable with the corresponding values in the complexes **4c** and **5c** (and in **4b**, where appropriate).[11] These parameters are also identical with those found in the bis-*S*,*S*′-chelated Li^+ derivative $[Li(TMEDA)]_2$**3c**.[9] The Tl–S distances between the thallium centre and two sulfur atoms from the one terminus of the dianionic ligand range from 2.953(3) to 3.128(3) Å and are similar to those seen in the ladder polymer $\{Tl[(SP^iPr_2)_2N]\}_\infty$ (2.920(1) and 2.922(2) Å) in which the Tl atoms are also four-coordinate.[14] The Tl–S bond lengths between thallium and one sulfur atom from the opposite terminus of the dianionic ligand are longer (3.289(4) and 3.380(4) Å) and approach weak van der Waals interaction [$\sum_{(cov)} = 2.47$; $\sum_{(vdW)} = 3.76$].[27,28] They are comparable to those seen in thioether complexes of Tl(I) centres, *e.g.* $[Tl([18]aneS_6)][PF_6]$ (3.164(5)–3.370(5) Å)[29] and $[Tl([24]aneS_8)][PF_6]$ (3.2851(3)–3.473(2) Å).[30] The Tl–Se distances of 3.203(2) and 3.221(2) Å in **9c** also represent moderately weak interactions, *cf.* the Tl(I)–Se interactions in **8** (Table 2). Consistently, the (C)Se–Se(C) bond length of 2.531(2) Å in **9c** is only slightly elongated (by *ca.* 0.02 Å) compared to the corresponding distance in the bis-*S*,*S*′-chelated dilithium reagent $[Li(TMEDA)]_2$**3c**.[9]

The $^{31}P\{^1H\}$ NMR spectrum of **9c** exhibited a broad singlet at δ 47.3 ppm ($\Delta w_{\frac{1}{2}} \approx 950$ Hz) at room temperature, indicating fluxionality in solution. However, upon cooling to −60 °C, this resonance was resolved into two doublets at δ 50.4 [$^2J(^{31}P,^{31}P) = 55$ Hz] and 49.2 [$^2J(^{31}P,^{31}P) = 59$ Hz], and the mutually coupled pairs of these doublets appear as an overlapping doublet at *ca.* 41.2 ppm without clear resolution of the two distinct $^2J(^{31}P,^{31}P)$ couplings (see Supplementary Information†).[31] Two of the phosphorus atoms (P2 and P4) in the solid-state structure of **9c** are constituents of 5-membered rings while the other two phosphorus centres (P1 and P3) are components of 6-membered rings, thereby resulting in two discrete environments for these two pairs of phosphorus atoms (Fig. 3 and Scheme 2). Consequently, while the P1···Tl2 and P1···Se2 contacts for phosphorus atom P1 are 5.723(4) and 3.958(4) Å respectively, the corresponding interactions for P2 are P2···Tl2 = 3.819(4) Å and P2···Se2 = 4.726(4) Å. Similar disparity in P···Tl and P···Se interactions is evident between P3 and P4 atoms [P3···Tl1 5.748(3) and P3···Se1 3.975(4) Å; P4···Tl1 3.800(4) and P4···Se1 4.703(4) Å]. In summary, the low-temperature ^{31}P NMR spectrum of **9c** is consistent with the solid-state structure.

The reaction of $[Li(TMEDA)]_2$**3b** with TlOEt in a 1 : 2 molar ratio yielded a orange-red powder with elemental (C, H, N) analysis that is consistent with the formation of the dinuclear complex $Tl_2[(SPh_2P)_2CSSC(PPh_2S)_2]$ (**9b**) analogous to the selenium congener **9c**. The room temperature $^{31}P\{^1H\}$ NMR spectrum of **9b** showed one broad resonance at δ 48.3 ($\Delta w_{\frac{1}{2}} \approx 250$ Hz) which, although substantially narrower than the resonance observed for **9c** (*vide supra*), is also indicative of fluxional behaviour. Variable temperature NMR experiments, however, indicate a structural disparity between **9b** and **9c** in solution. After cooling the solution of **9b** to −80 °C, only a partial resolution into five broad resonances in the region of 63.9–40.1 ppm was observable (see Supplementary Information†), *cf.* two pairs of mutually coupled doublets for **9c** (*vide supra*). Unfortunately, despite numerous attempts, X-ray quality crystals of **9b** could not be obtained so the nature of the structural differences in the solid state between **9b** and **9c** could not be ascertained, although it is likely associated with the change in the carbon-bound chalcogen from Se in **9c** to S in **9b**.

Synthesis, spectroscopic characterization and crystal structures of (TMEDA)InCl[(E′)C(PPh$_2$E)$_2$] (10a, E = E′ = Se; 10b, E = E′ = S; 10c, E = S, E′ = Se)

The reaction of [Li(TMEDA)]**1** with $InCl_3$ in a 2 : 1 molar ratio at 50 °C results in a selenium–proton exchange to give the heteroleptic complex $(TMEDA)InCl[(Se)C(PPh_2Se)_2]$ (**10a**) as a pale yellow powder in 70% yield (Scheme 3). The related sulfur-containing complexes $(TMEDA)InCl[(S)C(PPh_2S)_2]$ (**10b**) and $(TMEDA)InCl[(Se)C(PPh_2S)_2]$ (**10c**) were obtained in 70 and 80% yields *via* metathetical reaction of $[Li(TMEDA)]_2$**2b** or $[Li(TMEDA)]_2$**2c** with $InCl_3$, respectively (Scheme 3). Previous examples of the formation of the triseleno dianion $[(Se)C(PPh_2Se)_2]^{2-}$



Scheme 3

Table 4 Selected bond lengths (Å) and bond angles (deg) in (TMEDA)InCl[(Se)C(PPh$_2$Se)$_2$] (**10a**), (TMEDA)InCl[(S)C(PPh$_2$S)$_2$] (**10b**) and (TMEDA)InCl[(Se)C(PPh$_2$S)$_2$] (**10c**)

	10a (E = E′ = Se)	**10b** (E = E′ = S)	**10c** (E = S; E′ = Se)
In1–E1	2.725(1)	2.619(2)	2.637(2)
In1–E2	2.745(9)	2.650(2)	2.626(3)
In1–E′	2.664(11)	2.540(2)	2.660(2)
In1–N1	2.441(6)	2.434(6)	2.392(9)
In1–N2	2.425(6)	2.390(7)	2.410(9)
In1–Cl1	2.506(2)	2.483(2)	2.491(2)
E1–P1	2.189(2)	2.034(3)	2.031(3)
E2–P2	2.190(2)	2.028(2)	2.028(4)
C1–E′	1.973(7)	1.803(7)	1.938(9)
C1–P1	1.741(7)	1.753(7)	1.735(9)
C1–P2	1.725(7)	1.739(6)	1.745(9)
C1–P1–E1	115.9(2)	114.9(2)	117.2(3)
C1–P2–E2	117.2(2)	116.2(2)	115.5(3)
P1–C1–E′	107.0(3)	107.3(4)	106.0(4)
P2–C1–E′	106.2(4)	106.9(3)	107.4(5)
P1–C1–P2	124.1(4)	122.0(4)	122.3(5)

from reactions of [Li(TMEDA)]**1** and p-block metal halides (see ref. 6 and the synthesis of **8** in this work) involve both Se–H$^+$ and redox disproportionation of the metal centre. In these examples the reagents used involved group 13, 14 or 16 metal centres in low oxidation states [Tl(I), Sn(II) or Te(II)]. By contrast, the formation of **10a** from [Li(TMEDA)]**1** and the In(III) reagent InCl$_3$ is not accompanied by a redox process at the metal centre.[32] Consistently, the Sn(IV) complex Sn(**2a**)$_2$ is obtained in higher yields from [Li(TMEDA)]**1** by using SnCl$_4$ rather than SnCl$_2$ as the tin source.[33] Interestingly, Leung and co-workers have shown that the reaction of [Li(THF)(Et$_2$O)][HC(PPh$_2$S)$_2$], the dithio analogue of **1**, with InCl$_3$ in a 2 : 1 molar ratio produces the *S*,*C*,*S*′-bonded dimer [InCl{C(PPh$_2$S)$_2$}]$_2$ *via* a process that probably involves metathesis followed by dehydrochlorination by the second equivalent of the lithium reagent.[34]

The crystal structures of **10a–c** were determined by X-ray crystallography. All three complexes crystallize in the space group $P2_1/c$ and form an isostructural series. A representative thermal ellipsoid plot is shown in Fig. 4, and selected bond lengths and angles are compared in Table 4. The solid-state structures of **10a–c** reveal discrete molecules in which the indium(III) centre is hexa-coordinated by one tridentate [(E′)C(PPh$_2$E)$_2$]$^{2-}$ ligand, one bidentate TMEDA molecule and one chloride ligand, giving a slightly distorted octahedral geometry for the metal. A similar tridentate bonding mode of the [(E′)C(PPh$_2$S)$_2$]$^{2-}$ (E′ = S, Se) dianions to a metal centre prevails in the homoleptic complexes Sn(**2a**)$_2$,[6] Pb(**2b**) and Pb(**2c**),[35] as well as for the Tl[(Se)C(PPh$_2$Se)$_2$]$_2^-$ anion in **8**. While the differences in In–N and In–Cl bond lengths between **10a–c** are insignificant, the In–E and In–E′ bond distances increase as expected with the size of the chalcogens. The P–Se and P–C bond lengths in **10a** are similar to those seen in Sn(**2a**)$_2$,[6] but slightly shorter that the values observed in **8**, whereas the C–Se distance in **10a** exhibits a slight increase of *ca.* 0.04–0.07 Å compared to those in Sn(**2a**)$_2$[6] and **8**. The P–S and P–C bond lengths in **10b** and **10c** are essentially equal at *ca.* 1.74 and 2.03 Å, respectively, and in agreement with the corresponding mean values of 1.74 and 2.04 Å reported for both Pb(**2b**) and Pb(**2c**).[35] The C–E′ distances in **10b** and **10c** (**10b**, E′ = S: 1.8037(7) and **10c**, E′ = Se: 1.938(9) Å) are also very similar to those seen in Pb(**2b**) and Pb(**2c**).[35] In addition, the PCP carbons in **10a–c** all exhibit a significant distortion from planarity ($\sum\angle$C is *ca.* 336°) that is found to be typical for the metal-coordinated tridentate dianions **2a–c**.[6,11,35]

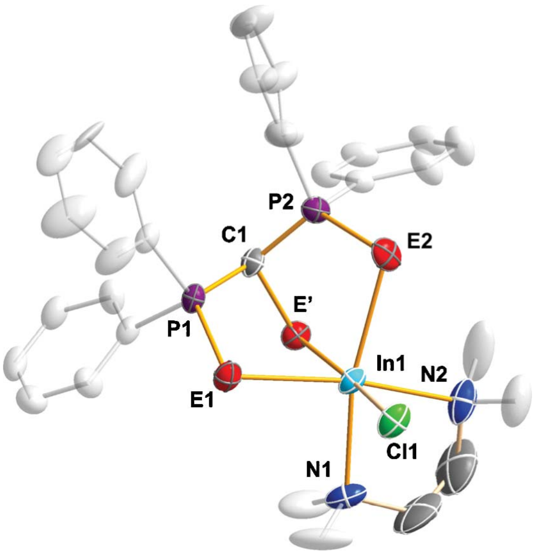


Fig. 4 Molecular structure of (TMEDA)InCl[(Se)C(PPh$_2$Se)$_2$] (**10a**) with atomic numbering scheme as representative of compounds (TMEDA)InCl[(E′)C(PPh$_2$E)$_2$] (**10a**, E = E′ = Se; **10b**, E = E′ = S; **10c**, E = S, E′ = Se). Thermal ellipsoids have been drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Only the higher occupancy portion of the disordered phenyl groups is shown.

The ^{31}P{^{1}H} NMR spectra of **10a–c** each displayed a single resonance at δ 50.2, 48.0 and 48.4 ppm, respectively. The ^{77}Se satellites were also observed for **10a** [$^1J(^{31}\mathrm{P},^{77}\mathrm{Se})$ = 512 Hz, $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ = 29 Hz]. The $^1J(^{31}\mathrm{P},^{77}\mathrm{Se})$ and $^2J(^{31}\mathrm{P},^{31}\mathrm{P})$ coupling constants are somewhat smaller than the values observed for homoleptic tin and thallium complexes, Sn(**2a**)$_2$[6] and **8**, respectively. In the ^{1}H NMR spectra of **10a–c** two sets of singlets were observed for the methyl and methylene protons of the TMEDA ligand, in addition to the characteristic signal pattern for phenyl groups of the chalcogenocarbonyl dianion. The NMR spectral features thus indicate that the four N-methyl groups and four methylene protons have two mutually different environments in solution. One of the N-methyl groups in each terminus of the ligand and one hydrogen atom in both CH$_2$-groups are on the same side of the indium coordination plane as the chlorine atom and the other two N-methyl groups and methylene hydrogens of TMEDA are on the same side of the coordination plane as the PCP carbon-bound chalcogen of the [E′C(PPh$_2$E)$_2$]$^{2-}$ ligand.

Conclusions

The reaction of TlOEt with the anion [HC(PPh$_2$Se)$_2$]$^-$ produces a homoleptic thallium(I) complex as an adduct with LiOEt which, upon mild heating, undergoes selenium–proton exchange and redox disproportionation of the thallium centres to give the mixed-valent complex {[Tl][Tl{(Se)C(PPh$_2$Se)$_2$}$_2$]}$_\infty$; the latter exhibits an intriguing one-dimensional polymeric structure. By contrast, treatment of TlOEt with the dimeric anions $[(SPh_2P)_2CE'E'C(PPh_2S)_2]^{2-}$ (E′ = S, Se) yields polycyclic, binuclear Tl(I)/Tl(I) complexes in which the dimeric ligands remain intact with little change in the central chalcogen–chalcogen bond length for E = Se. Reaction of $InCl_3$ with $[HC(PPh_2Se)_2]^-$ generates the heteroleptic, mononuclear In(III) complex (TMEDA)InCl[(Se)C(PPh$_2$Se)$_2$] *via* selenium–proton exchange with no detectable intermediate. An alternative route to similar In(III) complexes is the metathesis of $InCl_3$ with the tridentate dianions $[(E')C(PPh_2S)_2]^{2-}$ (E′ = S, Se). These monofunctional complexes (In–Cl linkage) offer scope for further investigations of reaction chemistry at indium(III) centres harnessed by tridentate chalcogen-centred ligands.

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