Synthesis of Phosphinochalcogenoic Amidato Complexes of Zinc and Cadmium. The Crystal and Molecular Structure of $[\mathrm{Zn}\{\mathrm{Bu^t_2P(Se)NPr^i}\}_2]$†

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The protolysis of zinc and cadmium amides $[\mathrm{M}\{\mathrm{N(SiMe_3)_2}\}_2]$ with 2 equivalents of phosphinochalcogenoic amides $\mathrm{Bu^t_2P(E)NHR}$ (E = Se or Te, R = $\mathrm{Pr^i}$ or $\mathrm{C_6H_{11}}$) gave the complexes $[\mathrm{M}\{\mathrm{Bu^t_2P(E)NR}\}_2]$ (M = Zn or Cd). The thermally stable compounds are monomeric and sublime readily. If the protolysis reaction is carried out in a molar ratio of 1 : 1, the mixed-ligand compounds $[\mathrm{Zn}\{\mathrm{N(SiMe_3)_2}\}\{\mathrm{Bu^t_2P(E)NR}\}]$ can be isolated for zinc but not for cadmium. The crystal structure of $[\mathrm{Zn}\{\mathrm{Bu^t_2P(Se)NPr^i}\}_2]$ has been determined. The complex possesses a distorted tetrahedral structure. The ligands are bidentate, with short [1.981(3) Å] Zn–N and comparatively long [2.5375(9) Å] Zn–Se bonds.

Over the last few years there has been significant interest in the synthesis of molecular 'single-source' precursors for solid-state materials.[1] General requirements for successful precursors are a low degree of association and adequate volatility, at least sufficient for low-pressure deposition techniques. Steigerwald and co-workers[2] prepared a series of arenechalcogenolato complexes of zinc, cadmium and mercury suitable mainly for the preparation of nanoscale particles from solution thermolysis, and we have reported the synthesis of related sterically highly hindered mono- and di-meric arenechalcogenolato complexes $[\{\mathrm{M(EC_6H_2Bu^t_3)_2}\}_2]$ (M = Zn, Cd or Hg; E = S or Se) for the gas-phase deposition of II–VI (Group 12–16) films.[3] More recently, Arnold and co-workers[4] applied this principle of steric hindrance to the synthesis of low-co-ordinate silyltellurolato complexes. However, preventing intermolecular association by high steric hindrance has its limitations since it implies an increase in molecular weight, usually at the expense of volatility. The same objective may be achieved by the use of chelating ligands. For example, four-co-ordinate dithio- and diseleno-carbamates have proved sufficiently volatile for the growth of zinc and cadmium chalcogenide films.[5] We are particularly interested in readily accessible complexes of the heavier chalcogenide elements, notably tellurium, for materials applications and have recently reported the synthesis of phosphino-selenoic and -telluroic amides, $\mathrm{Bu^t_2P(E)NHR}$ (E = Se or Te).[6] Analogous sulfur compounds are known as usually bidentate S–N ligands, and a number of main group and transition-metal complexes have been reported.[7] By contrast, the possibility of using this ligand system for the synthesis of stable monomeric selenium and tellurium complexes has hardly been explored so far. We report here the synthesis of a number of zinc(II) and cadmium(II) complexes and the structure of a representative zinc–selenium complex.

Results and Discussion

Phosphinochalcogenoic amidato complexes of zinc and cadmium are conveniently prepared in high yields by protolysis of the corresponding metal bis(trimethylsilyl)amides in light petroleum at room temperature according to Scheme 1.

The complexes are moderately soluble in light petroleum and are obtained after recrystallisation from toluene as colourless (E = Se) or yellow (E = Te) crystals; the latter are, to our knowledge, the first examples of complexes of the phosphinotelluroic amidato ligand. The zinc–tellurium complexes **1c** and **1d** decompose above 135 and 150 °C, respectively; the other complexes are thermally more stable, with melting points >200 °C. All the complexes sublime readily at 100–200 °C under reduced pressure. Molecular-weight determinations are in agreement with a monomeric tetrahedral structure; this was confirmed by X-ray crystallography for complex **1a**.

The products obtained from ligand-exchange reactions between metal amides and chalcogenolato ligands, *i.e.* reactions of the type shown in Scheme 1, are usually the least soluble components of an equilibrium, and only rarely intermediates can be isolated. However, protolysis of $[\mathrm{Zn}\{\mathrm{N(SiMe_3)_2}\}_2]$ with only 1 equivalent of $\mathrm{Bu^t_2P(E)NHR}$ leads to the mixed-ligand zinc amido complexes $[\mathrm{Zn}\{\mathrm{N(SiMe_3)_2}\}\{\mathrm{Bu^t_2P(E)NR}\}]$ as hydrocarbon-soluble colourless to yellow crystals **3a**–**3d** (Scheme 2).

Cryoscopic molecular-weight determinations in benzene for **3c** indicated a mononuclear structure in solution, although it is likely that the compounds exist as chalcogenide-bridged dimers in the solid state. The preference of chalcogenolato over amido bridges has been observed for example in the recently reported manganese(II) complex $[\{\mathrm{Mn[N(SiMe_3)_2][SeC_6H_2Pr^i_3\text{-}2,4,6](thf)}\}_2]$[8] (thf = tetrahydrofuran) and in the trinuclear zinc complex $[\mathrm{Zn_3}\{\mathrm{N(SiMe_3)_2}\}_2\{\mathrm{SC_6H_2Pr^i_3\text{-}2,4,6}\}_4]$.[9] Unfortunately, in spite of numerous attempts crystals of **3** suitable for X-ray diffraction could not be obtained.

By contrast, the reaction of $[\mathrm{Cd}\{\mathrm{N(SiMe_3)_2}\}_2]$ with $\mathrm{Bu^t_2P(E)NHR}$ in a ratio of 1 : 1 only gave the complexes **2a**–**2d**; no intermediates analogous to **3** could be isolated. The analytical and physical data of all new compounds are collected in Table 1, spectroscopic data in Tables 2 and 3.

Crystal Structure of $[\mathrm{Zn}\{\mathrm{Bu^t_2P(Se)NPr^i}\}_2]$ (**1a**).—The molecular structure of **1a** is shown in Fig. 1, important bond lengths and angles are collected in Table 4. Dialkylphosphinothioic amidato complexes of divalent metals can possess square-planar or tetrahedral geometries and exist as monomers or ligand-bridged dimers, often in equilibrium with each other, depending on the nature of the phosphorus-alkyl substituents, with bulky ligands favouring monomeric tetrahedral structures.[7a] Complex **1a** belongs to this latter category. The $\mathrm{ZnN_2Se_2}$ core forms a flattened tetrahedron as the result of the small bite angle of the ligands (average

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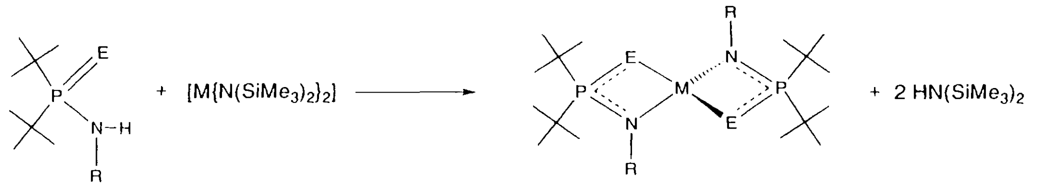
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.
Non-SI unit employed: Torr ≈ 133 Pa.

Table 1 Analytical data of phosphinochalcogenoic amidato complexes

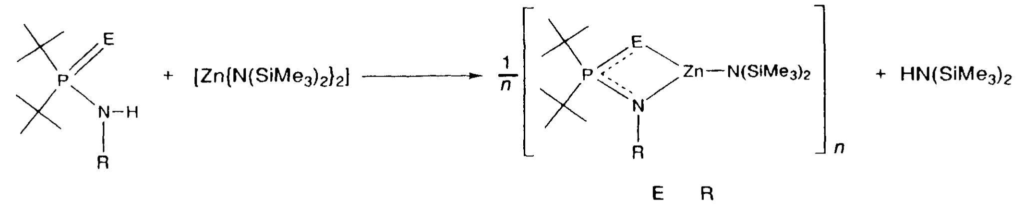
Compound	M.p./°C	Sublimation temperature[a]/°C	Yield (%)	Analysis[b] (%) C	H	N
1a $[Zn\{Bu^t_2P(Se)NPr^i\}_2]$	> 220	190	88	42.2 (42.1)	8.1 (8.0)	4.3 (4.5)
1b $[Zn\{Bu^t_2P(Se)N(C_6H_{11})\}_2]$	> 220	200	90	47.8 (47.5)	8.4 (8.3)	3.9 (4.0)
1c $[Zn\{Bu^t_2P(Te)NPr^i\}_2]$	135[c]		79	36.9 (36.4)	7.5 (7.0)	4.8 (4.8)
1d $[Zn\{Bu^t_2P(Te)N(C_6H_{11})\}_2]$	152[c]	115	69	42.6 (42.0)	8.2 (7.9)	3.8 (3.5)
2a $[Cd\{Bu^t_2P(Se)NPr^i\}_2]$	> 220	200	91	39.3 (39.2)	7.6 (7.5)	4.3 (4.2)
2b $[Cd\{Bu^t_2P(Se)N(C_6H_{11})\}_2]$	> 220	200	88	44.8 (44.5)	7.7 (7.7)	3.7 (3.7)
2c $[Cd\{Bu^t_2P(Te)NPr^i\}_2]$	188	115	85	34.5 (34.2)	6.4 (6.5)	3.6 (3.6)
2d $[Cd\{Bu^t_2P(Te)N(C_6H_{11})\}_2]$	213	180	83	39.6 (39.5)	6.8 (6.9)	3.5 (3.3)
3a $[Zn\{N(SiMe_3)_2\}\{Bu^t_2P(Se)NPr^i\}]$	> 220	200	65	40.3 (40.3)	8.4 (8.5)	5.2 (5.5)
3b $[Zn\{N(SiMe_3)_2\}\{Bu^t_2P(Se)N(C_6H_{11})\}]$	> 220	200	72	43.5 (43.9)	8.2 (8.6)	4.7 (5.1)
3c $[Zn\{N(SiMe_3)_2\}\{Bu^t_2P(Te)NPr^i\}]$	206	120	76	36.6 (36.7)	7.6 (7.8)	4.7 (5.0)
3d $[Zn\{N(SiMe_3)_2\}\{Bu^t_2P(Te)N(C_6H_{11})\}]$	> 220	200	70	40.6 (40.3)	7.8 (8.0)	4.6 (4.7)

[a] At *ca.* 10^{-6} Torr. [b] Calculated values in parentheses. [c] With decomposition.



	M	E	R
1a	Zn	Se	Pr^i
1b	Zn	Se	C_6H_{11}
1c	Zn	Te	Pr^i
1d	Zn	Te	C_6H_{11}
2a	Cd	Se	Pr^i
2b	Cd	Se	C_6H_{11}
2c	Cd	Te	Pr^i
2d	Cd	Te	C_6H_{11}

Scheme 1



	E	R
3a	Se	Pr^i
3b	Se	C_6H_{11}
3c	Te	Pr^i
3d	Te	C_6H_{11}

Scheme 2

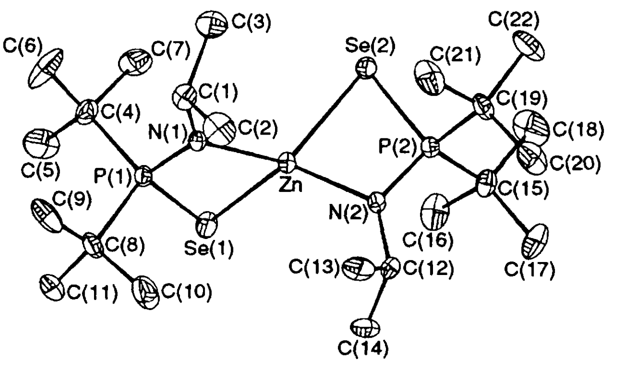


Fig. 1 Molecular structure of $[Zn\{Bu^t_2P(Se)NPr^i\}_2]$ **1a**, showing the atomic numbering scheme. Ellipsoids are drawn at 30% probability

N–Zn–Se angle 81.37°), leading to Se(1)–Zn–Se(2) and N(1)–Zn–N(2) angles of 120.00(3)° and 136.16(13)°, respectively. As a comparison with the structures of related complexes of Co^{II} and Ni^{II} (ref. 7*e*) shows, the geometric features are dictated primarily by steric factors (Table 5), and there is no discernible influence of changes in the d electron configuration from d^7 to d^{10}.

The Zn–Se distances in **1a** of (on average) 2.5375(9) Å are about 0.2 Å longer than Zn–Se bonds to terminal selenolato ligands in $[Zn(SeC_6H_2Bu^t_3\text{-}2,4,6)_2(OSC_4H_8)]$ [2.313(3) Å][10] and $[Zn(SeC_6H_2Bu^t_3\text{-}2,4,6)_2(CNBu^t)_2]$ [2.380(3) Å][11] but are comparable to the longer of the two bridging Zn–Se distances in $[Zn_2(SeC_6H_2Bu^t_3\text{-}2,4,6)_2(\mu\text{-}SeC_6H_2Bu^t_3\text{-}2,4,6)_2(OCHC_6H_4O\text{-}Me\text{-}4)_2]$ [2.552(4) Å].[12] By contrast, the Zn–N bonds in **1a** are relatively short, 1.981(3) Å. This distance is intermediate between typical terminal $Zn–N(SiMe_3)_2$ bonds (*ca.* 1.86 Å) and bonds

Table 2 Proton and ^{31}P NMR data[a]

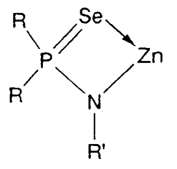
				C_6H_{11} = [CH^a(CH$^b{}_2$)$_2$(CH$^c{}_2$)$_2$CH$^d{}_2$]				
Complex	CMe$_3$	CH*Me*$_2$	C*H*Me$_2$	a	b	c	d	^{31}P
1a	1.55 (d, 36 H, $^3J_{PH}$ = 14.9)	1.36 (d, 12 H, $^4J_{PH}$ = 5.9)	3.60 (m, 2 H, $^3J_{PH}$ = 8.7)					99.86
1b	1.46 (d, 36 H, $^3J_{PH}$ = 14.8)			3.00 (m, 2 H)	2.03 (m, 8 H)	1.73 (m, 8 H)	1.10 (m, 4 H)	99.19
1c	1.50 (d, 36 H, $^3J_{PH}$ = 15.5)	1.23 (d, 12 H, $^4J_{PH}$ = 6.3)	3.35 (m, 2 H, $^3J_{PH}$ = 6.6)					93.39
1d	1.30 (d, 36 H, $^3J_{PH}$ = 15.8)			3.31 (m, 2 H)	2.02 (m, 8 H)	1.61 (m, 8 H)	1.11 (m, 4 H)	92.86
2a	1.52 (d, 36 H, $^3J_{PH}$ = 14.6)	1.27 (d, 12 H, $^4J_{PH}$ = 5.9)	3.68 (m, 2 H, $^3J_{PH}$ = 8.7)					103.37
2b	1.50 (d, 36 H, $^3J_{PH}$ = 14.8)			3.05 (m, 2 H)	2.05 (m, 8 H)	1.69 (m, 8 H)	1.31 (m, 4 H)	102.83 (J_{PSe} = 342)
2c	1.50 (d, 36 H, $^3J_{PH}$ = 14.8)	1.26 (d, 12 H, $^4J_{PH}$ = 6.6)	3.57 (m, 2 H, $^3J_{PH}$ = 6.6)					93.12
2d	1.46 (d, 36 H, $^3J_{PH}$ = 14.5)			3.08 (m, 2 H)	2.07 (m, 8 H)	1.69 (m, 8 H)	1.18 (m, 4 H)	92.59
3a[b]	1.47 (d, 18 H, $^3J_{PH}$ = 15.2)	1.21 (d, 6 H, $^4J_{PH}$ = 6.3)	3.45 (m, 1 H, $^3J_{PH}$ = 8.7)					106.87 (J_{PSe} = 478)
3b[b]	1.46 (d, 18 H, $^3J_{PH}$ = 15.2)			2.92 (m, 1 H)	2.08 (m, 4 H)	1.74 (m, 4 H)	1.16 (m, 2 H)	106.33 (J_{PSe} = 547)
3c[b]	1.50 (d, 18 H, $^3J_{PH}$ = 15.5)	1.22 (d, 6 H, $^4J_{PH}$ = 5.9)	3.37 (m, 1 H, $^3J_{PH}$ = 6.6)					93.26
3d[b]	1.50 (d, 18 H, $^3J_{PH}$ = 15.5)			2.84 (m, 1 H)	2.05 (m, 4 H)	1.73 (m, 4 H)	1.15 (m, 2 H)	92.85

[a] At 270 MHz, CDCl$_3$ solution, 25 °C; *J*/Hz. [b] SiMe$_3$ signal at δ 0.07–0.08 (s, 18 H).

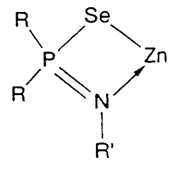
Table 3 Carbon-13 NMR data[a]

					C_6H_{11} = [CH^a(CH$^b{}_2$)$_2$(CH$^c{}_2$)$_2$CH$^d{}_2$]			
Compound	C*Me*$_3$	*C*Me$_3$	CH*Me*$_2$	*C*HMe$_2$	a	b	c	d
1a	29.5 (d, $^2J_{PC}$ = 2.4)	42.0 (d, $^1J_{PC}$ = 31.7)	28.5 (d, $^3J_{PC}$ = 2.4)	50.5 (d, $^2J_{PC}$ = 9.8)				
1b	29.5 (d, $^2J_{PC}$ = 2.4)	42.2 (d, $^1J_{PC}$ = 31.7)			59.1 (d, $^2J_{PC}$ = 9.7)	39.3 (s)	26.3 (s)	25.7 (s)
1c	30.1 (d, $^2J_{PC}$ = 2.4)	42.5 (d, $^1J_{PC}$ = 21.9)	28.9 (d, $^3J_{PC}$ = 6.1)	53.4 (d, $^2J_{PC}$ = 9.18)				
1d	28.1 (d, $^2J_{PC}$ = 2.5)	39.4 (d, $^1J_{PC}$ = 34.3)			55.7 (d, $^2J_{PC}$ = 12.2)	35.9 (d, $^3J_{PC}$ = 2.4)	25.5	25.1
2a	29.7 (d, $^2J_{PC}$ = 2.5)	42.6 (d, $^1J_{PC}$ = 32.9)	29.6 (d, $^3J_{PC}$ = 7.3)	50.3 (d, $^2J_{PC}$ = 10.9)				
2b	30.4 (d, $^2J_{PC}$ = 2.5)	43.8 (d, $^1J_{PC}$ = 20.8)			61.7 (d, $^2J_{PC}$ = 14.6)	40.2 (d, $^3J_{PC}$ = 6.1)	26.2	25.6
2c	30.3 (d, $^2J_{PC}$ = 2.4)	43.6 (d, $^1J_{PC}$ = 22.0)	29.3 (d, $^3J_{PC}$ = 8.5)	53.2 (d, $^2J_{PC}$ = 13.4)				
2d	29.7 (d, $^2J_{PC}$ = 2.4)	42.7 (d, $^1J_{PC}$ = 33.0)			58.7 (d, $^2J_{PC}$ = 12.2)	40.6 (d, $^3J_{PC}$ = 6.1)	26.1	25.6
3a[b]	29.5 (d, $^2J_{PC}$ = 2.4)	41.8 (d, $^1J_{PC}$ = 31.8)	29.0 (d, $^3J_{PC}$ = 6.1)	50.4 (d, $^3J_{PC}$ = 9.8)				
3b[b]	29.5 (d, $^2J_{PC}$ = 2.5)	42.1 (d, $^1J_{PC}$ = 31.9)			58.8 (d, $^2J_{PC}$ = 9.8)	40.0 (d, $^3J_{PC}$ = 4.9)	26.1	25.5
3c[b]	30.1 (d, $^2J_{PC}$ = 2.4)	42.5 (d, $^1J_{PC}$ = 21.9)	28.9 (d, $^3J_{PC}$ = 7.3)	53.4 (d, $^2J_{PC}$ = 12.2)				
3d[b]	30.2 (d, $^2J_{PC}$ = 2.4)	42.6 (d, $^1J_{PC}$ = 22.0)			61.8 (d, $^2J_{PC}$ = 12.2)	39.8 (d, $^3J_{PC}$ = 6.1)	26.1	25.4

[a] 67.8 MHz, CDCl$_3$ solution, 25 °C; *J*/Hz. [b] SiMe$_3$, δ 5.1 (s).



A



B

between zinc and typical N-donor ligands which range from 2.04 to 2.14 Å.[10] This bond length distribution suggests that the nitrogen in **1a** has essentially amido character whereas the selenium acts mainly as an n-donor rather than a selenolato ligand, *i.e.* structure **A** is more representative of the bonding in **1a** than **B**.

The nitrogen is trigonal planar (angle sum 359.9°), with rather wide exocyclic P–N–C and C–N–Zn angles of *ca.* 128°. The angles around the phosphorus atom are close to tetrahedral.

Conclusions.—The protolysis of zinc and cadmium amides with dialkylphosphino-selenoic and -telluroic amides provides a convenient salt-free route for the preparation of phosphinochalcogenoic amidato complexes in high yield. The reaction proceeds stepwise, and in the case of zinc mixed-ligand intermediates are isolable. The bis(phosphinochalcogenoic amidato) complexes are monomeric and sufficiently volatile to be of interest as promising single-source precursors for the gas-phase deposition of metal selenide and telluride films.[13] An important advantage is the thermal stability of the tellurium derivatives; most tellurolato complexes have in the past proved either thermally unstable or non-volatile.

Experimental

All reactions were carried out under nitrogen using standard vacuum-line techniques. Solvents were distilled under nitrogen from sodium–benzophenone (diethyl ether, thf, light petroleum (b.p. 40–60 °C), sodium (toluene) or calcium hydride (dichloromethane). NMR solvents were stored over 4 Å molecular sieves and degassed by freeze-thaw cycles. NMR spectra were recorded using a JEOL EX270 instrument. $Bu^t_2P(E)NHR$ (E = Se or Te, R = Pr^i or C_6H_{11})[6] and $[M\{N(SiMe_3)_2\}_2]$ (M = Zn or Cd)[14] were prepared as described previously. Melting points are uncorrected.

Preparations.—$[Zn\{Bu^t_2P(Se)NPr^i\}_2]$ **1a**. To a suspension of $Bu^t_2P(Se)NHPr^i$ (0.433 g, 1.53 mmol) in light petroleum (10 cm^3) was added $[Zn\{N(SiMe_3)_2\}_2]$ (0.295 g, 0.77 mmol) at 0 °C. The mixture was stirred at 0 °C for 5 min and then warmed to room temperature and stirred. After 45 min at room temperature, all the suspension had dissolved and a white precipitate had begun to form. After stirring for 3 h the solvent was removed under reduced pressure and the crude product recrystallised from toluene (5 cm^3) to give colourless crystals after cooling to − 16 °C. Yield 0.423 g (0.67 mmol, 88%), m.p. > 220 °C. Sublimes at 190 °C at 4.0 × 10^{-6} Torr. IR (Nujol mull, cm^{-1}): 491m, 468s, 429w, 407w, 226m, 202vw, 188s and 149s.

$[Zn\{Bu^t_2P(Se)N(C_6H_{11})\}_2]$ **1b**. This compound was prepared following the procedure for **1a** from $Bu^t_2P(Se)NH(C_6H_{11})$ (0.937 g, 2.91 mmol) and $[Zn\{N(SiMe_3)_2\}_2]$ (0.56 g, 1.45 mmol) as colourless crystals (0.927 g, 1.31 mmol, 90%), m.p. > 220 °C. Sublimes at 200 °C at 1.5 × 10^{-6} Torr. IR (Nujol mull, cm^{-1}) 487m, 465s, 444m, 408w, 381m, 200s, 172m and 143s.

Table 4 Selected bond lengths (Å) and angles (°) for $[Zn\{Bu^t_2P(Se)NPr^i\}_2]$ **1a**

Zn–N(2)	1.980(3)	Zn–N(1)	1.982(4)
Zn–Se(2)	2.5372(9)	Zn–Se(1)	2.5377(9)
Se(1)–P(1)	2.173(2)	Se(2)–P(2)	2.1766(13)
P(1)–N(1)	1.611(3)	P(1)–C(4)	1.875(4)
P(1)–C(8)	1.887(4)	P(2)–N(2)	1.614(3)
P(2)–C(19)	1.883(4)	P(2)–C(15)	1.884(5)
N(1)–C(1)	1.491(5)	N(2)–C(12)	1.494(5)
N(2)–Zn–N(1)	136.16(13)	N(2)–Zn–Se(2)	81.58(9)
N(1)–Zn–Se(2)	121.01(9)	N(2)–Zn–Se(1)	122.10(10)
N(1)–Zn–Se(1)	81.16(9)	Se(2)–Zn–Se(1)	120.00(3)
P(2)–Se(2)–Zn	72.92(4)	P(1)–Se(1)–Zn	73.22(4)
N(1)–P(1)–C(8)	112.5(2)	N(1)–P(1)–C(4)	113.1(2)
N(1)–P(1)–Se(1)	102.39(13)	C(4)–P(1)–C(8)	112.2(2)
C(8)–P(1)–Se(1)	107.9(2)	C(4)–P(1)–Se(1)	108.1(2)
N(2)–P(2)–Se(2)	102.69(13)	C(1)–N(1)–P(1)	128.5(3)
C(1)–N(1)–Zn	128.2(3)	P(1)–N(1)–Zn	103.2(2)
P(2)–N(2)–Zn	102.7(2)		

$[Zn\{Bu^t_2P(Te)NPr^i\}_2]$ **1c**. To a yellow solution of $Bu^t_2P(Te)NHPr^i$ (1.789 g, 5.41 mmol) in light petroleum (20 cm^3) $[Zn\{N(SiMe_3)_2\}_2]$ (1.05 g, 2.72 mmol) was added at −78 °C *via* syringe and the mixture stirred rapidly. A yellow precipitate formed immediately. The reaction mixture was warmed to room temperature and stirred for 2 h. The precipitate was filtered off and recrystallised from toluene to give yellow crystals (1.55 g, 2.14 mmol, 79%), m.p. 135 °C (decomp.).

$[Zn\{Bu^t_2P(Te)N(C_6H_{11})\}_2]$ **1d**. From $Bu^t_2P(Te)NH(C_6H_{11})$ (0.647 g, 1.74 mmol) and $[Zn\{N(SiMe_3)_2\}_2]$ (0.35 g, 0.91 mmol) as yellow crystals (0.483 g, 0.60 mmol, 69%), m.p. > 152 °C (decomp.). Sublimes at 115 °C at 2.7 × 10^{-6} Torr.

$[Cd\{Bu^t_2P(Se)NPr^i\}_2]$ **2a**. From $Bu^t_2P(Se)NHPr^i$ (0.421 g, 1.49 mmol) and $[Cd\{N(SiMe_3)_2\}_2]$ (0.323 g, 0.745 mmol); colourless crystals (0.458 g, 0.68 mmol, 91%), m.p. > 220 °C. Sublimes at 200 °C at 1.5 × 10^{-6} Torr. IR (Nujol mull, cm^{-1}): 489m, 464s, 415m, 376w, br, 223m, 211 (sh), 182s, 152m and 137m.

$[Cd\{Bu^t_2P(Se)N(C_6H_{11})\}_2]$ **2b**. From $Bu^t_2P(Se)NH(C_6H_{11})$ (0.478 g, 1.48 mmol) and $[Cd\{N(SiMe_3)_2\}_2]$ (0.32 g, 0.74 mmol); colourless crystals (0.492 g, 0.65 mmol, 88%), m.p. > 220 °C. Sublimes at 200 °C at 1.3 × 10^{-6} Torr. IR (Nujol mull, cm^{-1}) 484m, 462s, 445m, 408w, 377s, 199m, 184s, 144m and 129m.

$[Cd\{Bu^t_2P(Te)NPr^i\}_2]$ **2c**. To a yellow solution of $Bu^t_2P(Te)NHPr^i$ (1.533 g, 4.64 mmol) in light petroleum (20 cm^3) $[Cd\{N(SiMe_3)_2\}_2]$ (1.00 g, 2.31 mmol) was added *via* syringe at 0 °C and the reaction mixture stirred vigorously. A yellow precipitate formed instantaneously. The reaction mixture was warmed to room temperature and stirred for 2 h. The precipitate was filtered off and recrystallised from warm toluene to give yellow crystals (1.516 g, 1.96 mmol, 85%), m.p. 188 °C. Sublimes at 115 °C at 1.5 × 10^{-5} Torr. IR (Nujol mull, cm^{-1}): 487m, 462s, 413m, 370m (br), 215m, 160s and 118m.

$[Cd\{Bu^t_2P(Te)N(C_6H_{11})\}_2]$ **2d**. From $Bu^t_2P(Te)NH(C_6H_{11})$ (0.449 g, 1.21 mmol) and $[Cd\{N(SiMe_3)_2\}_2]$ (0.25 g, 0.58 mmol); yellow crystals (0.408 g, 0.48 mmol, 83%), m.p. 213–216 °C. Sublimes at 180 °C at 7.5 × 10^{-6} Torr. IR (Nujol mull, cm^{-1}): 479m, 460s, 443m, 431m, 377s, 246m, 179m, 157s and 117m.

$[Zn\{N(SiMe_3)_2\}\{Bu^t_2P(Se)NPr^i\}]$ **3a**. To a suspension of $Bu^t_2P(Se)NHPr^i$ (1.415 g, 5.01 mmol) in light petroleum (25 cm^3) was added at room temperature $[Zn\{N(SiMe_3)_2\}_2]$ (1.95 g, 5.05 mmol) *via* syringe. The mixture was stirred for 3 h and centrifuged. The supernatant liquid was concentrated and cooled at − 16 °C to give white crystals (1.651 g, 3.26 mmol, 65%), m.p. > 220 °C. Sublimes at 200 °C at 4.6 × 10^{-6} Torr.

$[Zn\{N(SiMe_3)_2\}\{Bu^t_2P(Se)N(C_6H_{11})\}]$ **3b**. From $Bu^t_2P(Se)NH(C_6H_{11})$ (1.4516 g, 4.52 mmol) and $[Zn\{N(SiMe_3)_2\}_2]$ (1.75 g, 4.53 mmol); colourless crystals (1.780 g, 3.26 mmol, 72%), m.p. > 220 °C. Sublimes at 200 °C at 3.2 × 10^{-6} Torr.

$[Zn\{N(SiMe_3)_2\}\{Bu^t_2P(Te)NPr^i\}]$ **3c**. To a yellow suspension of $Bu^t_2P(Te)NHPr^i$ (0.80 g, 2.42 mmol) in light petroleum (30 cm^3) was added at room temperature $[Zn\{N(SiMe_3)_2\}_2]$ (0.95 g, 2.46 mmol) *via* syringe. The reaction mixture was stirred for 3 h, after which the suspension had dissolved. The solvent was removed under reduced pressure and the yellow residue recrystallised from hot toluene (10 cm^3) to give yellow

Table 5 Comparison of geometric parameters of bis(phosphinochalcogenoic amidato) metal complexes

M	N(1)–M–N(2)	E(1)–M–E(2)	E(1)–M–N(1)	E(1)–M–N(2)	Ref.
Co (E = S)	138.0(1)	119.5(1)	81.0	120.0(1)	7*e*
Ni (E = S)	139.5(1)	121.2(1)	80.7(1)	120.1(1)	7*e*
Zn (E = Se)	136.16(13)	120.00(3)	81.16(9)	122.10(10)	This work

Table 6 Atomic coordinates (× 10^4) for **1a**

Atom	x	y	z
Zn	8 170(1)	8 867(1)	2 472(1)
Se(1)	7 279(1)	8 892(1)	3 779(1)
Se(2)	7 544(1)	8 148(1)	1 110(1)
P(1)	7 642(1)	10 628(1)	3 534(1)
P(2)	8 634(1)	7 093(1)	1 402(1)
N(1)	8 221(2)	10 505(3)	2 718(2)
N(2)	8 998(2)	7 655(3)	2 249(2)
C(1)	8 641(3)	11 412(4)	2 228(3)
C(2)	9 590(3)	11 205(5)	2 204(3)
C(3)	8 282(3)	11 463(5)	1 345(3)
C(4)	6 654(3)	11 467(4)	3 339(3)
C(5)	6 054(4)	11 477(7)	4 069(3)
C(6)	6 849(3)	12 678(5)	3 057(4)
C(7)	6 192(3)	10 877(5)	2 606(3)
C(8)	8 258(3)	11 159(4)	4 468(3)
C(9)	8 551(3)	12 387(5)	4 349(3)
C(10)	9 037(4)	10 390(6)	4 545(4)
C(11)	7 759(3)	11 050(5)	5 275(3)
C(12)	9 748(3)	7 284(4)	2 752(3)
C(13)	10 386(3)	8 232(5)	2 816(3)
C(14)	9 488(3)	6 914(5)	3 617(3)
C(15)	8 236(3)	5 612(4)	1 569(3)
C(16)	7 621(3)	5 694(5)	2 291(3)
C(17)	8 948(3)	4 786(4)	1 811(4)
C(18)	7 768(4)	5 148(5)	809(3)
C(19)	9 403(3)	7 198(4)	516(3)
C(20)	10 203(3)	6 504(5)	665(3)
C(21)	9 635(4)	8 466(5)	455(3)
C(22)	9 000(3)	6 840(6)	−320(3)

crystals (1.02 g, 1.84 mmol, 76%), m.p. 206–208 °C. Sublimes at 120 °C at 8.5 × 10^{-6} Torr. Cryoscopic molecular-weight determinations (benzene): Found 490. Calc. 555.7.

$[Zn\{N(SiMe_3)_2\}\{Bu^t{}_2P(Te)N(C_6H_{11})\}]$ **3d**. From $Bu^t{}_2P(Te)NH(C_6H_{11})$ (1.298 g, 3.50 mmol) and $[Zn\{N(SiMe_3)_2\}_2]$ (1.40 g, 3.63 mmol); yellow crystals (1.46 g, 2.45 mmol, 70%), m.p. > 220 °C. Sublimes at 200 °C at 3.4 × 10^{-6} Torr.

X-Ray Crystallography.—$[Zn\{Bu^t{}_2P(Se)NPr^i\}_2]$ **1a**: $C_{22}H_{50}N_2P_2Se_2Zn$, $M = 627.87$, monoclinic, space group $P2_1/a$, $a = 15.815(5)$, $b = 11.848(8)$, $c = 16.041(5)$ Å, $\beta = 90.56(2)°$, $U = 3006(2)$ Å^3, $Z = 4$, $D_c = 1.388$ g cm^{-3}, $F(000) = 1296$; absorption coefficient 3.357 mm^{-1}. Colourless crystal of dimensions 0.24 × 0.18 × 0.14 mm.

Data collection and refinement. The X-ray data were collected at 120 K using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo-Kα radiation [λ(Mo-Kα) = 0.710 69 Å], $2.14 \leqslant \theta \leqslant 25.05$, index range $-18 \leqslant h \leqslant 17$, $-12 \leqslant k \leqslant 12$, $-18 \leqslant l \leqslant 18$. 11708 Reflections collected of which 4442 were independent. $R_{int} = 0.0746$, with 278 parameters. The structure was solved by the Patterson method using SHELXS[15] and refined by full-matrix least-squares techniques using SHELX 80.[16] The F_o data were corrected for absorption using the DIFABS[17] procedure at the isotropic refinement stage. Calculations were made on a 486DX266 PC. Hydrogen atoms were allowed to ride on their parents [$d_{CH} = 0.96$ Å] in calculated positions, a common U_{iso} being refined for all. Goodness of fit on F^2 was 0.964. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0406$, $wR_2 = 0.0955$; final R indices for all data $R_1 = 0.0524$, $wR_2 = 0.0983$ $\{w = [\sigma^2(F_o)^2 + (0.0505P)^2]^{-1}$, where $P = [\max(F_o)^2 + 2(F_c)^2]/3\}$; $R_1 = \Sigma w(|F_o| - |F_c|)/\Sigma w|F_c|$, $wR_2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. The largest difference peak and hole were 0.808 and −0.496 e Å^{-3}. Atomic coordinates are given in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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