Synthesis of Selenophosphinic and Tellurophosphinic Amides and Amidato Complexes. Crystal Structures of $Bu^t_2P(Te)NH(C_6H_{11})$, $[Ti(\eta\text{-}C_5H_5)Cl_2\{Bu^t_2P(Se)NPr^i\}]$ and $[TiCl_2\{Bu^t_2P(Se)N(C_6H_{11})\}_2]\cdot C_7H_8$†

Manfred Bochmann,*,[a] Gabriel C. Bwembya,[a] Nicola Whilton,[a] Xuejing Song,[a]
Michael B. Hursthouse,[b] Simon J. Coles[b] and Alexander Karaulov[b]
[a] *School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK*
[b] *School of Chemistry and Applied Chemistry, University of Wales, Cardiff, PO Box 912, Cardiff CF1 3TB, UK*

The reaction of Bu^t_2PNHR' with selenium or tellurium affords the chalcogenophosphinic amides $Bu^t_2P(E)NHR'$ (E = Se or Te; R' = Pr^i or *cyclo*-C_6H_{11}). The compounds $[Bu^t_2P(E)NHCH_2]_2$ were prepared similarly. The crystal structure of $Bu^t_2P(Te)NH(C_6H_{11})$ was determined; it shows a short P–Te bond of 2.371(1) Å and a rather long P–N bond of 1.781(4) Å. The lithium salts $Li[Bu^t_2P(Se)NR']$ react with $[TiCl_3(cp)]$ (cp = η-C_5H_5) to give $[TiCl_2(cp)\{Bu^t_2P(Se)NR'\}]$. The reaction of $Li[Bu^t_2P(Se)NPr^i]$ with $[TiCl_4(thf)_2]$ (thf = tetrahydrofuran) affords $[TiCl_3\{Bu^t_2P(Se)NPr^i\}]$, while a similar reaction with $Li[Bu^t_2P(Se)N(C_6H_{11})]$ leads to the isolation of $[TiCl_2\{Bu^t_2P(Se)N(C_6H_{11})\}_2]$. The structures of $[TiCl_2(cp)\{Bu^t_2P(Se)NPr^i\}]$ and $[TiCl_2\{Bu^t_2P(Se)N(C_6H_{11})\}_2]\cdot C_7H_8$ have been determined by X-ray crystallography. The selenophosphinic amidato ligands are bidentate in all cases. The former complex adopts a distorted square-pyramidal geometry with apical cp, while the latter is octahedral with *cis*-Cl ligands and *trans* stereochemistry for the nitrogen donors.

Thiophosphinic amides of the general formula $R_2P(S)NHR'$ are accessible either from the reaction of the corresponding aminophosphine R_2PNHR' with sulfur, or from $R_2P(S)Cl$ and primary amines.[1] They are readily deprotonated, and numerous complexes are known which contain bidentate thiophosphinic amidato ligands, notably those of late transition metals, *e.g.* $[M\{R_2P(S)NR'\}_2]$ (M = Co^{II} or Ni^{II}).[2,3] To our knowledge examples for early transition metal complexes are restricted to compounds of trivalent metals, such as Ti^{III}, V^{III} and Cr^{III}.[3] By contrast, the reaction of $R_2P(S)N(SiMe_3)_2$ (R = Ph or Pr^i) with $TiCl_4$ gives complexes with Ti–N double bonds in which the sulfur atom is not co-ordinated.[4]

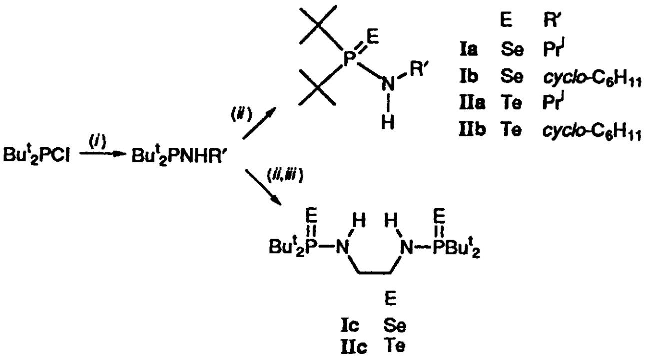
Whereas thiophosphinic amides have been studied extensively, there is only scant detail on the preparation of the analogous selenium and tellurium compounds[1c] and their metal complexes. In the course of our studies on the use of metal chalcogenolato complexes as single-source precursors for the gas-phase deposition of films of solid-state materials[5] we have become interested in the synthesis of complexes of ligands such as $[R_2P(E)NR']^-$, particularly where E = Se or Te. We report here the synthesis of a range of these ligands and of some complexes of Ti^{IV}, including their structural characterisation.

Results and Discussion

It is known from studies of complexes of divalent metals $[M\{R_2P(S)NR'\}_2]$ that the degree of association depends on the steric requirements of R, such that complexes with R = Me tend to form dimers, while with R = Pr^i or Bu^t the compounds are monomeric in solution and in the solid state.[2a,b] Judging that higher degrees of association might be undesirable for potential applications in materials synthesis, we synthesized a series of *tert*-butyl-substituted compounds $Bu^t_2P(E)NHR'$ (E = Se or Te) as shown in Scheme 1.

The ligands are readily prepared from Bu^t_2PCl in a one-pot reaction. The addition of Bu^t_2PCl to lithium amides LiNHR' leads smoothly to the formation of the aminophosphines Bu^t_2PNHR' (R = Pr^i or *cyclo*-C_6H_{11}). Refluxing the reaction mixture in toluene with finely powdered selenium or tellurium gives the chalcogenophosphinic amides $Bu^t_2P(E)NHR'$ (E = Se, R' = Pr^i **Ia** or *cyclo*-C_6H_{11} **Ib**; E = Te, R' = Pr^i **IIa** or *cyclo*-C_6H_{11} **IIb**) as white (E = Se) to yellow (E = Te) crystalline solids in good yields. The potentially tetradentate ligands $Bu^t_2P(E)NHCH_2CH_2P(E)Bu^t_2$ (E = Se **Ic** or Te **IIc**) were prepared in an analogous manner. The spectroscopic and analytical data for the new compounds are given in Tables 1 and 2, respectively.

The reaction of **I** or **II** with 1 equivalent of $LiBu^n$ in tetrahydrofuran (thf) at 0 °C affords yellow solutions of $Li[Bu^t_2P(E)NR']$ (E = Se **1** or Te **2**). Treatment of **1a** and **1b** with $[TiCl_3(cp)]$ (cp = η-C_5H_5) in thf gives the complexes



Scheme 1 (*i*) LiNHR', toluene, reflux, 1 h, R' = Pr^i or *cyclo*-C_6H_{11}; (*ii*) E_n (E = Se or Te), Et_2O, reflux 2 h; (*iii*) R' = C_2H_4

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Spectroscopic data for chalcogenophosphinic amides and amidato complexes (*J*/Hz)

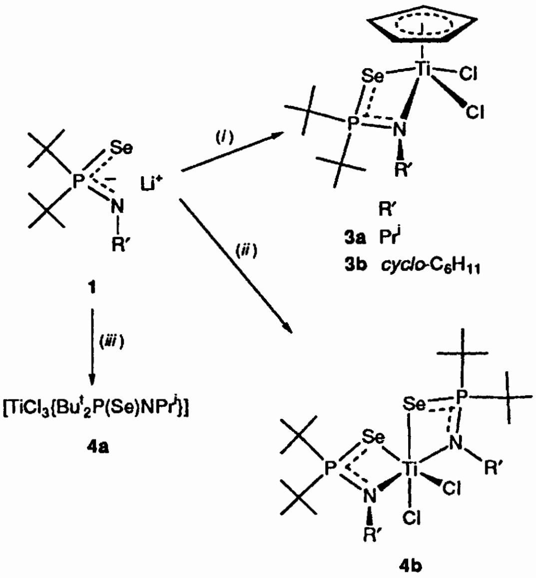
Compound	^1H NMR (δ)	^{13}C NMR (δ)	^{31}P NMR (δ)
Ia $Bu^t_2P(Se)NHPr^i$	1.22 (d, 6 H, $CHMe_2$, $^3J_{PH}$ 6.3) 1.35 (d, 18 H, Bu^t, $^3J_{CH}$ 15.5) 3.82 (m, 1 H, $CHMe_2$)	25.8 (d, $CHMe_2$, $^3J_{PC}$ 3.6) 27.6 (d, CMe_3, $^2J_{PC}$ 2.5) 39.6 (d, CMe_3, $^1J_{PC}$ 47.6) 45.8 (s, $CHMe_2$)	97.6 ($^1J_{PSe}$ 400)
Ib $Bu^t_2P(Se)NH(C_6H_{11})$	1.10 (m, 4 H, C_6H_{11}) 1.29 (d, 18 H, Bu^t, $^3J_{CH}$ 15.5) 1.62 (m, 4 H, C_6H_{11}) 1.99 (m, 2 H, C_6H_{11}) 3.88 (m, 1 H, C_6H_{11})	25.2 (s, 2 C, C_6H_{11}) 25.6 (s, 1 C, C_6H_{11}) 27.6 (s, CMe_3) 36.4 (d, 2 C, C_6H_{11}, $^3J_{PC}$ 3.7) 39.6 (d, CMe_3, $^1J_{PC}$ 46.0) 52.2 (d, CHC_5H_{10}, $^3J_{PC}$ 2.4)	97.0 ($^1J_{PSe}$ 364)
Ic $[Bu^t_2P(Se)NHCH_2]_2$	1.30 (d, 18 H, Bu^t, $^3J_{CH}$ 15.5) 2.52 (m, 1 H, NH) 3.27 (m, 2 H, $-CH_2-$)	27.8 (s, CMe_3) 40.1 (d, CMe_3, $^1J_{PC}$ 45.2) 46.0 (d, $^3J_{PC}$ 4.9)	101.5 ($^1J_{PSe}$ 356)
IIa $Bu^t_2P(Te)NHPr^i$	1.17 (d, 6 H, $CHMe_2$, $^3J_{PH}$ 6.6) 1.31 (d, 18 H, Bu^t, $^3J_{CH}$ 16.0) 3.71 (m, 1 H, $CHMe_2$)	25.2 (d, $CHMe_2$, $^3J_{PC}$ 3.6) 28.0 (d, CMe_3, $^2J_{PC}$ 2.5) 39.4 (d, CMe_3, $^1J_{PC}$ 47.6) 49.4 (s, $CHMe_2$)	79.3
IIb $Bu^t_2P(Te)NH(C_6H_{11})$	1.12 (m, 4 H, C_6H_{11}) 1.31 (d, 18 H, Bu^t, $^3J_{CH}$ 15.8) 1.61 (m, 4 H, C_6H_{11}) 2.04 (m, 2 H, C_6H_{11}) 3.32 (m, 1 H, C_6H_{11})	25.1 (s, 2 C, C_6H_{11}) 25.5 (s, 1 C, C_6H_{11}) 28.2 (d, CMe_3, $^2J_{PC}$ 2.4) 35.8 (d, 2 C, C_6H_{11}, $^3J_{PC}$ 2.4) 39.5 (d, CMe_3, $^1J_{PC}$ 34.2) 55.7 (br, 1 C, CHC_5H_{10})	79.0
IIc $[Bu^t_2P(Te)NHCH_2]_2$	1.40 (d, 18 H, Bu^t, $^3J_{CH}$ 15.8) 2.29 (m, 1 H, NH) 3.34 (m, 2 H, $-CH_2-$)		77.3
3a $[TiCl_2(cp)\{Bu^t_2P(Se)NPr^i\}]$	1.50 (d, 6 H, $CHMe_2$, $^3J_{PH}$ 6.0) 1.52 (d, 18 H, Bu^t, $^3J_{CH}$ 16) 4.05 (m, 1 H, $CHMe_2$) 6.81 (s, 5 H, cp)	27.0 (s, $CHMe_2$) 29.1 (d, CMe_3, $^2J_{PC}$ 3.0) 42.8 (d, CMe_3, $^1J_{PC}$ 25) 57.4 (d, $CHMe_2$, $^2J_{PC}$ 5) 121.8 (s, cp)	78.6
3b $[TiCl_2(cp)\{Bu^t_2P(Se)N(C_6H_{11})\}]$	1.15 (m, 4 H, C_6H_{11}) 1.52 (d, 18 H, Bu^t, $^3J_{CH}$ 16) 1.82 (m, 4 H, C_6H_{11}) 2.33 (m, 2 H, C_6H_{11}) 3.50 (m, 1 H, C_6H_{11}) 6.81 (s, 5 H, cp)	25.2 (s, 1 C, C_6H_{11}) 26.9 (s, 2 C, C_6H_{11}) 29.2 (d, CMe_3, $^2J_{PC}$ 3.0) 33.7 (s, br, 2 C, C_6H_{11}) 42.9 (d, CMe_3, $^1J_{PC}$ 26) 68.0 (d, 1 C, CHC_5H_{10}, $^3J_{PC}$ 4.9) 121.7 (s, cp)	79.5
4a $[TiCl_3\{Bu^t_2P(Se)NPr^i\}]$	1.54 (d, 18 H, Bu^t, $^3J_{CH}$ 17) 1.80 (d, 6 H, $CHMe_2$, $^3J_{PH}$ 7.0) 4.20 (m, 1 H, $CHMe_2$)	24.5 (s, $CHMe_2$) 28.8 (d, CMe_3, $^2J_{PC}$ 3.0) 43.0 (d, CMe_3, $^1J_{PC}$ 23) 58.2 (d, $CHMe_2$, $^2J_{PC}$ 6)	81.8 ($^1J_{PSe}$ 229.5)
4b $[TiCl_2\{Bu^t_2P(Se)N(C_6H_{11})\}_2]$	1.12 (m, 4 H, C_6H_{11}) 1.31 (d, 18 H, Bu^t, $^3J_{CH}$ 15.8) 1.61 (m, 4 H, C_6H_{11}) 2.04 (m, 2 H, C_6H_{11}) 3.32 (m, 1 H, C_6H_{11})	25.1 (s, 1 C, C_6H_{11}) 26.6 (s, 1 C, C_6H_{11}) 27.2 (s, 1 C, C_6H_{11}) 29.8 (s, CMe_3) 30.6 (s, CMe_3) 34.0 (d, 1 C, C_6H_{11}, $^3J_{PC}$ 4.0) 37.2 (d, 1 C, C_6H_{11}, $^3J_{PC}$ 4.0) 68.8 (d, 1 C, CHC_5H_{10}, $^3J_{PC}$ 4.9)	81.4

Table 2 Analytical and physical data

				Elemental analysis * (%)			
Compound	Colour	Yield (%)	M.p./°C	C	H	N	Other
Ia	White	67	106–108	47.1 (46.8)	9.2 (9.2)	4.7 (5.0)	
Ib	White	59	128	52.0 (52.2)	9.5 (9.4)	4.3 (4.35)	
Ic	White	26.5	208	42.7 (42.5)	8.1 (8.7)	5.3 (5.5)	
IIa	Yellow	71	109–113 (decomp.)	40.3 (39.9)	7.6 (7.9)	4.0 (4.2)	
IIb	Yellow	69	122 (decomp.)	45.6 (45.3)	8.2 (8.15)	3.6 (3.8)	
IIc	Yellow	45	74 (decomp.)	36.2 (35.8)	7.0 (7.0)	4.65 (4.6)	
3a	Red	49		41.6 (41.3)	6.6 (6.5)	2.8 (3.0)	Cl 14.9 (15.3)
3b	Red	45		45.5 (45.2)	6.6 (6.8)	2.7 (2.8)	Cl 14.1 (14.0)
4a	Orange	30		30.7 (30.3)	5.6 (5.7)	3.1 (3.2)	Cl 23.0 (24.4)
4b·C_7H_8	Red	52		48.4 (49.2)	7.3 (7.8)	3.0 (3.3)	Cl 8.5 (8.3)

* Calculated values in parentheses.

$[TiCl_2(cp)\{Bu^t_2P(Se)NR'\}]$ (R′ = Pr^i **3a** or *cyclo*-C_6H_{11} **3b**) respectively as red crystalline solids (Scheme 2). Similarly, the reaction of 2 equivalents of **Ib** with $[TiCl_4(thf)_2]$ in thf gives $[TiCl_2\{Bu^t_2P(Se)N(C_6H_{11})\}_2]$ **4b** as a dark red solid which is recrystallised from toluene. The compound retains one molecule of toluene of crystallisation. The analogous reaction



Scheme 2 (*i*) [TiCl$_3$(cp)], thf; (*ii*) [TiCl$_4$(thf)$_2$], thf, R' = *cyclo*-C$_6$H$_{11}$; (*iii*) [TiCl$_4$(thf)$_2$], thf, R' = Pr^i

of [TiCl$_4$(thf)$_2$] with **1a** gave a mixture of red and orange crystals which proved difficult to separate. Analyses of the latter are consistent with the formulation as the 1 : 1 complex, [TiCl$_3${Bu$^t_2$P(Se)NPr^i}] **4a**. The compound is monomeric in benzene.

The reaction of [TiCl$_3$(cp)] with **2a** (R' = Pr^i) at room temperature in thf gives a purple solution. During the course of the reaction the ^{31}P NMR signal of **2a** (δ 69.8) is replaced by a new signal at δ 75.5 which is comparable to the ^{31}P resonance of the selenium complex **3a** at δ 78.6 and indicates the formation of the desired titanium complex. However, slow reduction to titanium(III) took place in solution, and no tractable product could be isolated. The reaction between [TiCl$_3$(cp)] and **2b** (R' = *cyclo*-C$_6$H$_{11}$) proceeds similarly.

Structural Studies.—Since to our knowledge tellurophosphinic acids and their derivatives have not yet been structurally characterised, the crystal structure of compound **IIb** was determined as a representative example. The molecular geometry is shown in Fig. 1. Selected bond lengths and angles are collected in Table 3. The compound has a P–Te bond length of 2.371(1) Å, approximately comparable to the shorter of the Te–P distances in the (disordered) structure of Ph$_3$P=Te $\cdots$ PPh$_3$ (2.27–2.42 Å)[6] but significantly shorter than in the phosphine telluride complex [W(CO)$_5$(Te=PBu$^t_3$)] [2.439(2) Å].[7] The P–N bond distance of 1.781(4) Å is significantly longer than that found in the related compound Me$_2$P(S)NH(SiMe$_3$) [1.634(6) Å],[8] possibly as the result of increased steric congestion around P in the case of **IIb**. The conformations of the P–NH–R' moieties are very similar in both compounds, with the NH hydrogen positioned approximately *trans* to the P=E vector.

Crystals of complex **3a** suitable for X-ray diffraction were obtained by recrystallisation from dichloromethane–light petroleum. The molecular structure is shown in Fig. 2, and selected bond lengths and angles are collected in Table 4. The complex has a distorted square-pyramidal geometry, with the cp ligand at the apex. The structure confirms the bidentate nature of the Se–N ligand, with a Se–Ti–N angle of 75.21(13)°. The Ti–N distance of 2.068(5) Å is rather long compared with Ti–N distances in amido complexes such as [{TiCl(μ-Cl)$_2$(NEt$_2$)}] [1.852(4) Å],[9] [Ti{(NSiMe$_3$)$_2$C$_2$H$_4$}$_2$] [1.903(1) Å][10] and [TiCl{N(SiMe$_3$)$_2$}$_3$] [1.940(10) Å].[11] The Ti–Se bond length is 2.675(2) Å. The Ti–Cl distances of 2.353(2) and 2.322(2) Å in **3a**, formally a 14-electron complex, compare well with those in the electonically more saturated compound [TiCl$_2$(cp)$_2$], 2.364 Å on average, although the Cl–Ti–Cl angle in **3a** is rather more acute (86.63 *vs.* 94.5°).[12]

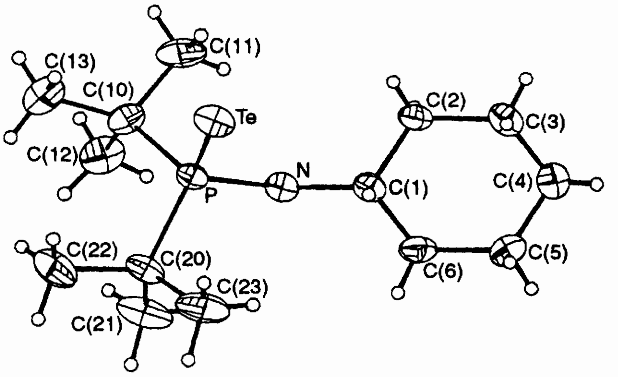


Fig. 1 Molecular structure of Bu$^t_2$P(Te)NH(C$_6$H$_{11}$) **IIb**, showing the atomic numbering scheme. Ellipsoids are drawn at 30% probability

Table 3 Selected bond lengths (Å) and angles (°) for Bu$^t_2$P(Te)-NH(C$_6$H$_{11}$) **IIb**

Te–P	2.371(1)	P–C(10)	1.845(5)
P–N	1.781(4)	P–C(20)	1.844(4)
N–C(1)	1.598(5)		
N–P–C(20)	108.6(2)	C(10)–P–C(20)	105.2(2)
N–P–Te	108.58(13)	C(10)–P–Te	110.26(14)
P–N–C(1)	134.0(3)	C(2)–C(1)–N	117.3(2)

Table 4 Selected bond lengths (Å) and angles (°) for [TiCl$_2$(cp){Bu$^t_2$P-(Se)NPr^i}] **3a**

Ti–N	2.068(5)	Ti–Cl(1)	2.353(2)
Ti–Se	2.675(2)	Ti–Cl(2)	2.322(2)
Ti–C(12)	2.382(7)	Se–P	2.153(2)
N–P	1.665(5)	P–C(1)	1.868(7)
N–C(9)	1.492(7)		
N–Ti–Se	75.21(13)	Cl(1)–Ti–Cl(2)	86.63(7)
Cl(1)–Ti–N	129.6(2)	Cl(2)–Ti–N	68.68(14)
Cl(1)–Ti–Se	80.04(6)	Cl(2)–Ti–Se	144.24(7)
C(9)–N–Ti	134.1(4)	N–P(1)–Se	99.6(2)

The structure of complex **4b**·C$_7$H$_8$ is shown in Fig. 3, bond lengths and angles are given in Table 5. The complex has distorted octahedral geometry, with the two chloride ligands in *cis* position. The Ti–N bond lengths of on average 2.076 Å are somewhat longer than in **3a**, while the Ti–Se distances are shorter, with an average of 2.648 Å. The two nitrogen atoms are *trans* to each other, although the N(1)–Ti–N(2) arrangement deviates significantly from linearity, with an angle of 159.56(12)°. The Se–Ti–Cl angles are less distorted, with values close to 170°. The N–Ti–Se 'bite' angles of *ca.* 75° are essentially identical to that in **3a**. The cyclohexyl substituents adopt the chair conformation.

Experimental

General Procedures.—All reactions were carried out under argon 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). The NMR solvents were stored over 4 Å molecular sieves and degassed by freeze-thaw cycles. The NMR spectra were recorded using JEOL EX90Q and EX270 instruments. Both Bu$^t_2$PCl[1a] and [TiCl$_3$(cp)][13] were prepared as described previously.[4] Melting points are uncorrected.

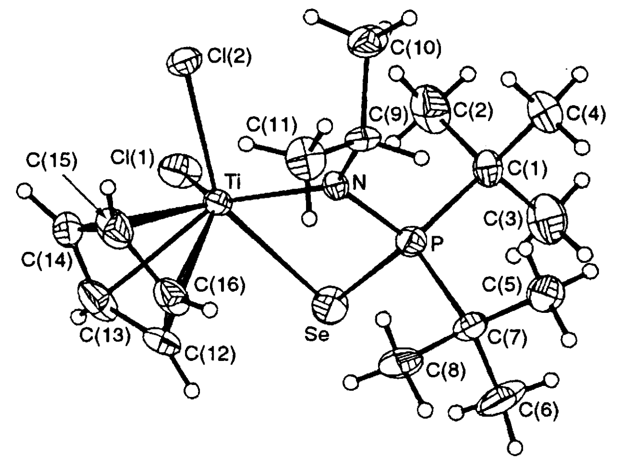


Fig. 2 Molecular structure of $[TiCl_2(cp)\{Bu^t{}_2P(Se)NPr^i\}]$ **3a**

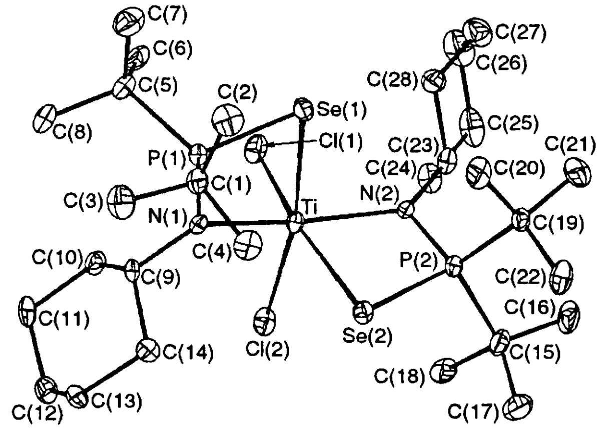


Fig. 3 Molecular structure of $[TiCl_2\{Bu^t{}_2P(Se)N(C_6H_{11})\}_2]\cdot C_7H_8$ **4b**$\cdot C_7H_8$

Table 5 Selected bond lengths (Å) and angles (°) for $[TiCl_2\{Bu^t{}_2P(Se)N(C_6H_{11})\}_2]\cdot C_7H_8$ **4b**$\cdot C_7H_8$

Ti–N(1)	2.078(3)	Ti–N(2)	2.073(3)
Ti–Cl(1)	2.3231(12)	Ti–Cl(2)	2.3292(13)
Ti–Se(1)	2.6592(12)	Ti–Se(2)	2.6379(8)
Se(1)–P(1)	2.1602(12)	Se(2)–P(2)	2.1665(13)
N(1)–P(1)	1.664(3)	P(1)–C(5)	1.885(4)
P(1)–C(1)	1.894(4)	N(2)–P(2)	1.649(3)
N(1)–C(9)	1.492(5)	N(2)–C(23)	1.496(5)
N(1)–Ti–N(2)	159.56(12)	N(2)–Ti–Cl(1)	94.67(9)
Cl(1)–Ti–N(1)	98.28(9)	Cl(2)–Ti–N(2)	101.54(10)
Cl(2)–Ti–N(1)	94.67(10)	Cl(1)–Ti–Cl(2)	88.02(4)
N(2)–Ti–Se(2)	75.24(9)	N(1)–Ti–Se(2)	93.14(9)
Cl(1)–Ti–Se(2)	168.17(4)	Cl(2)–Ti–Se(2)	88.01(4)
N(2)–Ti–Se(1)	89.27(9)	N(1)–Ti–Se(1)	74.82(9)
Cl(1)–Ti–Se(1)	90.90(4)	Cl(2)–Ti–Se(2)	169.18(4)
Se(1)–Ti–Se(2)	95.06(3)	P(1)–Se(1)–Ti	77.57(4)
P(1)–N(1)–Ti	108.8(2)	N(1)–P(1)–C(1)	113.7(2)
C(9)–N(1)–Ti	131.6(2)	N(1)–P(1)–Se(1)	98.82(12)
C(1)–P(1)–C(5)	111.7(2)	C(1)–P(1)–Se(1)	109.09(13)

Preparation of Chalcogenophosphinic Amides.—The preparative procedures are similar in all cases and exemplified below for $Bu^t{}_2P(Se)NHPr^i$ **Ia**.

$Bu^t{}_2P(Se)NHPr^i$ **Ia**. To 13.5 cm^3 of a 2.5 mol dm^{-3} solution of *n*-butyllithium in hexanes (33.0 mmol) was added dropwise at 0 °C Pr^iNH_2 (2.0 g, 33.9 mmol) in diethyl ether (100 cm^3). The mixture was warmed to room temperature and stirred for 1 h before the solvent was removed *in vacuo*. The resulting $LiNHPr^i$ was suspended in toluene (100 cm^3), and $Bu^t{}_2PCl$ (6 g, 33.0 mmol) was added. The mixture was heated to reflux for 1 h and filtered. To the filtrate was added at room temperature 2.6 g of selenium powder (33.0 g-atom), followed by a 2 h reflux and filtration. The filtrate was concentrated to give $Bu^t{}_2P(Se)NHPr^i$ **Ia** as a white crystalline solid on cooling (6.2 g, 22.1 mmol, 67%).

$Bu^t{}_2P(Te)NHPr^i$ **IIa**. This compound was prepared in an analogous manner to **Ia**. The reaction with tellurium powder requires 3 h reflux.

Preparation of $[TiCl_2(cp)\{Bu^t{}_2P(Se)NPr^i\}]$ **3a**.—To a solution of $Bu^t{}_2P(Se)NHPr^i$ (1.13 g, 4.0 mmol) in thf (30 cm^3) was added at 0 °C 1.6 cm^3 of a 2.5 mol dm^{-3} solution of $LiBu^n$ in hexanes (4.0 mmol) to give a yellow solution. This solution was added to $[TiCl_3(cp)]$ (0.8 g, 4.0 mmol) in thf (30 cm^3). The mixture was stirred for 3 h and the solvent removed *in vacuo*. The residue was extracted with toluene (30 cm^3) and centrifuged to remove LiCl. The supernatant was concentrated and cooled to give red crystals of **3a** (0.9 g, 1.94 mmol, 49%). Crystals suitable for X-ray crystallography were grown from dichloromethane–light petroleum.

Preparation of $[TiCl_2(cp)\{Bu^t{}_2P(Se)N(C_6H_{11})\}]$ **3b**.—The same preparative method as described for **3a** was used to give **3b** as red crystals (45%).

Preparation of $[TiCl_3\{Bu^t{}_2P(Se)NPr^i\}]$ **4a**.—To a thf solution of $Li[Bu^t{}_2P(Se)NPr^i]$ **Ia** prepared from $Bu^t{}_2P(Se)NHPr^i$ (1.4 g, 5.0 mmol) and $LiBu^n$ as described above, was added $[TiCl_4(thf)_2]$ (1.68 g, 5.0 mmol). The mixture was stirred for 3 h and concentrated to give a mixture of red and orange crystals. These partially dissolved in toluene from which **4a** was obtained as fine orange needles in 30% yield. The complex was sufficiently soluble for molecular weight determinations in benzene (calculated for monomer: 435.4; found 405).

Preparation of $[TiCl_2\{Bu^t{}_2P(Se)N(C_6H_{11})\}_2]$ **4b**.—To a mixture of $LiBu^n$ in hexanes (2.5 mol dm^{-3}, 1.9 cm^3, 4.7 mmol) and $Bu^t{}_2P(Se)NH(C_6H_{11})$ (1.5 g, 4.7 mmol) in thf (30 cm^3) was added $[TiCl_4(thf)_2]$ (1.6 g, 4.7 mmol). A dark red solution resulted which was stirred at room temperature for 3 h. Concentration yielded deep red crystals which were recrystallised from toluene. In spite of the stoichiometry used, the isolated product was the dihalide **4b**$\cdot C_7H_8$, with one molecule of toluene of crystallisation.

X-Ray Crystallography.—$Bu^t{}_2P(Te)NH(C_6H_{11})$ **IIb**, $C_{14}H_{30}NPTe$, $M = 370.96$, monoclinic, $a = 9.1573(14)$, $b = 11.8809(4)$, $c = 16.918(2)$ Å, $\beta = 95.49(1)°$, $U = 1832.2(3)$ Å^3, $Z = 4$, space group $P2_1/c$, $D_c = 1.345$ g cm^{-3}, $F(000) = 752$, $\mu = 1.696$ mm^{-1}. Colourless crystals of dimensions 0.1 × 0.1 × 0.06 mm.

$[TiCl_2(cp)\{Bu^t{}_2P(Se)NPr^i\}]$ **3a**, $C_{16}H_{30}Cl_2NPSeTi$, $M = 465.12$, orthorhombic, $a = 8.813(7)$, $b = 15.0422(5)$, $c = 31.232(10)$ Å, $U = 4140(3)$ Å^3, $Z = 8$, space group $Pcab$, $D_c = 1.492$ g cm^{-3}, $F(000) = 1904$, $\mu = 2.426$ mm^{-1}. Red crystals of dimensions 0.1 × 0.2 × 0.25 mm.

$[TiCl_2\{Bu^t{}_2P(Se)N(C_6H_{11})\}_2]\cdot C_7H_8$ **4b**$\cdot C_7H_8$, $C_{35}H_{66}Cl_2N_2P_2Se_2Ti$, $M = 853.56$, orthorhombic, $a = 13.233(7)$, $b = 17.2161(10)$, $c = 35.163(11)$ Å, $U = 8011(5)$ Å^3, $Z = 8$, space group $Pbca$, $D_c = 1.415$ g cm^{-3}, $F(000) = 3552$, $\mu = 2.271$ mm^{-1}. Red crystals of dimensions 0.2 × 0.1 × 0.07 mm.

Data collection and refinement. All structures were determined using an Enraf-Nonius FAST TV area detector diffractometer and graphite-monochromated Mo-Kα radiation [λ(Mo-Kα) = 0.710 69 Å]. The structures were solved by the Patterson method using SHELX-S[14] and refined by full-matrix least squares techniques using SHELX 80.[15] The F_o data were corrected for absorption using the DIFABS[16] procedure at the isotropic refinement stage. Calculations were made on a

Table 6 Atomic coordinates (× 10^4) for compound **IIb**

Atom	*x*	*y*	*z*
Te	2116(1)	952(1)	7415(1)
P	2008(1)	−974(1)	7760(1)
N	512(4)	−1608(3)	7172(2)
C(1)	−432(4)	−1266(3)	6364(2)
C(2)	−1932(5)	−765(3)	6428(2)
C(3)	−2915(7)	−446(5)	5581(4)
C(4)	−3191(6)	−1403(5)	4994(4)
C(5)	−1720(6)	−1912(5)	4935(3)
C(6)	−715(6)	−2231(4)	5772(3)
C(10)	1789(6)	−1124(4)	8828(3)
C(11)	200(6)	−656(5)	8803(4)
C(12)	1868(8)	−2355(4)	9119(3)
C(13)	2968(7)	−433([illegible])	9448(3)
C(20)	3698(5)	−1754(4)	7605(3)
C(21)	3530(8)	−3032(4)	7670(5)
C(22)	5164(6)	−1384(6)	8196(5)
C(23)	3767(8)	−1481(5)	6729(4)

Table 7 Atomic coordinates (× 10^4) for complex **3a**

Atom	*x*	*y*	*z*
Ti	1813(1)	1161(1)	859(1)
Se	1873(1)	2064(1)	1597(1)
Cl(1)	−346(2)	560(1)	1195(1)
Cl(2)	2149(2)	−231(1)	552(1)
N	4059(5)	1130(3)	1050(2)
P	4175(2)	1605(1)	1530(1)
C(1)	4565(7)	772(5)	1960(2)
C(2)	3324(8)	42(5)	1915(2)
C(3)	4454(8)	1192(6)	2396(2)
C(4)	6159(7)	315(5)	1926(2)
C(5)	5483(7)	2604(4)	1563(2)
C(6)	4949(9)	3235(5)	1914(3)
C(7)	7162(7)	2387(5)	1630(3)
C(8)	5333(9)	3084(4)	1123(3)
C(9)	5490(7)	802(4)	849(2)
C(10)	5646(7)	−220(4)	851(2)
C(11)	5693(7)	1138(5)	399(2)
C(12)	1206(10)	2623(5)	622(3)
C(13)	−80(8)	2097(6)	542(3)
C(14)	320(9)	1468(5)	238(3)
C(15)	1829(9)	1605(5)	139(2)
C(16)	2360(8)	2310(5)	377(3)

Table 8 Atomic coordinates (× 10^4) for compound **4b**·C_7H_8

Atom	*x*	*y*	*z*
Ti	−440(1)	229(1)	3556(1)
Se(1)	1094(1)	843(1)	3942(1)
Se(2)	−825(1)	1495(1)	3160(1)
Cl(1)	−441(1)	−854(1)	3950(1)
Cl(2)	−1547(1)	−435(1)	3157(1)
P(1)	1844(1)	313(1)	3462(1)
P(2)	−1761(1)	1653(1)	3659(1)
N(1)	840(2)	−36(2)	3239(1)
N(2)	−1435(2)	860(2)	3891(1)
C(1)	2538(3)	1090(2)	3184(1)
C(2)	3149(3)	1611(2)	3453(1)
C(3)	3242(3)	762(2)	2878(1)
C(4)	1748(3)	1602(2)	2996(1)
C(5)	2729(3)	−469(2)	3636(1)
C(6)	2152(3)	−982(2)	3914(1)
C(7)	3628(3)	−95(3)	3852(1)
C(8)	3156(3)	−989(2)	3317(1)
C(9)	982(3)	−530(2)	2895(1)
C(10)	657(3)	−1368(2)	2968(1)
C(11)	791(3)	−1872(2)	2613(1)
C(12)	222(3)	−1532(2)	2280(1)
C(13)	607(3)	−718(2)	2197(1)
C(14)	459(3)	−189(2)	2544(1)
C(15)	−3132(3)	1672(2)	3505(1)
C(16)	−3855(3)	1865(3)	3832(1)
C(17)	−3288(3)	2258(3)	3177(1)
C(18)	−3380(3)	867(2)	3343(1)
C(19)	−1416(3)	2580(2)	3919(1)
C(20)	−274(3)	2603(2)	3954(1)
C(21)	−1865(3)	2652(2)	4318(1)
C(22)	−1747(3)	3282(2)	3678(1)
C(23)	−1858(3)	719(2)	4280(1)
C(24)	−2557(3)	4(2)	4292(1)
C(25)	−2969(3)	−120(2)	4692(1)
C(26)	−2142(4)	−167(3)	4990(1)
C(27)	−1482(4)	548(3)	4977(1)
C(28)	−1027(3)	666(2)	4583(1)
C(50)	−4551(2)	1529(2)	5011(1)
C(51)	−5342(3)	1276(1)	4782(1)
C(52)	−5834(2)	1797(2)	4543(1)
C(53)	−5537(2)	2571(2)	4534(1)
C(54)	−4747(2)	2824(1)	4763(1)
C(55)	−4254(2)	2303(2)	5002(1)
C(56)	−3380(4)	2570(3)	5239(2)

486DX266 PC. Hydrogen atoms were allowed to ride on their parents (r_{CH} = 0.96 Å) in calculated positions, a common U_{iso} being refined for all. Atomic coordinates are given in Tables 6–8.

IIb. Data were collected at 150 K. θ Range 2.1 ⩽ θ ⩽ 26.3°; index range $-9 \leqslant h \leqslant 10$; $-9 \leqslant k \leqslant 12$; $-19 \leqslant 1 \leqslant 18$. 6180 Reflections collected of which 2650 were independent, R_{int} = 0.0513, with 194 parameters. Maximum and minimum DIFABS correction factors were 1.12 and 0.823, respectively. Goodness-of-fit on F^2 was 0.619. Final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.0341, wR_2 = 0.0835; final *R* indices for all data: R_1 = 0.0414, wR_2 = 0.0894 [$w = 1/\sigma^2(F_o)^2$]. The largest difference peak and hole were 0.517 and −0.491 e Å^{-3}.

3a. Data were collected at room temperature. θ Range 2.61 ⩽ θ ⩽ 25.07°; index range $-9 \leqslant h \leqslant 7$; $-16 \leqslant k \leqslant 17$; $-36 \leqslant l \leqslant 35$. 14 743 Reflections collected at 293 K of which 3269 were independent, R_{int} = 0.0911. The data-to-parameter ratio was 3257/207. Maximum and minimum DIFABS correction factors were 1.15 and 0.869, respectively. Goodness-of-fit on F^2 was 0.816. Final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.0497, wR_2 = 0.1015; final *R* indices for all data: R_1 = 0.1186, wR_2 = 0.1313 [$w = 1/\sigma^2(F_o)^2 + (0.047P)^2$] (*P* as defined in SHELXL 93[17]). The largest difference peak and hole were 0.561 and −0.376 e Å^{-3}.

4b·C_7H_8. Data were collected at 120 K. θ Range 1.93 ⩽ θ ⩽ 25.15°; index range $-15 \leqslant h \leqslant 10$; $-9 \leqslant k \leqslant 19$; $-41 \leqslant l \leqslant 40$. 36 613 Reflections collected of which 6457 were independent, R_{int} = 0.0786. The data-to-parameter ratio was 6452/398. Maximum and minimum DIFABS correction factors were 1.16 and 0.868, respectively. Goodness-of-fit on F^2 was 0.971. Final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.042, wR_2 = 0.0829; final *R* indices for all data: R_1 = 0.0736, wR_2 = 0.0906 [$w = 1/\sigma^2(F_o)^2 + (0.0415P)^2$]. The largest difference peak and hole were 0.736 and −0.365 e Å^{-3}.

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

Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council. G. C. B. thanks the Beit Trust for a studentship.

References

1 (*a*) O. J. Scherer and G. Schieder, *Chem. Ber.*, 1968, **101** 4184; (*b*) H. Steinberger and W. Kuchen, *Z. Naturforsch., Teil B*, 1974, **29**, 611; (*c*) W. McFarlane and B. Wrackmeyer, *J. Chem. Soc., Dalton Trans.*, 1976, 2351; (*d*) W. Kuchen, D. Langsch and W. Peters, *Phosphorus, Sulfur and Silicon*, 1990, **54**, 55.

2 (*a*) E. Lindner and H. M. Ebinger, *Chem. Ber.*, 1974, **107**, 448; (*b*) M. Fuchs, W. Kuchen and W. Peters, *Chem. Ber.*, 1986, **119**, 1569; (*c*) A. Deeg, W. Kuchen, D. Langsch, D. Mootz, W. Peters and H. Wunderlich, *Z. Anorg. Allg. Chem.*, 1991, **606**, 119; (*d*) N. Kuhn, A. Kuhn and P. Sartori, *Chem.-Ztg.*, 1988, **112**, 251.

3 M. Fuchs, W. Kuchen and W. Peters, *Z. Anorg. Allg. Chem.*, 1987, **545**, 75; H. H. Schmidtke, T. Schoenherr, W. Kuchen and M. Fuchs, *Chem. Phys. Lett.*, 1986, **124**, 159.

4 H. Roesky, H. Voelker, M. Witt and M. Noltemeyer, *Angew. Chem.*, 1990, **102**, 712; *Angew. Chem. Int. Ed. Engl.*, 1990, **29**, 669; H. W. Roesky, T. Raubold, M. Witt, R. Bohra and M. Noltemeyer, *Chem. Ber.*, 1991, **124**, 1521.

5 M. Bochmann, K. Webb, M. Harman and M. B. Hursthouse, *Angew. Chem.*, 1990, **102**, 703; *Angew. Chem. Int. Ed. Engl.* 1990, **29**, 638; M. Bochmann and K. J. Webb, *Mat. Res. Soc. Symp. Proc.*, 1991, **204**, 149; M. Bochmann, K. J. Webb, J. E. Hails and D. Wolverson, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 155.

6 T. Austad, T. Rød, K. Åse, J. Songstad and A. H. Norbury, *Acta Chem. Scand.*, 1973, **27**, 1939.

7 N. Kuhn, H. Schumann and G. Wolmershäuser, *J. Chem. Soc., Chem. Commun.* 1985, 1595.

8 N. S. Hosmane, A. M. Arif and A. H. Cowley, *Acta Crystallogr., Sect. C*, 1987, **43**, 2013.

9 J. Fayos and D. Mootz, *Z. Anorg. Allg. Chem.*, 1971, **380**, 196.

10 W. A. Herrmann, M. Denk, R. W. Albach, J. Behm and E. Herdtweck, *Chem. Ber.*, 1991, **124**, 683.

11 C. Airoldi, D. C. Bradley, H. Chudzynska, M. B. Hursthouse, K. M. A. Malik and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1980, 2010.

12 A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal and I. Bernal, *Can. J. Chem.*, 1975, **53**, 1622.

13 A. M. Cardoso, R. J. H. Clark and S. Moorhouse, *J. Chem. Soc., Dalton Trans.*, 1980, 1156.

14 G. M. Sheldrick, SHELX-S, University of Göttingen, 1986.

15 G. M. Sheldrick, SHELX 80, University of Göttingen, 1980.

16 N. Walker, D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158 (adapted for FAST geometry by A. Karaulov, University of Cardiff, 1990).

17 G. M. Sheldrick, SHELXL 93, *J. Appl. Crystallogr.*, in the press.

Received 13*th January* 1995; *Paper* 5/00212E