Synthesis and Crystal Structures of Three Four-membered Ring Compounds containing PN$_2$Ti Skeletons†

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Depending on the reaction conditions, Ph$_2$P(=NSiMe$_3$)[N(SiMe$_3$)$_2$] reacts with TiCl$_4$ to form the titanadiazaphosphetidines Ph$_2$P[μ-N(SiMe$_3$)]$_2$TiCl$_3$MeCN (1) and Ph$_2$P[μ-N(SiMe$_3$)]$_2$TiCl$_2$-[NPPh$_2$N(SiMe$_3$)$_2$] (2). Compound (1) dimerises slowly in solution with elimination of Me$_3$SiCl to yield a tricyclic system containing a central Ti$_2$N$_2$ ring (3). X-Ray analyses of these compounds show (1) and (3) to be monoclinic, space group $P2_1/n$, while (2) is triclinic, space group $P\bar{1}$. Compound (2) has a Ti–N–P angle of 170.3(7)° and a short exocyclic Ti–N bond of 179.2(9) pm.

Recently we were able to incorporate Group 5—7 transition metals in S–N[1] and P–N systems to form six-[2] and eight-membered[3] heterocycles which may possess delocalised electronic systems. Group 4 elements like titanium should react in a different manner because double bonds are unfavourable, as has been shown in the reaction of TiCl$_4$ with silylated amidines[4] and di-iminophosphoranes[5] where zwitterionic four-membered rings were formed with rather long Ti–N bond distances, thus indicating partial donor character.[6] Since the reaction of Ph$_2$P(=NSiMe$_3$)[N(SiMe$_3$)$_2$][7] with VOCl$_3$ afforded an eight-membered ring with two metal atoms,[3] we expected the corresponding reaction with the valence isoelectronic TiCl$_4$ to yield compounds with unusual properties which might make them useful as catalysts in organic synthesis.[8]

in MeCN at ambient temperature, bright orange cubes were obtained by crystallisation at −25 °C. Elemental and X-ray analyses of this material, which showed a singlet in the ^{31}P n.m.r. spectrum at +25 p.p.m., indicated the formation of (1) [equation (1)]. Compound (1) decomposes above 105 °C. Prolonged heating in MeCN and crystallisation at −25 °C affords yellow needles with a ^{31}P n.m.r. signal at +37 p.p.m. X-Ray structure analysis showed this compound (3) to have a tricyclic skeleton generated by dimerisation of (1) with elimination of Me$_3$SiCl [equation (2)]. Repeating the reaction in MeCN in a 1:1 ratio as well as with an excess of the amino-iminophosphorane affords yellow crystals melting at 135 °C. Phosphorus-31 n.m.r. investigations showed that this compound possesses two different phosphorus atoms, one giving a

(1)

(3)
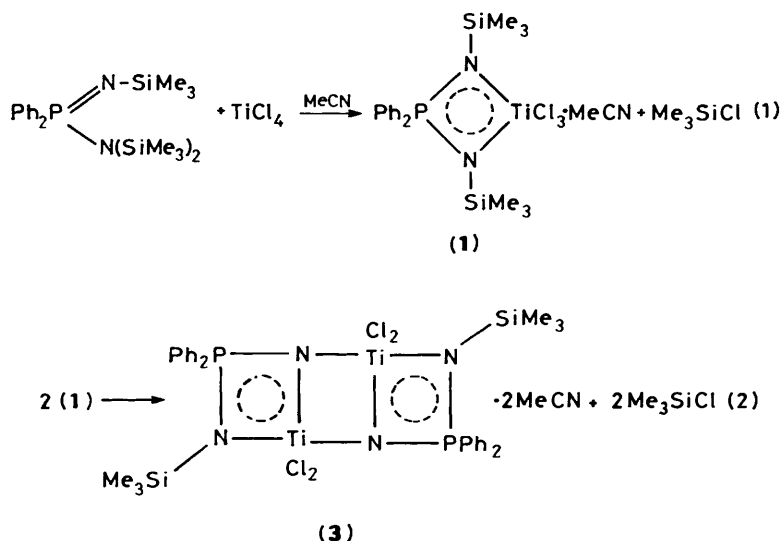
Results and Discussion

The reaction of Ph$_2$P(=NSiMe$_3$)[N(SiMe$_3$)$_2$] with TiCl$_4$ in CH$_2$Cl$_2$ at 0 °C yields a dark red solution which shows four independent signals in the ^{31}P n.m.r. spectrum. After stripping off the solvent and dissolving the amorphous orange-red residue

sharp singlet (+25.3 p.p.m.), the other a broad singlet (+2.7 p.p.m.). X-Ray structural analysis confirmed the formation of a 2:1 adduct [equation (3)]. The structure of this compound is somewhat surprising, since the corresponding reaction of TiCl$_4$ with excess of amidine yields a spirocyclic system [equation (4)].[4]

Compounds (2) and (3) could not be purified sufficiently for elemental analyses. All three compounds decompose in a mass spectrometer. The common feature of all three compounds
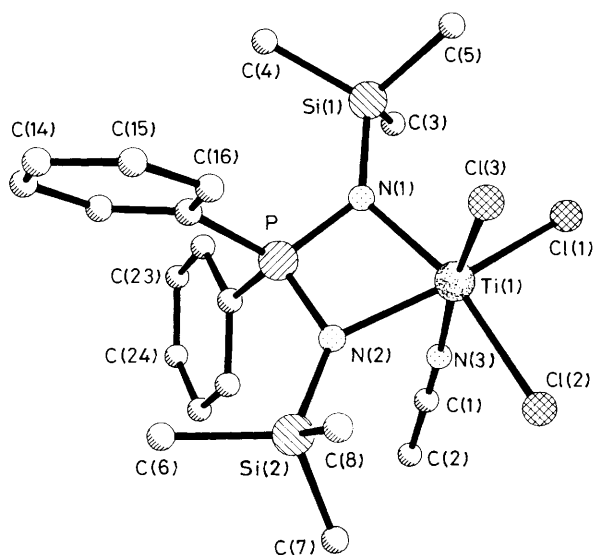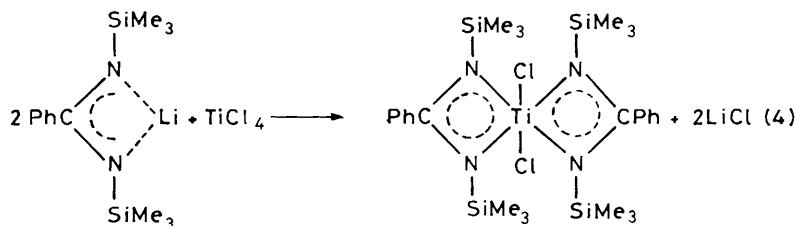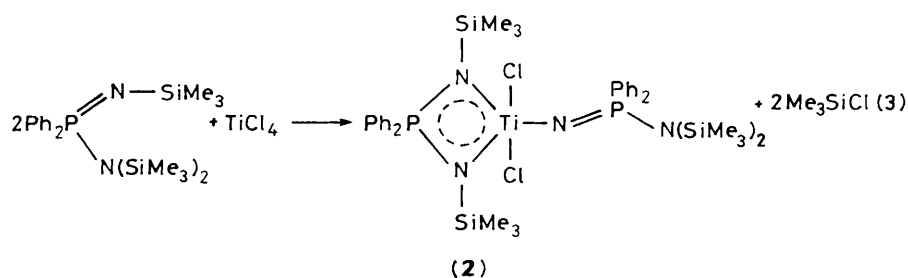

Figure 1. The molecule of compound (1) in the crystal, with non-hydrogen atoms labelled
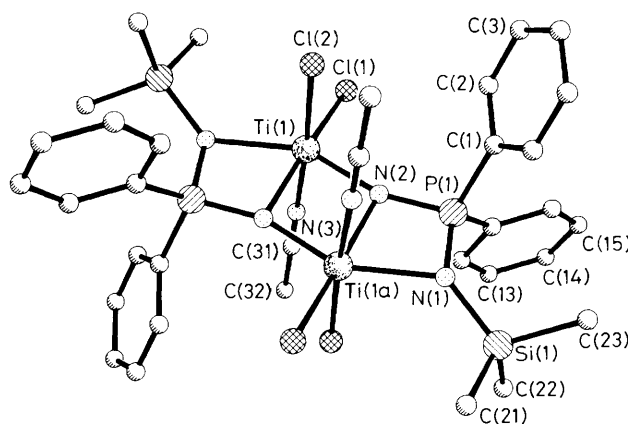

Figure 3. The molecule of compound (3) in the crystal, with independent non-hydrogen atoms labelled

Figure 2. The molecule of compound (2) in the crystal

(Figures 1—3) is a cyclic PN_2Ti ring skeleton, planar within tolerances; (1) has C_s and (3) D_{2h} molecular symmetry within experimental error. The Ti atoms of (1) and (3) have distorted octahedral environments with the Cl atoms all cis, the sixth position being occupied by a co-ordinated MeCN molecule. The Ti atom in (2) exhibits square pyramidal geometry with the exocyclic N atom occupying the apical position. The central Ti_2N_2 ring in (3) is also planar and is tilted to the two parallel PN_2Ti rings by 22.6°.

All the N atoms bearing Me_3Si groups exhibit essentially planar co-ordination; the N–Si bonds are slightly shorter than the sum of the covalent radii of 187 pm.[9,10] The P–N bond lengths in the rings lie between typical single and double bond lengths, and are comparable with those in cyclic phosphazenes.[11] The angles at the P-atoms lie around 100°, at the N atoms >90°, and at the Ti atoms between 72.5 and 74.1°, respectively. Though the P–Ti separations (approximately 270 pm) are smaller than the sum of van der Waals radii,* a direct bonding interaction can be excluded, as well as in the central Ti_2N_2 ring in (3), where the Ti ••• Ti distance [301.4(2) pm]

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* Though exact values for covalent and van der Waals radii are not available for covalently bound Ti, the sum of van der Waals radii of P and Ti can be estimated to exceed 300 pm.[9,12]

Table 1. Crystallographic data for compounds (1)—(3)

Compound	(1)	(2)	(3)
Sum Formula	$C_{20}H_{31}Cl_3N_3PSi_2Ti$	$C_{38}H_{59}Cl_2N_5P_2Si_4Ti$	$C_{34}H_{44}Cl_4N_6P_2Si_2Ti_2$
M	554.87	879.02	892.46
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/pm	953.0(2)	1 141.5(4)	938.4(2)
b/pm	1 778.5(3)	1 250.2(5)	1 638.5(3)
c/pm	1 608.0(2)	1 828.2(8)	1 459.7(3)
$\alpha/°$	90	78.18(3)	90
$\beta/°$	96.70(3)	82.06(2)	101.42(2)
$\gamma/°$	90	71.20(2)	90
U/nm³	2.71	2.41	2.20
Z	4	2	2
D_c/Mg m⁻³	1.362	1.211	1.347
μ/mm⁻¹	0.77	0.48	0.76
Crystal size (mm)	0.6 × 0.65 × 0.7	0.2 × 0.3 × 0.3	0.3 × 0.3 × 0.2
Reflections, unique	3 322	6 251	2 854
observed	2 941	3 553	2 174
R	0.037	0.103	0.049
R'	0.038	0.076	0.047
Weighting scheme, $w^{-1} = \sigma^2(F) + gF^2$ with g =	0.0002	0.0006	0.0006
Refined parameters	271	469	226

Table 2. Atomic co-ordinates (× 10⁴) for compound (1)

Atom	x	y	z	Atom	x	y	z
Ti	1 011(1)	7 042(1)	1 721(1)	C(6)	−511(4)	5 936(2)	4 310(2)
Cl(1)	2 189(1)	7 501(1)	643(1)	C(7)	121(4)	7 594(2)	4 165(2)
Cl(2)	37(1)	8 182(1)	2 066(1)	C(8)	−2 310(4)	6 860(2)	3 035(3)
Cl(3)	−1 000(1)	6 708(1)	883(1)	C(11)	545(3)	4 966(2)	2 718(2)
Si(1)	2 928(1)	5 547(1)	1 011(1)	C(12)	959(3)	4 372(2)	3 251(2)
Si(2)	−495(1)	6 741(1)	3 569(1)	C(13)	9(3)	3 805(2)	3 383(2)
N(1)	1 985(3)	6 026(2)	1 731(1)	C(14)	−1 358(4)	3 837(2)	2 991(2)
N(2)	641(3)	6 540(2)	2 805(1)	C(15)	−1 765(4)	4 414(2)	2 441(2)
N(3)	2 901(3)	7 488(2)	2 526(1)	C(16)	−830(3)	4 981(2)	2 295(2)
C(1)	3 717(3)	7 721(2)	3 031(2)	C(21)	3 136(3)	5 740(2)	3 417(2)
C(2)	4 737(4)	8 013(2)	3 695(2)	C(22)	4 237(3)	5 255(2)	3 292(2)
P	1 583(1)	5 808(1)	2 654(1)	C(23)	5 470(4)	5 255(2)	3 848(2)
C(3)	4 771(4)	5 894(2)	1 117(2)	C(24)	5 585(4)	5 730(2)	4 532(2)
C(4)	2 877(4)	4 517(2)	1 199(2)	C(25)	4 500(4)	6 200(2)	4 666(2)
C(5)	2 044(4)	5 680(2)	−75(2)	C(26)	3 272(4)	6 210(2)	4 108(2)

Table 3. Atomic co-ordinates (× 10⁴) for compound (2)

Atom	x	y	z	Atom	x	y	z
Ti	3 071(2)	326(2)	2 274(1)	C(22)	5 087(11)	−1 452(11)	4 037(8)
Si(1)	884(3)	1 678(3)	3 617(2)	C(23)	5 603(13)	−1 320(12)	4 636(11)
Si(2)	1 938(3)	891(3)	475(2)	C(24)	5 331(16)	−1 816(16)	5 342(12)
Si(3)	3 993(3)	−3 718(3)	2 220(2)	C(25)	4 467(16)	−2 413(14)	5 477(9)
Si(4)	6 147(3)	−3 932(3)	3 127(2)	C(26)	3 950(12)	−2 557(12)	4 868(9)
Cl(1)	4 712(2)	−97(3)	1 367(2)	C(31)	233(9)	3 070(9)	1 596(6)
Cl(2)	4 011(2)	1 364(3)	2 782(2)	C(32)	−819(10)	3 666(10)	1 196(7)
P(1)	3 583(3)	−2 248(3)	3 366(2)	C(33)	−1 047(13)	4 809(11)	906(8)
P(2)	701(2)	1 550(3)	1 966(2)	C(34)	−283(15)	5 373(12)	1 029(9)
N(1)	1 326(6)	1 280(7)	2 744(5)	C(35)	774(15)	4 813(13)	1 403(10)
N(2)	1 822(6)	845(7)	1 445(5)	C(36)	1 030(11)	3 664(11)	1 677(8)
N(3)	3 256(7)	−1 073(7)	2 822(5)	C(41)	361(9)	1 410(10)	119(7)
N(4)	4 520(8)	−3 342(7)	2 993(5)	C(42)	2 786(10)	1 891(10)	−11(7)
C(1)	2 171(10)	−2 603(11)	3 710(6)	C(43)	2 724(10)	−570(9)	225(6)
C(2)	2 195(13)	−3 732(12)	4 038(8)	C(51)	1 854(10)	634(10)	4 317(6)
C(3)	1 105(18)	−3 958(15)	4 264(9)	C(52)	−757(9)	1 754(13)	3 935(8)
C(4)	−30(17)	−3 094(21)	4 166(10)	C(53)	1 026(14)	3 106(11)	3 633(8)
C(5)	−82(12)	−2 001(16)	3 847(9)	C(61)	7 004(11)	−2 907(11)	2 639(8)
C(6)	1 029(12)	−1 760(12)	3 634(7)	C(62)	6 490(11)	−4 385(11)	4 135(8)
C(11)	−665(8)	1 051(9)	2 053(7)	C(63)	6 820(12)	−5 292(10)	2 743(8)
C(12)	−519(10)	−16(10)	1 912(7)	C(71)	3 961(13)	−5 233(11)	2 453(9)
C(13)	−1 523(12)	−455(11)	2 014(8)	C(72)	5 015(12)	−3 438(12)	1 371(7)
C(14)	−2 647(12)	187(13)	2 267(8)	C(73)	2 390(11)	−2 861(11)	1 998(8)
C(15)	−2 805(10)	1 248(13)	2 400(8)	N(5)	6 666(21)	3 937(24)	253(20)
C(16)	−1 812(9)	1 699(10)	2 289(7)	C(81)	5 844(28)	3 447(26)	575(21)
C(21)	4 265(10)	−2 079(10)	4 144(8)	C(82)	4 905(24)	3 006(23)	799(14)

Table 4. Atomic co-ordinates (× 10⁴) for compound (3)

Atom	x	y	z	Atom	x	y	z
Ti	426(1)	315(1)	4 123(1)	C(11)	2 994(5)	1 211(3)	6 788(3)
Cl(1)	2 196(1)	1 127(1)	3 629(1)	C(12)	3 880(5)	538(3)	6 748(3)
Cl(2)	−1 359(1)	1 257(1)	3 580(1)	C(13)	5 348(5)	579(3)	7 125(4)
P	1 066(1)	1 086(1)	6 379(1)	C(14)	5 934(5)	1 291(3)	7 550(3)
N(1)	310(4)	511(2)	7 034(2)	C(15)	5 058(6)	1 967(3)	7 589(4)
N(2)	750(4)	585(2)	5 406(2)	C(16)	3 589(5)	1 924(3)	7 207(3)
Si	676(1)	381(1)	8 242(1)	C(21)	−749(6)	−260(4)	8 573(4)
C(1)	297(5)	2 095(2)	6 174(3)	C(22)	2 465(6)	−101(4)	8 677(4)
C(2)	621(5)	2 564(3)	5 445(3)	C(23)	701(7)	1 385(3)	8 848(4)
C(3)	29(6)	3 330(3)	5 275(3)	N(3)	2 284(4)	−546(2)	4 439(2)
C(4)	−883(6)	3 642(3)	5 816(4)	C(31)	3 136(5)	−1 022(3)	4 671(3)
C(5)	−1 219(6)	3 175(3)	6 537(4)	C(32)	4 239(6)	−1 658(3)	4 967(4)
C(6)	−631(5)	2 404(3)	6 711(3)				

Table 5. Selected bond lengths (pm) and angles (°) for compound (1)

Ti–N(1)	203.3(3)	Ti–N(3)	223.7(2)
Ti–N(2)	202.6(2)	N(1)–P	162.2(2)
Ti–Cl(1)	232.0(1)	N(2)–P	161.6(3)
Ti–Cl(2)	232.4(1)	N(1)–Si(1)	176.6(3)
Ti–Cl(3)	228.9(1)	N(2)–Si(2)	176.5(3)
Ti–N(1)–P	93.6(1)	N(1)–P–N(2)	98.0(1)
Ti–N(1)–Si(1)	133.7(1)	Si(1)–N(1)–P	132.7(2)
Ti–N(2)–P	94.0(1)	Si(2)–N(2)–P	131.6(2)
Ti–N(2)–Si(2)	133.8(1)	C(11)–P–C(21)	108.4(1)
Ti–N(3)–C(1)	169.0(3)	N–P–C(average)	112.5
N(1)–Ti–N(2)	74.1(1)		

Table 6. Selected bond lengths (pm) and angles (°) for compound (2)

Ti–N(1)	213.1(7)	N(2)–Si(2)	175.0(10)
Ti–N(2)	208.5(9)	Ti–N(3)	179.2(9)
Ti–Cl(1)	232.3(3)	N(3)–P(1)	156.1(9)
Ti–Cl(2)	231.7(4)	P(1)–N(4)	164.9(9)
N(1)–P(2)	160.4(9)	N(4)–Si(3)	180.8(12)
N(2)–P(2)	161.3(8)	N(4)–Si(4)	179.6(9)
N(1)–Si(1)	172.9(10)		
Ti–N(1)–P(2)	92.2(4)	N(2)–Ti–Cl(1)	89.9(2)
Ti–N(1)–Si(1)	131.3(5)	N(2)–Ti–Cl(2)	130.8(3)
Ti–N(2)–P(2)	93.6(4)	Cl(1)–Ti–Cl(2)	91.7(1)
Ti–N(2)–Si(2)	135.5(4)	N(3)–Ti–Cl(1)	100.2(3)
Ti–N(3)–P(1)	170.3(7)	N(3)–Ti–Cl(2)	111.5(4)
N(1)–Ti–N(2)	72.5(3)	N(3)–P(1)–N(4)	115.2(5)
N(1)–P(2)–N(2)	101.6(4)	N(3)–P(1)–C(average)	108.4
Si(1)–N(1)–P(2)	136.2(4)	N(4)–P(1)–C(average)	108.1
Si(2)–N(2)–P(2)	128.9(5)	C(1)–P(1)–C(21)	108.5(6)
N(1)–Ti–N(3)	101.4(3)	P(1)–N(4)–Si(3)	117.5(5)
N(2)–Ti–N(3)	116.6(4)	P(1)–N(4)–Si(4)	123.9(5)
N(1)–Ti–Cl(1)	156.6(2)	Si(3)–N(4)–Si(4)	116.5(5)
N(1)–Ti–Cl(2)	88.7(3)		

exceeds the sum of two covalent single bond radii (*ca.* 265 pm[9]).

Although the Ti–N bonds in compound (1) have to be considered single bonds [r_{cov}(Ti) + r_{cov}(N) ≈ 203 pm[9]],* and are comparable with those in the PN₂Ti ring reported by Niecke *et al.*,[5] the endocyclic Ti–N bonds in (2) [208.5(9) pm and 213.1(7) pm] are definitively longer than single bonds, but resemble those found in the bis(amidine) chelate complex [TiCl₂{PhC(NSiMe₃)₂}₂] (206.6 and 210.1 pm).[4] The exocyclic Ti–N bond [179.2(9) pm] is among the shortest Ti–N bonds known so far; only the bonds in [Ti(cp)Cl₂(NPPh₃)] (cp = η-C₅H₅) [177.5(13) pm] [20] and [Ti(cp)Cl₂{NPPh₂NS(O)Me₂}] [176.4(2) pm] [21] are shorter. The Ti–N–P linkage is almost linear [170.3(7)°]; similar bond angles in Ti–N compounds have been found only in the two cases mentioned above. The *sp²* hybridisation of the N atom suggests a strong donor capacity that has been found in a wide variety of transition metal–nitrogen bonds.[22] The P–N bond adjacent to the Ti atom [156.1(9) pm] could be described as a P^V=N double bond.

Another unusual structure feature of (2) is the five-co-ordinated Ti atom.

Five-co-ordinated Ti atoms in four-membered rings have been observed in *e.g.* [{TiCl₃(OR)}₂] with Ti–O–Ti bridges

(R = Et or Ph),[23] in the PN₂Ti ring reported by Niecke *et al.*,[5] and in [{TiCl₂(NSiMe₃)}₂] with Ti–N–Ti linkages connected by Cl bridges to form linear chains.[14] Besides partial disorder in the chains, the two independent units in one polymer strand were found to differ considerably in corresponding Si–N and Ti–N bond lengths (169 *vs.* 183 and 194 *vs.* 199 pm), but the mean values of 176 and 196 pm, respectively, seem plausible.[14] The Ti₂N₂ core of tricyclic (3) shows somewhat longer Ti–N distances, 189.0(3) pm for the bonds connecting the two PN₂Ti moieties, and 204.2(4) pm for the bonds common to two rings. While the first is shorter than a typical single bond, the second lies in the range common to the other PN₂Ti four-membered rings described in this paper and in ref. 5.

Experimental

Syntheses.—All reactions were carried out under nitrogen or argon, solvents were purified and dried according to literature methods, degassed, and stored under nitrogen or vacuum. The compound Ph₂P(=NSiMe₃)[N(SiMe₃)₂] was prepared according to ref. 7; TiCl₄ was fractionally condensed *in vacuo*. N.m.r. spectra were recorded on a Bruker AM 250 spectrometer.

Compound (1). Titanium tetrachloride (1.9 g, 10 mmol) and CH₂Cl₂ (100 cm³) were condensed in a flask (250 cm³) at −190 °C *in vacuo*, the mixture flushed with nitrogen, and Ph₂P(=NSiMe₃)[N(SiMe₃)₂] (4.3 g, 10 mmol) added with a syringe. After re-evacuation the system was slowly warmed up

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* The Ti–N single bond length has been previously estimated to be 196 pm.[13] Such bond lengths are strongly dependent on the geometry of Ti, the direction of the bond, and the donor capacity of N.[14] For a listing of different types of Ti–N bonds see refs. 15 and 16 and literature cited therein. A Ti–N single bond length of 203 pm would also be consistent with Ti–C distances of about 210 pm,[8,17] where dative interactions can be excluded. The mean Ti–C bond length in [{Ti(OMe)₂(μ-OMe)(μ-CH₂PMe₂CH₂)}₂] is extended to 225 pm;[18] the CH₂PMe₂CH₂ bridge is isoelectronic to μ-(Me₃SiN)₂PPh₂ in our compounds. In [Ti(cp)₂(CO)₂], where back donation may be postulated, the Ti–C bond is shortened to 203 pm.[19]

Table 7. Selected bond lengths (pm) and angles (°) for compound (**3**)

Ti(1)–Cl(1)	235.0(1)	N(1)–P(1)	160.4(4)
Ti(1)–Cl(2)	230.0(1)	N(1)–Si(1)	174.3(3)
Ti(1)–N(1A)	216.7(3)	N(2)–P(1)	161.7(3)
Ti(1)–N(2)	189.0(3)	Ti(1)–N(3)	221.9(4)
Ti(1)–N(2A)	204.2(4)		
Ti(1a)–N(1)–P(1)	90.7(2)	N(2)–Ti(1)–N(2a)	80.0(1)
Ti(1a)–N(1)–Si(1)	132.9(2)	N(2a)–Ti(1)–Cl(1)	167.0(1)
N(1)–P(1)–N(2)	101.6(2)	N(2a)–Ti(1)–Cl(2)	101.3(1)
P(1)–N(1)–Si(1)	130.8(2)	N(2a)–Ti(1)–N(3)	85.7(1)
P(1)–N(2)–Ti(1a)	95.0(2)	Cl(1)–Ti(1)–Cl(2)	91.5(1)
P(1)–N(2)–Ti(1)	162.8(2)	Cl(1)–Ti(1)–N(2)	100.8(1)
N(1a)–Ti(1)–N(2)	151.9(1)	Cl(1)–Ti(1)–N(3)	81.4(1)
N(1a)–Ti(1)–N(2a)	72.6(1)	Ti(1)–N(2)–Ti(1a)	100.0(1)
N(1a)–Ti(1)–Cl(1)	104.5(1)	N(3)–Ti(1)–N(2)	88.6(1)
N(1a)–Ti(1)–Cl(2)	93.0(1)	Cl(2)–Ti(1)–N(2)	98.5(1)
N(1a)–Ti(1)–N(3)	83.2(1)	Cl(2)–Ti(1)–N(3)	170.7(1)

to 0 °C, and held at this temperature for 2 h. All volatiles were pumped off, and MeCN (80 cm^3) was condensed at −190 °C. After warming and dissolving the orange-red residue, the flask was cooled to −25 °C. Several days later orange cubes began to separate from the solution, m.p. 105 °C (decomp.) (Found: C, 43.8; H, 5.6; Cl, 19.2; N, 7.1. $C_{20}H_{31}Cl_3N_3PSi_2Ti$ requires C, 43.3; H, 5.6; Cl, 19.2; N, 7.6%). δ(P)(CDCl$_3$–CH$_2$Cl$_2$) 24.7 p.p.m.

Compound (**2**). To a solution of Ph$_2$P(=NSiMe$_3$)[N(SiMe$_3$)$_2$] 8.6 g, 20 mmol) in MeCN (120 cm^3) a solution of TiCl$_4$ (1.9 g, 10 mmol) in CH$_2$Cl$_2$ (10 cm^3) was slowly added at 0 °C. After stirring for 12 h at ambient temperature all volatile material was evaporated and the solid residue dissolved in MeCN (50 cm^3). On cooling, compound (**2**) crystallised in dark yellow blocks melting at 135 °C. δ(P)(CDCl$_3$–CH$_2$Cl$_2$) 2.7 (P chain, s) and 25.3 p.p.m. (P ring, s).

Compound (**3**). Compound (**1**) (1.1 g, 2 mmol) was dissolved in MeCN (50 cm^3) and heated to 60 °C for 3 h. After several days at −25 °C a mixture of crystals of (**1**) and (**3**) precipitated which after filtration were manually separated. δ(P)(CD$_3$CN–CH$_2$Cl$_2$) 36.7. p.p.m.

X-Ray Structure Analyses.—All crystals were obtained by fractional crystallisation from MeCN. All structures were measured on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo-$K_α$ radiation. Data were collected at −85 [(**1**) and (**3**)] and 18 °C [(**2**)] with a profile fitting method,[24] $2\theta_{max.} = 45°$, and reflections with $|F| > 3\sigma(F)$ were treated as observed. The structures were solved by Patterson and Fourier methods, and refined by full-matrix least squares (on F), with all non-hydrogen atoms anisotropic. A riding model was employed for the H atoms with idealised geometry. Structure (**2**) contains one molecule of acetonitrile [N(5), C(81), and C(82)] per asymmetric unit, which exhibits high thermal motion and presumably accounts for the relatively high R index. All calculations were performed with SHELX 76[25] and SHELX 86.[26] Crystallographic data for compounds (**1**)—(**3**) are shown in Table 1, atomic co-ordinates in Tables 2—4, and selected bond lengths and angles in Tables 5—7.

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

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