Four- and Eight-membered Cyclic Phosphazene Derivatives of Zirconium, Titanium and Vanadium. Crystal Structures of the Complexes [ZrCl₃(Me₃SiNPPh₂NSiMe₃)]·MeCN and [{TiCl₂(OPPh₂N)}₂]·4MeCN†

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The reaction of $ZrCl_4$ with $(Me_3Si)_2NPPh_2NSiMe_3$ 1 yields the four-membered heterocycle [ZrCl₃(Me₃SiNPPh₂NSiMe₃)]. An improved synthesis of the aminoiminophosphorane 1 is described. The compound $TiCl_4$ reacts with $Me_3SiOPPh_2NSiMe_3$ unexpectedly with elimination of all Me_3Si groups to yield the eight-membered heterocycle [{TiCl₂(OPPh₂N)}₂]. A vanadium-containing dimetallacyclophosphazene [{VCl₂(NPPh₂N)}₂] has been synthesised from [VCl₃(NSiMe₃)] and ClPPh₂NSiMe₃. The X-ray structures of [ZrCl₃(Me₃SiNPPh₂NSiMe₃)]·MeCN and [{TiCl₂-(OPPh₂N)}₂]·4MeCN have been determined. While the cyclic Zr–N distances in the former have to be considered as single bonds, the short Ti–N of the latter (almost planar) suggest double-bond character.

The incorporation of transition metals as building blocks of cyclic[1–6] and acyclic[5–7] phosphazene systems has found increasing interest over the past few years. For example, phosphazene polymers with metals in the skeleton have been synthesised.[8] In the course of our investigations we were interested in including other transition metals and other building units, e.g. oxygen instead of nitrogen.

Results and Discussion

In 1989 we reported on the reaction of $TiCl_4$ with $(Me_3Si)_2NPPh_2NSiMe_3$ 1, which under different reaction conditions yields three different products 2–4 all of which possess a planar, cyclic, PN_2Ti unit as the common feature.[4] Analogous reactions of silylated benzamidinates with other halides of Group 4 lead, depending on the stoichiometry, to the formation of four-membered cyclic (molar ratio 1:1) or spirocyclic compounds (molar ratio 1:2).[9] In the amino-iminophosphorane case, a 1:2 molar ratio led to double addition, 3, but only one ring was closed. Since the steric requirement of the aminoiminophosphorane chelate is greater than of the benzamidine ligand, a second ring closure to form the spirocyclic isomer of 3 might be unfavourable. We have investigated the analogous reaction with the slightly bigger zirconium [$r_{cov} \approx 136$ (Ti), ≈ 148 pm (Zr)[10]]. Independent of the molar ratio, a 1:1 reaction product 5 is formed in up to 80% yield, which after recrystallisation from MeCN has been isolated and characterised by means of X-ray analysis as the MeCN adduct 5a [equation (1)]. Compounds of type 5 are of interest as potential catalysts in organic chemistry.[11]
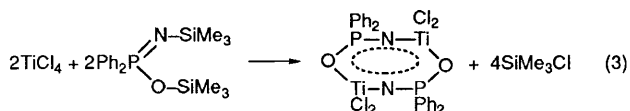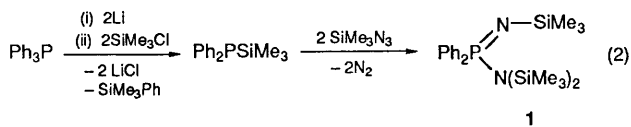
During the course of our investigations we found a straightforward two-step synthesis of compound 1 [equation (2)], which so far was only accessible via two independent multistep procedures;[12] a total yield up to 80% was achieved.

Since the primary reactions to form compounds 5 and 3 involve only the cleavage of one Me_3Si unit per molecule, it was interesting to replace the amino-function by a trimethylsilyloxy group. Surprisingly, in the solid residue of the reaction (3) of $TiCl_4$ with $Me_3SiOPPh_2NSiMe_3$ 6,[13] no Me_3Si groups could
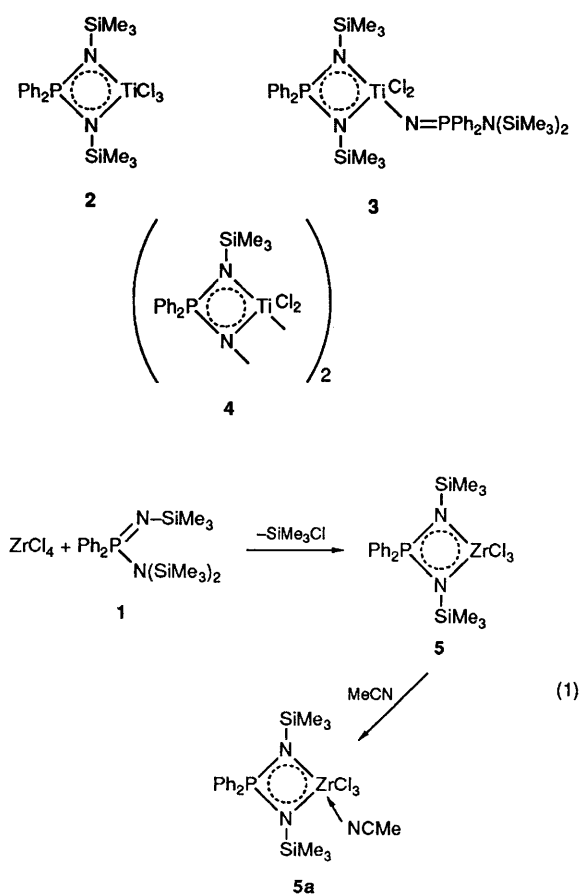
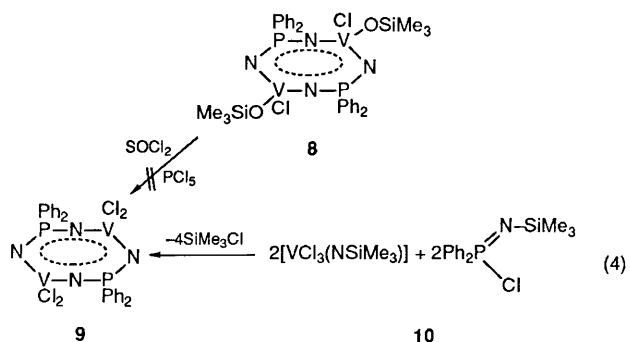be detected spectroscopically. The structure of compound 7 has been determined by means of a low-temperature single-crystal X-ray analysis of the MeCN adduct 7a, which forms yellow blocks after recrystallisation from MeCN. The structure analysis reveals the presence of an almost planar, eight-membered heterocycle with very short Ti–N bonds and P–N–Ti units close to linearity. Thus, 7 is valence isoelectronic with a

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$$Ph_3P \xrightarrow[\substack{-2\,LiCl \\ -SiMe_3Ph}]{\substack{(i)\ 2Li \\ (ii)\ 2SiMe_3Cl}} Ph_2PSiMe_3 \xrightarrow[-2N_2]{2\,SiMe_3N_3} Ph_2P\underset{N(SiMe_3)_2}{\overset{N-SiMe_3}{\lessgtr}} \quad (2)$$

1

$$2TiCl_4 + 2Ph_2P\underset{O-SiMe_3}{\overset{N-SiMe_3}{\lessgtr}} \longrightarrow 7 + 4SiMe_3Cl \quad (3)$$

6 **7**

8

$$2[VCl_3(NSiMe_3)] + 2Ph_2P\underset{Cl}{\overset{N-SiMe_3}{\lessgtr}} \xrightarrow{-4SiMe_3Cl} 9 \quad (4)$$
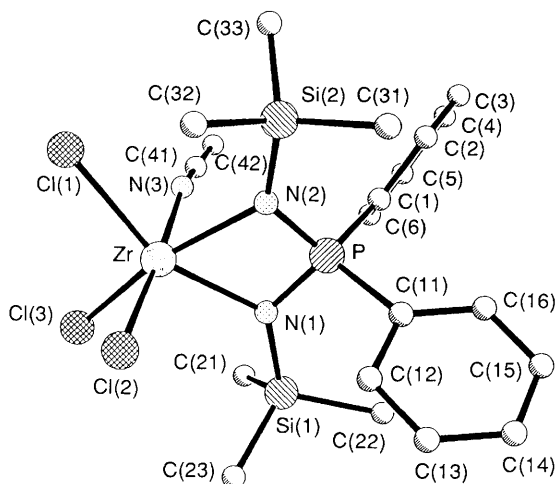
9 **10**

Fig. 1 The molecule of compound **5a** in the crystal, with non-hydrogen atoms labelled

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

Zr–N(1)	217.2(4)	Zr–Cl(1)	243.7(1)
Zr–N(2)	218.4(4)	Zr–Cl(2)	241.1(1)
Zr–N(3)	236.4(4)	Zr–Cl(3)	244.0(2)
P–N(1)	161.5(5)	Si(1)–N(1)	175.7(4)
P–N(2)	160.0(5)	Si(2)–N(2)	176.4(4)
Zr–N(1)–P	95.0(2)	N(1)–P–N(2)	100.5(2)
Zr–N(1)–Si(1)	132.9(2)	P–N(1)–Si(1)	131.3(2)
Zr–N(2)–P	94.9(2)	P–N(2)–Si(2)	132.9(2)
Zr–N(2)–Si(2)	132.2(2)	C(1)–P–C(11)	107.6(2)
Zr–N(3)–C(41)	166.8(5)	N–P–C (average)	112.2
N(1)–Zr–N(2)	69.4(1)	sum ring	359.8

previously synthesised tetraazadiphosphadivanadocine **8**,[3] accessible by treating VOCl₃ with **1**. Attempts to exchange the Me₃SiO groups in **8** with chlorine by means of SOCl₂, PCl₅, etc. led to a total cleavage of the ring skeleton. Nevertheless, the tetrachlorinated derivative **9** can be synthesised by a double
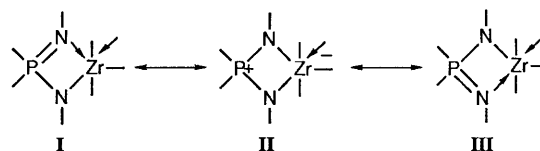
Scheme 1 Resonance forms of compound **5a**, outer ring atoms being omitted

Table 2 Comparison of the cell constants of compounds **5a** and **3**

	5a	**3**	Difference (%)
a/pm	941.7(2)	953.0(2)	−1.2
b/pm	1827.5(2)	1778.5(3)	2.7
c/pm	1638.2(2)	1608.0(2)	1.8
β/°	97.65(2)	96.70(3)	1.0
U/nm³	2.794	2.707	3.1

[2 + 2] cycloaddition from [VCl₃(NSiMe₃)][14] and the chlorophosphazene **10**[15] in high yield [equation (4)].

Compound **9**, a brick-red microcrystalline solid, is moderately stable in air, but suffers immediate decomposition in solution. An analogous eight-membered heterocycle bearing C₂F₅ groups on phosphorus has recently been synthesised by the same route and characterised by an X-ray structure analysis.[16] Unfortunately we were not able to grow single crystals of **9**, but the mass spectrum ($m/z = 670$, M, 23%) clearly supports the proposed structure. The formation of **9** sharply contrasts with the reactions of [VCl₃(NSiMe₃)] with ClP(CF₃)₂NSiMe₃ and of nitride halides of Group 6 with ClPPh₂NSiMe₃ **10** which lead to six-[2] and eight-membered[6] rings with only one metal atom in the skeleton. So far the eight-membered rings have only been characterised by ³¹P NMR and mass spectroscopy.

The molecular structure of compound **5a** (Fig. 1, Table 1) is composed of an almost planar four-membered ring (standard deviation 2.32 pm) with both silicon atoms lying also close to this plane [Si(1) and Si(2) deviate 2.8 and 9.0 pm from this plane respectively]. The phosphorus atom has an almost tetrahedral environment, while the geometry at zirconium consists of a distorted octahedron due to the small cyclic N–Zr–N angle of 69.4(1)°. The Zr–N–C angle of the co-ordinated MeCN is about 13° from linearity, the N≡C–C unit being tilted towards the ring. Similar deviations from 180° have also been found in the titanium compounds **3a**, **4** and **7a**.[4] While the Zr–N(3) bond has dative character, the Zr–N bonds in the ring have to be considered single bonds.[10] With the P–N bonds resembling those of cyclic phosphazenes,[17] and sp²-hybridised nitrogen atoms, the resonance forms in Scheme 1 can be drawn.

Compound **5a** is isomorphous with its titanium homologue **3**,[4] a comparison of the cell constants being given in Table 2. The unit-cell volume of **5a** is somewhat bigger due to the size of the metal atoms.

The single-crystal X-ray structure of compound **7a** (Fig. 2, Table 3) exhibits an almost planar eight-membered ring with two alternating Ti–N–P–O sequences. Compound **7a** is valence isoelectronic with its vanadium analogues **9** and **8**, the structure of the latter having been described earlier.[3] The molecule contains an inversion centre. The most striking feature in the structure of **7a** is the very short Ti–N bonds of 174.1(2) pm and the large P–N–Ti angles of 175.9(1)°, so that sp hybridisation can be attributed to the nitrogen atoms. The resonance forms in Scheme 2 can be assigned. From these it is clear that the Ti–N bonds have appreciable double-bond character. Thus, resonance form **IV** can be regarded as dominant. The Ti–N bond in [TiCl₂(NPPh₂S)]·3C₅H₅N, 172.0(2) pm [Ti–N–P 172.5(2)°], is probably best described as a double bond.[18] Similar bonding features have been observed[19] in some phosphoraneiminato
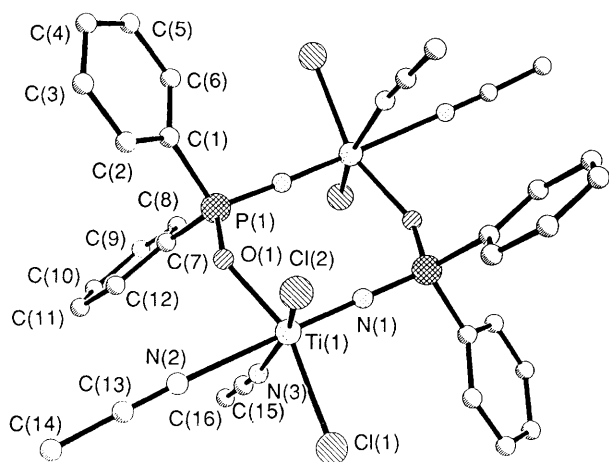
Fig. 2 The molecule of compound 7a in the crystal, with independent non-hydrogen atoms labelled

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

Ti(1)–N(1)	174.1(2)	Ti(1)–Cl(1)	237.2(1)
Ti(1)–O(1)	197.9(2)	Ti(1)–Cl(2)	233.7(1)
Ti(1)–N(2)	234.4(2)	P(1)–O(1)	151.7(2)
Ti(1)–N(3)	221.9(2)	P(1)–N(1A)	160.5(2)
Ti(1)–N(1)–P(1A)	175.9(1)	O(1)–Ti(1)–N(1)	98.7(1)
Ti(1)–O(1)–P(1)	141.7(1)	O(1)–P(1)–N(1A)	117.3(1)
Ti(1)–N(2)–C(13)	177.1(2)	O–P–C (average)	107.7
Ti(1)–N(3)–C(15)	171.7(2)	N–P–C (average)	108.7
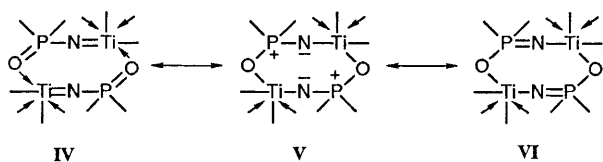
Scheme 2 Resonance forms of compound 7a, outer ring atoms being omitted for clarity

complexes of $[Ti(C_5H_5)Cl_2]^+$ and in 4.[4] A disordered structure has been reported for the polymeric $[\{[TiCl_2(NSiMe_3)]_2\}_x]$ where one set of Ti–N bonds was found to be 169 pm.[20]

The P–N distance in compound 7a [160.5(2) pm] is longer than in most other cyclic phosphazenes,[17] and the P–O separation [151.7(2) pm] is close to that calculated (150 pm) for a double bond. The Ti–O bond length of 197.9(2) pm is in the range found for titanium bonded to bridging sp²-hybridised oxygen atoms.[21] Since low-temperature data had been collected, a clear distinction between oxygen and nitrogen atoms could be made by comparison of the isotropic thermal parameters with those obtained by exchanging O and N. A strong *trans* effect is shown by the co-ordinated MeCN ligands, the Ti–N bond *trans* to the ring nitrogen being longer by 12.5(3) pm compared to the one in the *cis* position.

Experimental

All manipulations were performed in vessels predried and heated under dry nitrogen or argon or *in vacuo*. Solvents were dried and degassed by standard methods, $TiCl_4$ purified by condensation *in vacuo*, and commercially available $SiMe_3Cl$

* As a minor change, LiPh was not quenched with Bu^tCl and the resulting $SiMe_3Ph$ separated by fractional distillation.

Table 4 Crystallographic data for compounds 5a and 7a *

Compound	5a	7a
Formula	$C_{20}H_{31}Cl_3N_3PSi_2Zr$	$C_{32}H_{32}Cl_4N_6O_2P_2Ti_2$
M	598.2	832.2
a/pm	941.7(1)	999.5(1)
b/pm	1827.5(2)	1608.2(2)
c/pm	1638.2(2)	1287.4(1)
β/°	97.65(2)	101.31(2)
U/nm³	2.794	2.029
Z	4	2
$F(000)$	1224	848
D_c/Mg m⁻³	1.42	1.36
Crystal size (mm)	0.3 × 0.3 × 0.1	0.8 × 0.45 × 0.4
μ/mm⁻¹	0.83	0.77
Reflections		
unique	3631	3546
observed	3016	3134
R	0.046	0.036
R'	0.052	0.046
Goodness of fit	1.34	1.83
g in weighting scheme		
$w^{-1} = \sigma^2(F) + gF^2$	0.0008	0.0003
Refined parameters	274	219

* Details in common; crystal system monoclinic, space group $P2_1/n$.

and $SiMe_3N_3$ distilled prior to use. The compound $ZrCl_4$ was used as obtained, while Ph_2PSiMe_3,[22]* $[VCl_3(NSiMe_3)]$,[14] $Me_3SiOPPh_2NSiMe_3$ 6,[13] and $ClPPh_2NSiMe_3$ 10[15] were prepared according to the literature. The ³¹P NMR spectra were recorded on a Bruker AM 250 spectrometer; elemental analyses were carried out by Mikroanalytisches Labor Beller, Göttingen. The mass spectrum of compound 9 was recorded on a Finnigan Mat 8230 mass spectrometer. Only the highest peak of any isotope distribution is given. The boiling and melting points are listed without thermometer corrections.

Preparations.—[*Bis(trimethylsilyl)amino*]*diphenyl(trimethyl-silylimino)phosphorane* 1.—The compound Ph_2PSiMe_3 (51.5 g, 0.2 mol) and $SiMe_3N_3$ (*ca.* 80 cm³, 0.5 mol) were heated to 80 °C for 12 h and subsequently under reflux until nitrogen evolution had ceased. After removal of excess of $SiMe_3N_3$ the residue was carefully fractionated in high vacuum (1 Pa). The yield of compound 1 was 78 g (90%), as a colourless oily liquid of b.p. 125 °C (1 Pa), which solidified partially as colourless needles on prolonged standing. The properties are consistent with those given in ref. 12.

[$ZrCl_3(Me_3SiNPPh_2NSiMe_3)$]·MeCN 5a. The compound $ZrCl_4$(2.4 g, 10 mmol) and 1 (4.3 g, 10 mmol) were stirred in CH_2Cl_2 (100 cm³) at 0 °C for 2 h. After filtration of insoluble material, volatiles were evaporated and the residue redissolved in MeCN (80 cm³). After several days at −25 °C crystallisation started. Compound 5a crystallises as colourless needles of m.p. 135 °C (decomp.). Additional crops up to a total of 4.8 g (80%) can be obtained by concentrating the solution (Found: C, 40.3; H, 5.6; Cl, 17.7; N, 7.1. $C_{20}H_{31}Cl_3N_3PSi_2Zr$ requires C, 40.15; H, 5.20; Cl, 17.80; N, 7.00%), δ(P) ($CD_3CN–CH_2Cl_2$) 38.8 ppm.

[$\{TiCl_2(OPPh_2N)\}_2$]·4MeCN 7a. The compound $TiCl_4$ (3.8 g, 20 mmol) was transferred *in vacuo* into a mixture of $Me_3SiOPPh_2NSiMe_3$ 6 (7.2 g, 20 mmol) and MeCN (120 cm³) at −190 °C. After warming the solution was stirred at ambient temperature for 12 h. Insoluble material was filtered off and volatiles were removed. The yellowish brown residue was redissolved in a little MeCN and kept for crystallisation at −25 °C. Filtration and concentration of the mother-liquor gave a total yield of compound 7a of 5g (65%), m.p. 168 ± 2 °C (decomp.) (Found: C, 46.4; H, 4.2; Cl, 16.2; N, 9.0. $C_{32}H_{32}Cl_4N_6O_2P_2Ti_2$ requires C, 46.20; H, 3.90; Cl, 17.05; N, 10.10%), δ(P) ($CDCl_3–MeCN$) 35.4 ppm.

[$\{VCl_2(NPPh_2N)\}_2$] 9. The compound $[VCl_3(NSiMe_3)]$ (2.4

Table 5 Atomic coordinates ($\times 10^4$) for compound **5a**

Atom	x	y	z
Zr	8 964(1)	7 942(1)	8 327(1)
Cl(1)	7 653(1)	7 502(1)	9 416(1)
Cl(2)	11 133(1)	8 287(1)	9 194(1)
Cl(3)	9 968(2)	6 779(1)	7 949(1)
Si(1)	10 367(2)	8 299(1)	6 423(1)
Si(2)	7 062(2)	9 517(1)	8 959(1)
P	8 339(1)	9 201(1)	7 351(1)
N(1)	9 267(4)	8 485(2)	7 184(2)
N(2)	7 957(4)	9 021(2)	8 257(2)
N(3)	6 927(5)	7 495(2)	7 474(3)
C(1)	6 754(5)	9 286(3)	6 602(3)
C(2)	5 689(6)	9 786(3)	6 711(3)
C(3)	4 425(6)	9 813(3)	6 154(3)
C(4)	4 250(6)	9 341(3)	5 493(3)
C(5)	5 302(7)	8 849(3)	5 381(3)
C(6)	6 543(6)	8 814(3)	5 930(3)
C(11)	9 406(5)	10 017(3)	7 282(3)
C(12)	10 799(6)	10 009(3)	7 729(3)
C(13)	11 743(6)	10 567(3)	7 605(3)
C(14)	11 330(6)	11 125(3)	7 063(3)
C(15)	9 957(6)	11 148(3)	6 642(3)
C(16)	9 001(6)	10 593(3)	6 761(3)
C(21)	9 723(7)	7 456(3)	5 847(4)
C(22)	10 340(7)	9 074(3)	5 676(3)
C(23)	12 221(6)	8 175(3)	6 939(4)
C(31)	7 206(8)	10 520(3)	8 787(4)
C(32)	7 958(7)	9 353(3)	10 026(3)
C(33)	5 159(6)	9 217(4)	8 865(4)
C(41)	6 120(6)	7 273(3)	6 952(3)
C(42)	5 128(6)	6 989(3)	6 292(3)

Table 6 Atomic coordinates ($\times 10^4$) for compound **7a**

Atom	x	y	z
Ti(1)	2218(1)	4983(1)	1272(1)
Cl(1)	2960(1)	4751(1)	3115(1)
Cl(2)	3546(1)	3911(1)	783(1)
P(1)	875(1)	5880(1)	−1004(1)
O(1)	1972(2)	5533(1)	−127(1)
N(1)	632(2)	4501(1)	1124(1)
C(1)	1474(2)	5754(1)	−2223(2)
C(2)	2849(3)	5638(2)	−2216(2)
C(3)	3306(3)	5582(2)	−3166(2)
C(4)	2398(3)	5645(2)	−4114(2)
C(5)	1033(3)	5764(2)	−4126(2)
C(6)	553(3)	5814(2)	−3186(2)
C(7)	754(2)	6982(1)	−803(2)
C(8)	−491(3)	7392(2)	−1113(2)
C(9)	−569(3)	8247(2)	−984(2)
C(10)	579(3)	8690(2)	−544(2)
C(11)	1813(3)	8294(2)	−233(2)
C(12)	1916(3)	7435(2)	−364(2)
N(2)	4181(2)	5813(1)	1493(2)
C(13)	5159(3)	6188(2)	1625(2)
C(14)	6422(3)	6673(2)	1815(3)
N(3)	1392(2)	6173(1)	1752(2)
C(15)	886(3)	6786(2)	1875(2)
C(16)	213(3)	7579(2)	2002(3)

X-Ray Structure Analyses.—Crystals of compounds **5a** and **7a** suitable for diffraction studies were obtained by crystallisation from MeCN at −25 °C. Both structures were studied on a Stoe-Siemens four-circle diffractometer with graphite-monochromated Mo-Kα radiation. Data were collected at −85 °C with a profile-fitting method,[23] $2\theta_{max} = 45°$ for **5a** and 50° for **7a**, and reflections with $|F| > 3\sigma F$ for **5a** and $|F| > 4\sigma F$ for **7a** respectively 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. All calculations were performed with the programs SHELXS 86[24] and SHELX 76.[25] Crystallographic data for compounds **5a** and **7a** are shown in Table 4, atomic coordinates in Tables 5 and 6.

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

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g, 10 mmol) and $ClPPh_2NSiMe_3$ **10** (3.1 g, 10 mmol) in MeCN (120 cm³) were warmed to 40 °C for 4 h. The brick-red solid was filtered off, washed with a little MeCN, and dried *in vacuo*. The yield of analytically pure compound **9**, m.p. 235 °C (decomp.), was 2.5 g (75%) (Found: C, 42.2; H, 3.2; Cl, 21.3; N, 8.4. $C_{24}H_{20}Cl_4N_4P_2V_2$ requires C, 43.00; H, 3.00; Cl, 21.15; N, 8.35%), $\delta(P)$ (CDCl$_3$–CH$_2$Cl$_2$) −10.2 ppm, $w_{\frac{1}{2}} \approx 1500$ Hz. EI MS: m/z 670 (M, 23), 533 (M − NVCl$_2$, 100), 497 (M − NVCl$_2$ − HCl, 79), and 456 (M − NVCl − Ph, 37%).

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