3476 *Inorg. Chem.* **1997,** *36,* 3476−3479

Synthesis and Structural Characterization of P-Functionalized Metallacyclophosphazenes[†]

Michael Witt, Herbert W. Roesky,* and Matthias Noltemeyer

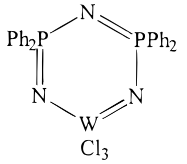
Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

Received October 24, 1996[⊗]

A facile, high-yield synthesis of $Cl_3VNSiMe_3$ (**1**) is reported. **1** and the metal nitride halides Cl_3MoN and Cl_3WN react with $[\{(Me_2N)_2PNH_2\}_2N]^+Cl^-$ to form the six-membered metallacyclophosphazenes $[(Me_2N)_2PN]_2VCl_2$ (**2**), $[(Me_2N)_2PN]_2MoCl_3{\cdot}MeCN$ (**3**), and $[(Me_2N)_2PN]_2WCl_3{\cdot}MeCN$ (**4**), respectively. The X-ray structure determinations of **2** and **3** show the compounds to have planar six-membered rings of distorted geometry.

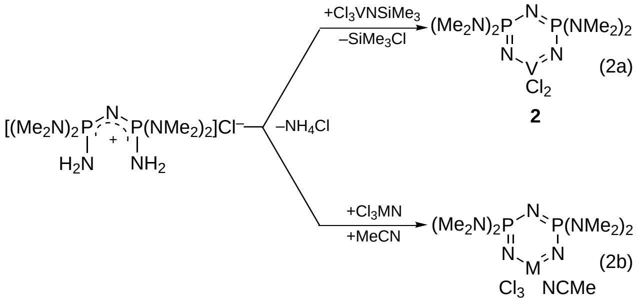
Introduction

In 1986 we described the first metallacyclophosphazene **A** prepared by reaction of an acyclic phosphazene precursor using tungsten hexachloride under evolution of hydrogen chloride.[1] Subsequently, other metals like V, Nb, Mo, and Re were incorporated into the phosphazene skeleton.[2] Variation of the substituents on phosphorus was limited to carbon species such as CF_3,[3] Me, 4-ClC_6H_4,[4] and a cyclic amine, $N(CH_2)_2O$,[5] respectively. The chemistry of these systems was limited to ligand exchange at the metal center[2b,6] and polymerization reactions of the phenyl-substituted systems.[7] We were interested in elucidating the reactivity of the phosphorus-bound substituents under retention of the ring skeleton. Herein, we report on a dimethylamino-substituted phosphazene precursor. The amino group can be easily substituted by halides,[8] and the starting material is easily available.[9] Because of the instability of the P−N bond in the presence of hydrogen chloride, metal nitride halides were employed for synthesizing the six-membered heterocycles **2**−**4** according to eqs 2a and 2b. Moreover, a new route for the vanadium precursor **1** is described (eq 1). The X-ray structures of compounds **2** and **3** are also reported.



A

$$(Me_3SiO)_3V{=}NSiMe_3 + 3TiCl_4 \longrightarrow \underset{\mathbf{1}}{Cl_3V{=}NSiMe_3} + 3Me_3SiOTiCl_3 \quad (1)$$



M: Mo, **3**; W, **4**

Experimental Section

All manipulations were carried out in an atmosphere of dry nitrogen or argon. Solvents were distilled under dry nitrogen from the appropriate drying agents. The starting materials $[\{(Me_2N)_2PNH_2\}_2N]^+Cl^-$,[9] $(Me_3SiO)_3V{=}NSiMe_3$,[10] $Cl_3Mo{\equiv}N$,[11] and $Cl_3W{\equiv}N$[12] were synthesized according to the literature.

^1H, ^{29}Si, ^{31}P, and ^{51}V NMR spectra were recorded on Bruker AM 200, AM 250, and MSL 400 instruments, using $SiMe_4$, 85% H_3PO_4, and $VOCl_3$ as external standards, respectively. EI mass spectra were recorded on Varian MAT CH5 and Finnigan MAT 8230 systems, and infrared spectra on a Bio-Rad FTS-7 spectrophotometer as Nujol mulls between KBr plates. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie und Mikroanalytisches Laboratorium Beller, Göttingen, Germany. Melting points were determined on a digital HWS-SG 3000 apparatus in sealed capillaries.

Preparation of $Cl_3VNSiMe_3$ (1). $(Me_3SiO)_3VNSiMe_3$ (20.3 g, 50 mmol) was dissolved in hexane (150 mL), the solution was cooled to −40 °C, and excess $TiCl_4$ (e.g. 36 g, 190 mmol) was added using a dropping funnel at that temperature. The mixture was slowly warmed to room temperature and stirred for an additional 2 h. The solvent was slowly evaporated through a sublimation apparatus held at +5 °C. The temperature then was raised to 8−10 °C and the brownish-yellow residue fractionally sublimed in high vacuum to leave **1** as bright orange crystals in the sublimator and $TiCl_{4-x}(OSiMe_3)_x$ as opaque off-white crystals, which depending on the V/Ti ratio might liquefy in the trap

---

[†] Dedicated to Professor Klaus Weissermel on the occasion of his 75th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) Roesky, H. W.; Katti, K. V.; Seseke, U.; Witt, M.; Egert, E.; Herbst, R.; Sheldrick, G. M. *Angew. Chem.* **1986**, *98*, 447; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 477.

(2) (a) Roesky, H. W.; Katti, K. V.; Seseke, U.; Schmidt, H.-G.; Egert, E.; Herbst, R.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1987**, 847. (b) Katti, K. V.; Roesky, H. W.; Rietzel, M. *Inorg. Chem.* **1987**, *26*, 4032. (c) Olms, P.; Roesky, H. W.; Keller, K.; Noltemeyer, M.; Bohra, R.; Schmidt, H.-G.; Stalke, D. *Chem. Ber.* **1991**, *124*, 2655. (d) Hasselbring, R.; Roesky, H. W.; Noltemeyer, M. *Angew. Chem.* **1992**, *104*, 613; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 601.

(3) Roesky, H. W.; Olms, P.; Witt, M.; Keller, K.; Stalke, D.; Henkel, T.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1989**, 366.

(4) Liebermann, J. Dissertation, Universität Göttingen, 1989.

(5) Witt, M.; Roesky, H. W. *Polyhedron* **1989**, *8*, 1736.

(6) Rietzel, M. Dissertation, Universität Göttingen, 1989.

(7) Roesky, H. W.; Lücke, M. *Angew. Chem.* **1989**, *101*, 480; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493.

(8) Allen, C. W. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I., Sowerby, D. W., Eds.; Academic Press: London, 1987; Vol. 2, p 501.

(9) Schmidpeter, A.; Weingand, C.; Hafner-Roll, E. *Z. Naturforsch.* **1969**, *24B*, 799.

(10) Becker, F. *J. Organomet. Chem.* **1973**, *51*, C9.

(11) Dehnicke, K.; Weiher, U.; Strähle, J. *Z. Naturforsch.* **1977**, *32B*, 1484.

(12) Godemeyer, T.; Berg, A.; Gross, H.-D.; Müller, U.; Dehnicke, K. *Z. Naturforsch.* **1985**, *40B*, 999.

S0020-1669(96)01284-0 CCC: $14.00

Table 1. Crystal Data and Structure Refinement Details for $C_8H_{24}Cl_2N_7P_2V$ (**2**) and $C_{10}H_{27}Cl_3MoN_8P_2$ (**3**)

	2	**3**
fw	402.12	523.63
temp (°C)	−140(2)	−140(2)
wavelength (Å)	0.710 73	0.710 73
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
Z	4	8
a (Å)	10.763(3)	26.479(6)
b (Å)	9.572(2)	9.9570(10)
c (Å)	18.704(10)	17.136(2)
β (deg)	96.31(4)	94.411(10)
V (Å)	1915.3(12)	4504.5(12)
ρ_{calcd} (g cm^{-3})	1.395	1.544
abs coeff (mm^{-1})	0.965	1.091
$F(000)$	832	2128
crystal size	0.80 × 0.80 × 0.60	0.60 × 0.50 × 0.40
θ range (deg)	3.73 to 22.50	3.75 to 22.54
limiting indices	$-11 \leq h \leq 11$, $-10 \leq k \leq 10$, $-20 \leq l \leq 20$	$-28 \leq h \leq 28$, $-10 \leq k \leq 10$, $0 \leq l \leq 18$
no. of reflns collected	4734	2864
no. of independent reflns	2495 ($R_{int} = 0.0333$)	2857 ($R_{int} = 0.0093$)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	2494/0/189	2856/0/226
goodness-of-fit on F^2	1.054	1.099
final R indices [$I > 2\sigma(I)$]	R1 = 0.0483, wR2 = 0.1273	R1 = 0.0205, wR2 = 0.0514
R indices (all data)[a]	R1 = 0.0509, wR2 = 0.1331	R1 = 0.0222, wR2 = 0.0530
largest diff peak and hole (e nm^{-3})	756 and −720	354 and −360

[a] $wR2 = \{[\sum w(F_c^2 - F_o^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

on warming to room temperature. The product obtained from a single sublimation, 8.5 g (35 mmol, 70%), was sufficiently pure for further reactions; analytically pure **1** resulted from repeated sublimations.

Analytical data are consistent with those previously reported.[13,14] ^{29}Si NMR ($CDCl_3$, 49 MHz): δ 39 ppm, $\Delta_{1/2}$ ca. 150 Hz. ^{51}V NMR ($CDCl_3$, 65 MHz): 15.3 ppm, $\Delta_{1/2}$ ca. 240 Hz. MS (EI): *m/z* 245 (M, 2), 229 (M − Me − H, 100), 93 (Me_2SiCl, 80), 73 (Me_3Si, 55).

General Procedure for the Synthesis of 2−4. The metal nitride (10 mmol) and $[\{(Me_2N)_2PNH_2\}_2N]^+Cl^-$ (3.2 g, 10 mmol) were mixed in a glovebox, and CH_2Cl_2 (75 mL) was condensed into the mixture at −190 °C *in vacuo*. The mixture was slowly warmed to room temperature and stirred for 36 h, after which it was filtered to remove NH_4Cl. After removal of all volatiles, the foamy reddish to orange residues were redissolved in MeCN (50 mL), and the mixture was filtered through a layer of Celite. The yields of NH_4Cl and the purity of the crude heterocycles were >90% as seen from ^{31}P NMR spectra.

$[(Me_2N)_2PN]_2NVCl_2$ (2). The MeCN solution was concentrated to 25 mL and placed in a freezer at −35 °C. After several days, orange-yellow blocks had formed in ca. 40% yield (1.6 g, 4 mmol). These were filtered off in the cold and dried *in vacuo*. Mp: 155 °C. ^{1}H NMR (CD_3CN, 200 MHz): δ 2.61 ppm (pseudo-t). ^{31}P NMR (CD_3CN, 101 MHz): δ 40 ppm, $\Delta_{1/2}$ ca. 650 Hz. ^{51}V NMR (CD_3CN, 66 MHz): δ 7.7 ppm, $\Delta_{1/2}$ ca. 250 Hz. MS (EI): *m/z* 401 (M, 15), 358 (M − NMe_2 + H, 33) 322 (M − NMe_2 − Cl − 2H, 18), 315 (M − 2NMe_2 + 2H, 18), 279 (M − 3NMe_2 + 2H, 19), 44 (NMe_2, 100%). IR: ν 1302 vst, 1221 vst, 1178 vst, 1147 sh, 1065 vst, 994 vst, 943 vst, 851 st, 754 st, 729 st, 714 m, 628 st, 505 st, 444 m, 419 st, 406 m, 380 m cm^{-1}. Anal. Calcd for $C_8H_{24}Cl_2N_7P_2V$ (M_r = 402.12): C, 23.90; H, 6.02; N, 24.38; P, 15.40. Found: C, 23.7; H, 5.8; N, 23.2; P, 14.2.

$[(Me_2N)_2PN]_2NMoCl_3{\cdot}MeCN$ (3). The MeCN was evaporated and replaced by $CHCl_3$, the solution transferred to a two-legged Schlenk apparatus,[15] and the solvent slowly transferred *in vacuo* from one leg into the other using a temperature gradient of 20 → 18 °C. Residual mother liquor was filtered off, the solvent recondensed, and the procedure repeated twice. Finally, the solvent was stripped off to yield 2.9 g (55%, 5.5 mmol) of **3** as orange crystals. Mp: 212 °C dec. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.75 (s, CH_3CN), 2.69 (pseudo-t, CH_3N) ppm. ^{31}P NMR ($CDCl_3$, 101 MHz): δ 41.1 ppm. MS (EI): *m/z* 448 (M − MeCN − Cl, 12), 360 (M − MeCN − Cl − 2NMe_2, 6), 44 (NMe_2, 100%). IR: ν 1302 vst, 1242 vst, 1185 sh, 1171 st, 1057 vst, 996 vst, 842 m, 763 m, 718 st, 610 m, 510 st, 423 m, 370 st cm^{-1}. Anal. Calcd for $C_{10}H_{27}Cl_3MoN_8P_2$ (M_r = 523.63): C, 22.94; H, 5.20; Cl, 20.31; N, 21.40; P, 11.83. Found: C, 22.1; H, 4.0; Cl, 20.9; N, 20.4; P, 11.2.

$[(Me_2N)_2PN]_2NWCl_3{\cdot}MeCN$ (4). The procedure for the isolation of **4** was as described for **3**, leaving 2.2 g (36%, 3.6 mmol) **4** as light orange crystals. Mp: 226 °C dec. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 2.79 (s, CH_3CN), 2.70 (pseudo-t, CH_3N) ppm. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 39.7 ppm ($^2J_{^{31}P-^{183}W}$ 89 Hz). MS (EI): *m/z* 536 (M − MeCN − Cl, 100), 492 (M − MeCN − Cl − NMe_2, 8), 448 (M − MeCN − Cl − 2NMe_2, 13), 44 (NMe_2, 53%). IR: ν 1300 vst, 1239 vst, 1186 sh, 1171 vst, 1056 vst, 984 vst, 917 vst, 842 st, 763 st, 719 st, 701 m, 626 m, 609 st, 509 st, 450 m, 423 m, 372 st, 320 vst cm^{-1}. Anal. Calcd for $C_{10}H_{27}Cl_3N_8P_2W$ (M_r = 611.54): C, 19.64; H, 4.45; N, 17.03; P, 10.14. Found: C, 18.3; H, 5.01; N, 18.3; P, 9.5.

X-ray Data Collection, Structure Solution, and Refinement of 2 and 3. Crystals suitable of **2** and **3** for X-ray diffraction were obtained by treating pure samples as described in the respective sections. The crystals were mounted on glass fibers in a rapidly cooled perfluoro polyether.[16] Data were collected on a Siemens-Stoe AED four-circle diffractometer at 153 K with graphite-monochromated Mo Kα radiation (λ = 71.073 pm), on-line profile fitting,[17] and constant scan speed. The structure was solved by the Patterson method with SHELXS-90[18] and refined against F^2 on all data by full-matrix least-squares methods with SHELXL-93.[19] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined using a riding model.

Details of the crystal structure refinement of **2** and **3** are summarized in Table 1. Further details of the structure determination are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW, U.K., on quoting the full journal citation.

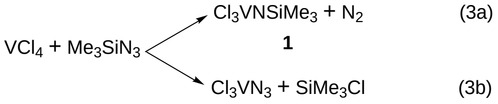
Results and Discussion

The synthesis of metallacyclophosphazenes bearing carbon on phosphorus proceeds straightforwardly from metal halides

---

(13) Schweda, E.; Scherfise, K. D.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *528*, 117.
(14) Critchlow, S. C.; Lerchen, M. E.; Smith, R. C.; Doherty, N. M. *J. Am. Chem. Soc.* **1988**, *110*, 8071.
(15) Hartmann, G.; Froböse, R.; Mews, R.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37B*, 1234.
(16) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.
(17) Clegg, W. *Acta Crystallogr.* **1981**, *A37*, 22.
(18) Sheldrick, G. M. SHELXS-90. *Acta Crystallogr.* **1990**, *A46*, 467.
(19) Sheldrick, G. M. SHELXL-93. University of Göttingen.

in their highest oxidation states with evolution of hydrogen chloride.[2] However, a different strategy has to be employed for P-functional heterocycles. The use of nitrogen bases as HCl scavengers only results in the formation of open-chain metallaphosphazenes.[5,20] The use of metal nitride halides provides an easy access to these systems. While high-yield syntheses for Cl_3MoN and Cl_3WN have been described, only two low-yield preparations of **1** (eqs 3a[13] and 4[14]) have been published.



$$VCl_4 + Me_3SiN_3 \begin{cases} \rightarrow \underset{\mathbf{1}}{Cl_3VNSiMe_3} + N_2 & (3a) \\ \rightarrow Cl_3VN_3 + SiMe_3Cl & (3b) \end{cases}$$

$$(Me_3SiO)_3VNSiMe_3 + 3VOCl_3 \longrightarrow \underset{\mathbf{1}}{Cl_3VNSiMe_3} + 3Me_3SiOV(O)Cl_2 \quad (4)$$

Several explosions occurred in our laboratory in the synthesis of **1** according to the competing formation of vanadium(+IV) azide trichloride (eq 3b) (and not vanadium trichloride as stated by Dehnicke et al.[13]). The second method is somewhat tedious because of low-temperature workup accompanied by substantial loss due to the excellent solubility even at that temperature. We re-examined this reaction using $TiCl_4$ instead of $VOCl_3$, since the volatility of $Me_3SiOTiCl_3$[21] is somewhat higher than that of the corresponding vanadyl ester.[22] By fractional sublimation through a condenser held at 8−10 °C, we were able to isolate **1** in 70% yield. The ^{51}V NMR spectrum recorded in $CDCl_3$ shows a downfield shift of ca. 5 ppm in comparison to the spectrum recorded in C_6D_6[14] with a half-width of ca. 240 Hz often found in tetracoordinated V(+V) compounds.[23] The ^{29}Si spectrum of **1** consists of an unresolved peak with a half-width of ca. 150 Hz.

When the metal nitride chlorides and the phosphazenium chloride are stirred in methylene chloride, clear dark brown solutions in the case of the group 6 metals and a dark red solution in the vanadium case result, from which ammonium chloride subsequently precipitates accompanied by a color change to red-orange. The first step of the reaction is the formation of the nitride chloride metalate anion by transferring the chloride to the metal (eq 5). Subsequently multistep transfer

$$[\{(Me_2N)_2PNH_2\}_2N]^+Cl^- + Cl_3WN \longrightarrow [\{(Me_2N)_2PNH_2\}_2N]^+[Cl_4WN]^- \quad (5)$$

of protons to the nitride results in the formation of the metallaheterocycles **2**−**4**. Filtration and evaporation of volatiles result in foamy orange residues which are soluble in polar solvents such as CH_3CN, CH_2Cl_2, $CHCl_3$, and THF and insoluble in ether and hydrocarbons. Mixture of polar and nonpolar solvents always yields red oily residues. As seen from the ^{31}P NMR spectra, the yields and purities of **2**−**4** exceed 90%; they can be purified by recrystallization from CH_3CN at −35 °C or by slow evaporation of the solvent in a temperature gradient with substantial loss. Impurities seem to increase the solubility; pure crystalline material of **2**−**4** redissolves only slowly. Monitoring the reaction by ^{31}P NMR spectroscopy shows the transient formation of a species with two different phosphorus atoms having doublets at ca. 42 and 36 ppm, respectively. The intensities of the transient signals decrease as the product signal increases. The ^{31}P signals of compounds **2**−**4** are shifted ca. 20 ppm downfield from that ofthe starting material to ca. 40 ppm. Similar shifting was observed previously for phenyl-[2] and morpholino-substituted phosphazenes.[5] The phosphorus resonance of **2** ought to show eight equidistant lines by coupling with the $S = {}^7/_2$ nucleus ^{51}V. Instead, a plateau-like signal with a half-width of ca. 650 Hz is observed due to a slow relaxation,[23] and the $^{31}P-^{51}V$ coupling constant can be estimated to be ca. 82 Hz. The $^{31}P-^{183}W$ coupling in **4** is well resolved with a value of 89 Hz. The ^1H spectra of **2**−**4** exhibit "virtual coupling"[24] of the protons to the more distant phosphorus atoms in the $A_{12}XX'A'_{12}$ systems, yielding "inverse" triplets (Figure 1).

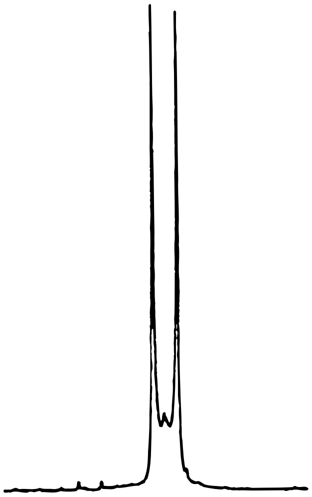


Figure 1. ^1H NMR of **3**.

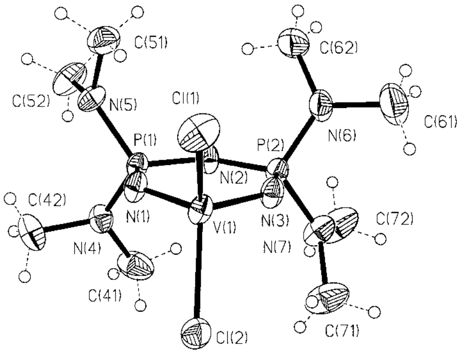


Figure 2. Crystal structure of **2**.

Cooling a solution of prepurified **2** to −35 °C yields crystals suitable for an X-ray structure determination (Figure 2). Selected bond lengths and angles are given in Table 2.

Crystals of **3** suitable for structural investigations were grown by slow evaporation of a concentrated $CHCl_3$ solution *in vacuo* in a temperature gradient of 20 → 18 °C. The crystal structure is shown in Figure 3, and selected bond lengths and angles are given in Table 3.

Both compounds exhibit an essentially planar six-membered ring with obtuse angles at the nitrogen atoms and acute angles at both the phosphorus and metal atoms, a feature that has been found also in the structures of the previously investigated phenyl-[2c] and CF_3-substituted vanadacyclophosphazenes[3] and the phenyl-substituted molybdenum heterocycle.[2a] Both compounds have almost planar NMe_2 groups, a common feature of dimethylamino heteroelement compounds.[25] Both compounds show strong dissymmetry in the solid state probably due to packing effects.

---

(20) Witt, M.; Roesky, H. W. Unpublished.
(21) Andrianov, K. A.; Dulova, V. G. *Izv. Akad. Nauk, Otd. Khim.* **1958**, 644; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1958**, 626.
(22) Schmidt, M.; Schmidbaur, H. *Angew. Chem.* **1959**, *71*, 220.
(23) Rehder, D. *Magn. Reson. Rev.* **1984**, *9*, 125.
(24) (a) Becker, E. D. *High Resolution NMR. Theory and Applications*, 2nd ed.; Academic Press: New York, 1980; p 163 f. (b) Diehl, P.; Harris, R. K.; Jones, R. G. *Prog. NMR Spectrosc.* **1967**, *3*, 1.
(25) E.g.: Bullen, G. J. *J. Chem. Soc.* **1962**, 3193.

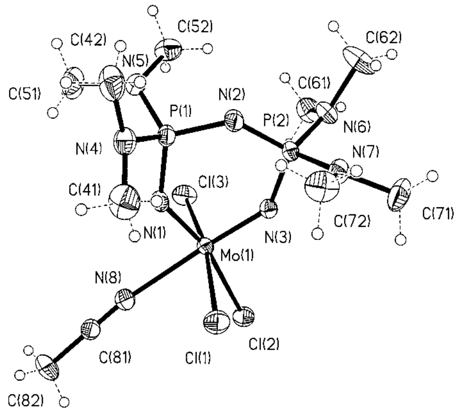


Figure 3. Crystal structure of **3**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

V(1)−N(1)	1.693(3)	V(1)−N(3)	1.693(3)
V(1)−Cl(1)	2.2335(12)	V(1)−Cl(2)	2.2368(14)
N(1)−P(1)	1.666(3)	N(2)−P(1)	1.583(3)
N(2)−P(2)	1.583(3)	N(3)−P(2)	1.666(3)
N(4)−P(1)	1.636(3)	N(5)−P(1)	1.643(3)
N(6)−P(2)	1.627(3)	N(7)−P(2)	1.632(3)
N(4)−C(41)	1.444(5)	N(4)−C(42)	1.461(5)
N(6)−C(61)	1.470(5)	N(6)−C(62)	1.438(5)

N(1)−V(1)−Cl(1)	1.1054(11)	N(1)−V(1)−Cl(2)	1.0899(11)
N(3)−V(1)−Cl(1)	1.1106(11)	N(3)−V(1)−Cl(2)	1.0827(10)
Cl(1)−V(1)−Cl(2)	1.1540(5)	N(1)−V(1)−N(3)	1.0167(14)
V(1)−N(1)−P(1)	1.332(2)	N(1)−P(1)−N(2)	1.111(2)
P(1)−N(2)−P(2)	1.292(2)	N(2)−P(2)−N(3)	1.116(2)
P(2)−N(3)−V(1)	1.328(2)	N(1)−P(1)−N(4)	1.120(2)
N(1)−P(1)−N(5)	1.041(2)	N(2)−P(1)−N(4)	1.086(2)
N(2)−P(1)−N(5)	1.158(2)	N(4)−P(1)−N(5)	1.051(2)
N(2)−P(2)−N(6)	1.072(2)	N(2)−P(2)−N(7)	1.161(2)
N(3)−P(2)−N(6)	1.131(2)	N(3)−P(2)−N(7)	1.041(2)
N(6)−P(2)−N(7)	1.047(2)	C(41)−N(4)−P(1)	1.216(3)
C(42)−N(4)−P(1)	1.206(3)	C(41)−N(4)−C(42)	1.152(3)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Mo(1)−N(1)	1.776(2)	Mo(1)−N(3)	1.754(2)
Mo(1)−Cl(1)	2.3965(7)	Mo(1)−Cl(2)	2.5100(7)
Mo(1)−Cl(3)	2.4068(8)	Mo(1)−N(8)	2.396(2)
N(1)−P(1)	1.663(2)	N(2)−P(1)	1.580(2)
N(2)−P(2)	1.579(2)	N(3)−P(2)	1.681(2)
N(4)−P(1)	1.634(2)	N(5)−P(1)	1.621(2)
N(6)−P(2)	1.624(2)	N(7)−P(2)	1.618(2)
N(4)−C(41)	1.460(4)	N(4)−C(42)	1.467(4)
N(6)−C(61)	1.461(3)	N(6)−C(62)	1.472(3)
N(8)−C(81)	1.134(3)		

Cl(1)−Mo(1)−Cl(2)	0.8494(2)	Cl(2)−Mo(1)−Cl(3)	0.8572(2)
N(1)−Mo(1)−Cl(1)	0.9374(7)	N(1)−Mo(1)−Cl(13)	0.9237(7)
N(1)−Mo(1)−N(8)	0.8649(8)	N(3)−Mo(1)−Cl(1)	0.9663(7)
N(3)−Mo(1)−Cl(2)	0.9865(2)	N(3)−Mo(1)−Cl(3)	0.9593(7)
N(1)−Mo(1)−N(3)	0.9632(9)	P(1)−N(1)−Mo(1)	1.3521(12)
N(1)−P(1)−N(2)	1.0959(11)	P(1)−N(2)−P(2)	1.3172(13)
N(2)−P(2)−N(3)	1.0912(10)	P(2)−N(3)−Mo(1)	1.3628(12)
N(1)−P(1)−N(4)	1.0465(11)	N(1)−P(1)−N(5)	1.1092(11)
N(2)−P(1)−N(4)	1.1626(12)	N(2)−P(1)−N(5)	1.0941(11)
N(4)−P(1)−N(5)	1.0588(11)	N(2)−P(2)−N(6)	1.1752(12)
N(2)−P(2)−N(7)	1.0908(11)	N(3)−P(2)−N(6)	1.0399(10)
N(3)−P(2)−N(7)	1.1141(11)	N(6)−P(2)−N(7)	1.0561(11)
C(41)−N(4)−P(1)	1.196(2)	C(42)−N(4)−P(1)	1.194(2)
C(41)−N(4)−C(42)	1.143(2)	C(81)−N(8)−Mo(1)	1.725(2)
N(8)−C(81)−C(82)	1.788(3)		

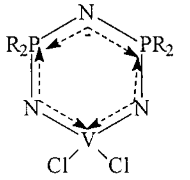
Table 4. Comparison of Bond Lengths (Å) and Angles (deg) in the Vanadacyclophosphazenes $(R_2PN)_2NVCl_2$

	R		
	Ph[2c,a]	NMe_2 (**2**)	CF_3[3]
V(1)−N(1)/V(1)−N(3)	1.689	1.693(3)	1.720(6)
N(1)−P(1)/N(3)−P(2)	1.666	1.666(3)	1.613(5)
N(2)−P(1)/N(2)−P(2)	1.582	1.583(3)	1.595(3)
V(1)−Cl	2.222	2.235	2.160(2)
N(1)−V(1)−N(3)	102.1	101.67(14)	104.2(4)
V(1)−N(1)−P(1)/V(1)−N(3)−P(2)	132.0	133.0	129.0(4)
N(1)−P(1)−N(2)/N(2)−P(2)−N(3)	112.9	111.4	118.1(3)
P(1)−N(2)−P(3)	126.7	129.2(2)	121.3(4)
Cl(1)−V(1)−Cl(2)	114.2	115.40(5)	111.9(1)[b]

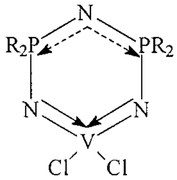
[a] Averaged over both molecules in the asymmetric unit. [b] Reference 27.

The NMe_2 groups of the two compounds have two different N−C distances; the difference is ca. 0.015 Å for **2** and ca. 0.01 Å for **3**. The exocyclic P−N bonds in **2** (average 1.635 Å) and **3** (average 1.625 Å) are shorter than a P(V)−N single bond (averaging 1.67−1.68 Å.[25,26]). A comparison of the bond lengths and angles of the three known six-membered vanadacyclophosphazenes (Table 4) shows that **2** resembles the phenyl-substituted system more closely than the CF_3-substituted system, besides not having C_{2v} symmetry.

Ehrig and Ahlrichs have calculated the electronic structure of the CF_3-substituted ring by population analysis. They concluded from their results a bonding situation where the nitrogen lone pairs are partially delocalized into low-lying orbitals of phosphorus and vanadium (**B**), which is consistent with the almost equal P−N distances. In contrast, the rather short P−N bonds opposite to the metal and the long P−N bonds adjacent and the shorter V−N bonds in **2** favor an electronic structure (**C**) with less delocalization. Both the V−N separations in **2** and the Mo−N bonds in **3** are on the upper limit for reported metal−nitrogen double bonds with the metals in their highest oxidation states.[28]



B



C

Compounds **2**−**4** seem to be suitable precursors for ligand exchange reactions at the phosphorus centers, e.g. with halides or alkoxides.[8] Preliminary investigations showed that the yellow compound **2** forms upon action of hydrogen chloride, even at −100 °C, an orange material of probably polymeric nature totally insoluble in common solvents. Further investigations are in progress.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of non-hydrogen coordinates and isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions and isotropic thermal parameters for **2** and **3** (8 pages). Ordering information is given on any current masthead page.

IC961284K

---

(26) Allcock, H. R. *Phosphorus-Nitrogen Compounds;* Academic Press: New York and London, 1972.

(27) Roesky, H. W.; Sheldrick, G. M. Private communication (from ref 28).

(28) Ehrig, M.; Ahlrichs, R. *Theor. Chim. Acta* **1992**, *81*, 245.

(29) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Double Bonds*; Wiley: New York, 1988.