# BIFUNCTIONAL PHOSPHAZENES—PRECURSORS FOR THE SYNTHESIS OF CYCLIC AND ACYCLIC METALLAPHOSPHAZENES

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Abstract—Several pathways for the synthesis of six-membered metallacyclophosphazenes  $Cl_xMPR_2NPR_2N$  with different substituents on phosphorus are reported. Acyclic intermediates are discussed. The reaction of a persilylated aminophosphazene, 7, with VOCl<sub>3</sub> affords the eight-membered ring  $(Cl_2VNPPh_2N-)_2$  (**6b**), WCl<sub>6</sub> yields an acyclic compound, 8, and group IV tetrachlorides lead to the formation of four-membered rings, 9, with a NPNM-skeleton. Me<sub>3</sub>SiOPPh<sub>2</sub>NSiMe<sub>3</sub> (**10**) and TiCl<sub>4</sub> form an eight-membered ring  $(Cl_2TiNPPh_2O-)_2$  (**11**) with the shortest Ti—N bond found so far. The X-ray structures of each type of metallacyclophosphazenes are discussed.

Depending on the nature of the ligands, metal chelates have been found useful catalysts in various aspects of organic chemistry.<sup>1</sup> Thus, we were interested in synthesizing metallaphosphazenes to test their applicability in catalysis. Furthermore, another crucial aspect of our work is the vast area of phosphazene chemistry, namely poly-<sup>2</sup> and cyclophosphazenes.<sup>2,3</sup> Incorporating metal centres in phosphazenes might afford materials with unusual properties depending on the metal atom and the substituents on both the metal and phosphorus centres. In this paper we summarize our present results in building up novel ring systems and open-chain compounds, as well as in attaching new organic groups on phosphorus.

# **RESULTS AND DISCUSSION**

Recently, we have reported the synthesis of metallatriazadiphosphorines, **2a**-e, from the reactions of  $[H_2NPPh_2NPPh_2NH_2]^+Cl^-$  (**1a**) with metal halides or metal nitride halides in their highest oxidation state, or by passing chlorine through solutions containing lower metal halides [eq. (1)]:<sup>4</sup>



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Starting from the *p*-chlorophenyl-, 1b, and methylsubstituted, 1c, precursors, the metallacycles 2f-jhave been synthesized according to method (ii). The phenoxy-substituted phosphazenium salt failed to form the expected rings.<sup>5</sup>

Since aminophosphazenes are known to be affected by both elemental chlorine and hydrogen chloride,<sup>2</sup> these conditions had to be avoided in the reactions of the amino-substituted phosphain the <sup>31</sup>P NMR spectrum.<sup>7</sup> In the reaction of 1e with NbCl<sub>5</sub> and pyridine an open chain compound, 4, has been isolated as the sole product as shown by <sup>31</sup>P NMR, IR and elemental analyses.<sup>6</sup> These facts give rise to the reaction sequence depicted in eq. (2):



zenium chlorides, 1d, e. The metallaphosphazenes 2k-n are accessible only to methods (iii) and (iv).<sup>6</sup>

Monitoring the progress of the reactions by  $^{31}P$ NMR spectroscopy showed the mechanism to be rather complex. The first intermediates identified or isolated were the hexachlorometallates **3**, which on heating, e.g. in CHCl<sub>3</sub>, subsequently yield two sets A somewhat surprising product has been found in the reaction of the CF<sub>3</sub>-substituted P-chlorophosphazene, **5a**, and Cl<sub>3</sub>V=NSiMe<sub>3</sub>: instead of the expected eight-membered ring system, **6** (vide infra), the CF<sub>3</sub>-substituted derivative, **2o**, was isolated in low yields as a volatile solid, melting with decomposition at 22.5°C:<sup>8</sup>



of pairs of doublets, indicating unsymmetric acyclic compounds disappearing with the growth of the singlets of **2**.

A second method to avoid acidic conditions,

The expected tetrazadiphosphadivanadocine, 6a, has been isolated in high yields as a brick-red microcrystalline solid from the reaction according to eq. (4):<sup>9</sup>



besides the use of metal nitrides, is the reaction in the presence of a tertiary base, e.g. pyridine. While with 1a and NbCl<sub>5</sub>, 2b is formed, TaCl<sub>5</sub> yields an inseparable mixture of the hexachlorotantalate, 3a, and two compounds showing two pairs of doublets A derivative, **6b**, is accessible via silyl migration from aminoiminophosphorane, **7**, and VOCl<sub>3</sub> in 80% yield, which after recrystallization from  $CH_2Cl_2$ -CH<sub>3</sub>CN forms translucent brick-red rhombs:<sup>9</sup>



Up until now, attempts to extend this synthetic pathway to other tetrazadiphosphadimetallocines have been unsuccessful. The reaction of 7 with WCl<sub>6</sub> yields an acyclic metal-substituted phosphazene, 8, characterized by elemental analysis and NMR spectroscopy [eq. (6)]:<sup>6</sup>



Since multiple bonds to group IV metals are rather unfavourable, the reactions of 7 with  $TiCl_4^{10}$  and  $ZrCl_4^6$  proceed in a different way [eq. (7)]:

## Spectroscopical and X-ray investigations

Mass spectroscopical measurements (EI, FI and FD techniques) show the parent ion or  $M^+ - Cl$  as the peaks with the highest masses for most of the six-membered rings, **2**. Of the eight-membered rings, only tetrazadiphosphadivanadocine, **6a**, gave the molecular ion, as well as the trichlorosubstituted four-membered rings, **9a**, **b**. The other metallaphosphazenes showed fragmentation and rearrangement patterns, e.g. in the EI mass spectrum of **6b**,  $M^+ - Cl$  for **2a** had been detected.<sup>6</sup> Interestingly, the open-chain intermediates  $[H_2N(PPh_2N)_2H_2]^+$   $MCl_6^-$  (**3b-d**) failed to show the signal for the cation. Instead, FI mass spectra consisted of the parent ions of the corresponding six-membered



While the reaction of 7 with  $ZrCl_4$  proceeds unequivocally, TiCl<sub>4</sub> yields a mixture of different products, **9b-d**. By varying the reaction conditions (see Experimental) the yields of the respective compounds could be optimized, the products have been isolated by fractional crystallization from CH<sub>3</sub>CN.

The analogous reaction of silyloxyphosphazene, 10, with  $TiCl_4$  leads to the unexpected formation of the eight-membered ring system, 11, besides several silicon-containing species which have not yet been identified :<sup>11</sup> rings, **2b**–**d**.<sup>6</sup> This is in contrast to the homologous compounds  $[H_2N(PPh_2N)_3H_2]^+MC_6^-$ , where the cation peak, together with the parent ions of the tetrazatriphosphametallocines with intensities between 0 and 30%, have been observed.<sup>12</sup>

<sup>31</sup>P NMR studies show downfield shifts for all metallaheterocycles compared to their acyclic phosphazene precursors. The chemical shifts of the six-membered rings, **2**, have been found 20–30 ppm downfield of the corresponding bis(amino-

$$2 \operatorname{Me_3SiOP} = \operatorname{NSiMe_3} + 2 \operatorname{TiCl_4} \longrightarrow \operatorname{Cl_2Ti\Theta} = \operatorname{O}^{\operatorname{Ph_2}} \operatorname{O}^{\operatorname{$$

phosphoranylidene)immonium precursors,  $1.^{4,5,8}$ While the <sup>31</sup>P signal of the open-chain compound, 8, is shifted downfield *ca* 50 ppm, compared to 7, an upfield shift of 17 ppm and line broadening has been observed for the phosphorus atom in 4 bearing the —N=NbCl<sub>4</sub> unit. The other phosphorus atom shows a signal at 14 ppm as does the precursor 2e.<sup>6</sup> Interestingly, the <sup>31</sup>P signals of the vanadium heterocycles 2l, 2o, 6a and 6b have halfwidths of *ca* 1000 c.p.s., which is not due to paramagnetic influence.<sup>13</sup>

X-ray crystallographic work on the four-membered rings, 9a-d, 10, 11 on the six-membered rings, 2c,<sup>4b</sup> 2d<sup>4a</sup> and 2o,<sup>8</sup> and on the eight-membered rings, **6b**,<sup>9</sup> and **11**,<sup>11</sup> has been done. All structures except that of 11 show the ring skeletons to be essentially planar. While donor solvents such as CH<sub>3</sub>CN are attached to the metals in the crystal state in 2c, d, 9a-c and 11 resulting in a distorted octahedral environment, the vanadium compounds, 20 and 6b, as well as the titanium heterocycle, 9d, contain no solvent in the crystals, thus resulting in distorted tetrahedral and trigonal-bipyramidal geometries, respectively. Compounds 9c, 6b and 11 are centrosymmetric and **20** contains a  $C_2$  axis through vanadium and the opposite nitrogen, causing pairwise equal bond lengths and angles. Trans-effects due to the CH<sub>3</sub>CN and Cl bond in the ring planes of 2c, d make the ring bonds and angles differ slightly. Due to steric effects a somewhat greater deviation from equality is found in the four-membered rings 9a, b, d. While bond lengths and angles in the P-N sections of the ring systems do not differ significantly from those of these non-metallated analogues, some unusual features have been found around the metal atoms. While the Ti-N and Zr-N bond lengths in the PN<sub>2</sub>M moiety in 9a-d can be regarded close to single bonds, the Ti—N bonds in the central  $Ti_2N_2$  ring of 9c are 189.0 pm, in the exocyclic  $Ti-N-PPh_2N(SiMe_3)_2$ moiety of **9d** are 179.2 pm, and in **11** are 173.9 pm, which are definitively shorter than single bonds, 11 having the shortest Ti-N distances found so far. The Ti-N-P angles in 9d (exocyclic) are 170.3° and in 11 are 175.9° and are almost linear. The angles at the ring nitrogen atoms adjacent to the metal atoms are also increased from 158.4° in 6b to  $129.0^{\circ}$  in **20**. The M-N separations in the fully unsaturated rings, 2 and 6b, have to be regarded as double bonds, the bond angles at the four coordinated vanadium atoms are close to the tetrahedral angle  $(104.2^{\circ} \text{ in } 20 \text{ and } 110.8^{\circ} \text{ in } 6b)$ , while the octahedral angles in 2c, d are slightly bigger than 90° and around 75° in the four-membered rings, 9ad. The exocyclic Si-O-V angles in 6b are almost linear.

#### EXPERIMENTAL

#### General methods

All manipulations were carried out under an atmosphere of dry argon or nitrogen or in vacuo. Solvents were dried and degassed by conventional methods and stored over molecular sieves. If not otherwise noted, solvents and volatile starting materials were transferred into the reaction vessel in vacuo at  $-190^{\circ}$ C and the reaction mixtures slowly warmed up to ambient temperatures, solids transferred to the flask in a dry box (prior to condensation) and liquids injected with a syringe. Metal halides and VOCl<sub>3</sub> were commercial products,  $Cl_3VNSiMe_3$ ,  $Cl_3MN$  (N = Mo, W), and the phosphazene precursors were prepared as described in the papers referred to in this article and the original papers cited therein. The syntheses of the six-membered rings, 2a-e, have been described elsewhere,<sup>4</sup> the syntheses of 2f-j<sup>5</sup> closely follow these procedures and are therefore omitted in this article. As a fully characterized example of an amino-substituted metallacyclophosphazene, the synthesis of 21 together with the  $CF_3$ -substituted 20 are given.

Synthesis of 2,2,4,4-tetramorpholino-1,3,5, $2\lambda^5$ , $4\lambda^5$ ,  $6\lambda^6$ -triazadiphosphatungstenine • THF (**21**)<sup>6</sup>

4.9 g (10 mmol) of 1e and 3.1 g (10 mmol) of NWCl<sub>3</sub> were refluxed in 100 cm<sup>3</sup> of CHCl<sub>3</sub> for 5 h. The solvent was evaporated and the remainder extracted with hot THF. 21 • THF precipitates as a microcrystalline, yellow solid in 26% (2.1 g) yield. Found for 21 • THF : C, 28.9; H, 5.1; Cl, 13.4; N, 11.9.  $C_{20}H_{10}Cl_{3}N_7O_5P_2W$  requires : C, 29.63; H, 4.97; Cl, 13.12; N, 12.09%.

Synthesis of 2,2,4,4-tetrakis(trifluoromethyl)-1,3,5,2 $\lambda^5$ ,4 $\lambda^5$ ,6 $\lambda^5$ -triazadiphosphavanadinine (**20**)<sup>8</sup>

2.4 g (10 mmol) of Cl<sub>3</sub>V=NSiMe<sub>3</sub> and 60 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> were cooled to  $-190^{\circ}$ C and 5.8 g (20 mmol) of **5a** were added. After warming up to room temperature the mixture was stirred for 5 h. Volatiles were removed at  $-10^{\circ}$ C *in vacuo* and the crude product was sublimed twice in a cold finger held at  $-10^{\circ}$ C. Compound **2o** was isolated as translucent yellow crystals, which melt at 22.5°C with decomposition, in 28% (1.4 g) yield. Found for **2o** : C, 9.7; Cl, 14.4; N, 8.4. C<sub>4</sub>Cl<sub>2</sub>F<sub>12</sub>N<sub>3</sub>P<sub>2</sub>V requires : C, 9.57; Cl, 14.13; N, 8.37%.

## Synthesis of the bis(aminodiphenylphosphoranylidene)immoniumhexachlorometallates $(3a-d)^6$

Of the intermediates, 3, only hexachlorotungstate, 3d, has been fully characterized. Equimolar amounts of **1a** and WCl<sub>6</sub> were stirred in CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 1 h. Cl<sub>2</sub> evolution was observed. After removal of the solvent, **3d** was recrystallized from CH<sub>3</sub>CN. It forms brown blocks melting at 239°C with decomposition. The yield (before recrystallization) was virtually quantitative. Found for **3d**: C, 34.8; H, 3.0; Cl, 27.2; N, 4.7. C<sub>24</sub>H<sub>24</sub>Cl<sub>6</sub>N<sub>3</sub>P<sub>2</sub>W requires: C, 35.46; H, 2.98; Cl, 26.16; N, 5.17%.

Synthesis of [(aminodimorpholinophosphoranylideneimino) aminodimorpholinophosphoranylideneim ino] aminoniobiumtetrachloride  $\cdot C_5 H_5 N (4)^6$ 

4.9 g (10 mmol) of 1e and 2.35 g (10 mmol) of NbCl<sub>5</sub> were refluxed in a mixture of 100 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> and 10 cm<sup>3</sup> of pyridine for 6 h. After cooling, pyridine hydrochloride was filtered off, the solution evaporated and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub>. The compound was isolated as yellow crystals in 15% (1.2 g) yield by slow diffusion of the solvent in an evacuated two legged Schlenk vessel from 21 to 18°C. Found for  $4 \cdot C_5H_5N$ : C, 34.1; H, 5.4; Cl, 19.2; N, 15.1. C<sub>21</sub>H<sub>39</sub>C<sub>14</sub>N<sub>8</sub>NbO<sub>4</sub>P<sub>2</sub> requires : C, 33.0; H, 5.14; Cl, 18.56; N, 14.66%.

Synthesis of 2,2,6,6-tetraphenyl-4,4,8,8-tetrachloro-1,3,5,7,2 $\lambda^5$ ,6 $\lambda^5$ ,4 $\lambda^5$ ,8 $\lambda^5$  - tetrazadiphosphadivanadocine (**6a**)<sup>9</sup>

2.4 g (10 mmol) of  $Cl_3V$ =NSiMe<sub>3</sub> and 3.1 g (10 mmol) of **5b** in 120 cm<sup>3</sup> CH<sub>3</sub>CN were heated for 4 h at 40°C. The solid was filtered off, washed with a little CH<sub>3</sub>CN and dried *in vacuo*. The brick-red microcrystalline powder, melting at 225°C with decomposition, was isolated analytically pure in 75% (5 g) yield. Found for **6a**: C, 42.2; H, 3.2; Cl, 21.3; N, 8.4.  $C_{24}H_{20}Cl_4N_4P_2N_2$  requires: C, 43.02; H, 3.01; Cl, 21.16; N, 8.36%.

Synthesis of 2,2,6,6-tetraphenyl-trans-4,8-dichloro-4,8 - bis(trimethylsilyloxy) - 1,3,5,7,2 $\lambda^5$ ,6 $\lambda^5$ ,4 $\lambda^5$ ,8 $\lambda^5$ tetrazadiphosphadivanadocine (**6b**)<sup>9</sup>

1.7 g (10 mmol) of VOCl<sub>3</sub> and 4.3 g (10 mmol) of 7 in 120 cm<sup>3</sup> of CH<sub>3</sub>CN were stirred at room temperature for 24 h. The residue was filtered off, washed with a little CH<sub>3</sub>CN, and then redissolved in CH<sub>2</sub>Cl<sub>2</sub> and a little CH<sub>3</sub>CN. At  $-30^{\circ}$ C **6b** crystallizes in brick-red rhombs of m.p. 206°C with decomposition. The yield of crude **6b** was 80% (6.2 g). Found for **6b**: C, 46.1; H, 4.9; Cl, 9.3; N, 7.3. C<sub>30</sub>H<sub>38</sub>C<sub>12</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>V<sub>2</sub> requires: C, 46.34; H, 4.93; Cl, 9.12; N, 7.4%.

Synthesis of N,N'-bis(trimethylsilyl)-N-pentachlorotungstenamino - P - diphenyliminophosphorane  $(8)^6$ 

7.9 g (20 mmol) of WCl<sub>6</sub> and 8.6 g (20 mmol) of 7 were stirred for 10 h in 150 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The volatiles were evaporated and the tarry dark-brown residue extracted several times with hot PCl<sub>3</sub>. An olive-yellow microcrystalline solid residue remained, which was dried thoroughly *in vacuo*. Elemental analysis showed this material to be analytically pure **8** in 55% (8.1 g) yield. Found for **8**: C, 31.3; H, 4.4; Cl, 25.0; N, 3.8. C<sub>18</sub>H<sub>30</sub>C<sub>15</sub>N<sub>2</sub>PSi<sub>2</sub>W requires: C, 29.92; H, 4.18; Cl, 24.53; N, 3.88%.

Synthesis of 1,3-bis(trimethylsilyl)-2,2-diphenyl-4,4, 4 - trichloro - 1,3,2 $\lambda^5$ ,4 $\lambda^4$  - diazaphosphazirconetidine · CH<sub>3</sub>CN (**9a**) and -titanetidine · CH<sub>3</sub>CN (**9b**)<sup>10</sup>

2.4 g (10 mmol) of  $ZrCl_4$  or 1.9 g (10 mmol) of TiCl<sub>4</sub>, respectively, and 4.3 g (10 mmol) of 7 were stirred at 0°C in 100 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub> for 2 h. Insoluble material was filtered off, volatiles were evaporated and 80 cm<sup>3</sup> of CH<sub>3</sub>CN added. After several days at  $-25^{\circ}$ C the products started to crystallize. Additional material has been obtained by partial removal of the solvent. The yields of 9a (colourless needles melting at 135°C with decomposition) and 9b (orange cubes melting at 105°C with decomposition) were 48% (2.9 g) and 42% (2.3 g), respectively. Found for 9a · CH<sub>3</sub>CN : C, 40.3; H, 5.6; Cl, 17.7; N, 7.1.  $C_{20}H_{31}Cl_3N_3PSi_2Zr$  requires: C, 40.17; H, 5.22; Cl, 17.78; N, 7.02%. Found for **9b** · **CH**<sub>3</sub>**CN**: C, 43.8; H, 5.7; Cl, 19.2; N, 7.1. C<sub>20</sub>H<sub>31</sub>Cl<sub>3</sub>N<sub>3</sub>PSi<sub>2</sub>Ti requires: C, 43.29; H, 5.63; Cl, 19.17; N, 7.57%.

Synthesis of 3,7-bis(trimethylsilyl)-2,2,6,6-tetraphenyl-4,4,8,8-tetrachloro-1,3,5,7,2 $\lambda^5$ ,6 $\lambda^5$ ,4 $\lambda^4$ ,8 $\lambda^4$ tetrazadiphosphadititanatricyclo[2, 2, 0, 0]octane · 2CH<sub>3</sub>CN (**9c**)<sup>10</sup>

1.1 g (2 mmol) of  $9b \cdot CH_3CN$  were dissolved in 50 cm<sup>3</sup> of CH<sub>3</sub>CN and heated to 60°C for 3 h. After several days at  $-25^{\circ}C$  a mixture of crystals of 9b and 9c precipitated, which after filtration were separated manually, but were not pure enough for elemental analysis.

Synthesis of 1,3-bis(trimethylsilyl)-2,2-diphenyl-4,4dichloro - 4 - [N,N - bis(trimethylsilyl)aminodiphenylphosphoranylideneimino] - N' - amino - 1,3,2 $\lambda^5$ ,4 $\lambda^4$  - diazaphosphatitanetidine · CH<sub>3</sub>CN (9d)<sup>11</sup>

8.6 g (20 mmol) of 7 and 1.9 g (10 mmol) of TiCl<sub>4</sub> were stirred at room temperature for 12 h.

Subsequently all volatiles were evaporated and the solid residue redissolved in 50 cm<sup>3</sup> of CH<sub>3</sub>CN. After cooling,  $9d \cdot CH_3CN$  crystallized in dark yellow blocks melting at 135°C. This was slightly contaminated with  $9b \cdot CH_3CN$  to give insufficient elemental analyses.

Synthesis of 2,2,6,6-tetraphenyl-4,4,8,8-tetrachloro-1,5,3,7,2 $\lambda^5$ ,6 $\lambda^5$ ,4 $\lambda^4$ ,8 $\lambda^4$  - dioxadiazadiphosphadititanocine · 4CH<sub>3</sub>CN (11)<sup>11</sup>

3.8 g (20 mmol) of TiCl<sub>4</sub> and 7.2 g (20 mmol) of 10 were stirred in 120 cm<sup>3</sup> of CH<sub>3</sub>CN at room temperature for 12 h. Insoluble material was filtered off and volatiles were evaporated. The residue was redissolved in a minimum amount of CH<sub>3</sub>CN and kept at  $-25^{\circ}$ C for crystallization. Found for 11 · 4CH<sub>3</sub>CN: C, 46.4; H, 4.2; Cl, 16.2; N, 9.0. C<sub>32</sub>H<sub>22</sub>Cl<sub>4</sub>N<sub>6</sub>O<sub>2</sub>P<sub>2</sub>Ti<sub>2</sub> requires: C, 46.19; H, 3.88; Cl, 17.04; N, 10.10%.

Acknowledgements—We are grateful to the Deutsche Forschungsgemeinschaft, VW-Stiftung and the Fonds der Chemischen Industrie for financial support.

#### REFERENCES

 (a) M. T. Reetz, Organotitanium Reagents in Organic Synthesis. Springer, Berlin (1986); M. T. Reetz, Top. Curr. Chem. 1986, 106, 1; (b) G. Wilkinson, F. G. A. Stone and E. W. Abel (Eds), Comprehensive Organometallic Chemistry, Vols 1-9. Pergamon Press, Oxford (1982).

- 2. H. R. Allcock, *Phosphorus–Nitrogen Compounds*. Academic Press, New York (1972).
- J. Haiduc and D. W. Sowerby, *The Chemistry of Inorganic Homo- and Heterocycles*. Academic Press, London (1987).
- (a) H. W. Roesky, K. V. Katti, U. Seseke, M. Witt, E. Egert, R. Herbst and G. M. Sheldrick, Angew. Chem. 1986, 98, 447; H. W. Roesky, K. V. Katti, U. Seseke, M. Witt, E. Egert, R. Herbst and G. M. Sheldrick, Angew. Chem. Int. Edn Engl. 1986, 25, 477; (b) H. W. Roesky, K. V. Katti, U. Seseke, H.-G. Schmidt, E. Egert, R. Herbst and G. M. Sheldrick, J. Chem. Soc., Dalton Trans. 1987, 847; (c) K. V. Katti, H. W. Roesky and M. Rietzel, Inorg. Chem. 1987, 26, 4032; (d) K. V. Katti, U. Seseke, M. Witt and H. W. Roesky, Phosphorus Sulfur 1987, 30, 421.
- 5. H. W. Roesky and J. Liebermann, unpublished results.
- 6. M. Witt and H. W. Roesky, unpublished results.
- 7. H. W. Roesky and M. Rietzel, unpublished results.
- 8. H. W. Roesky, P. Olms, M. Witt, K. Keller, D. Stalke, T. Henkel and G. M. Sheldrick, J. Chem. Soc., Chem. Commun., in press.
- M. Witt, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, Angew. Chem. 1988, 100, 852; M. Witt, H. W. Roesky, M. Noltemeyer and G. M. Sheldrick, Angew. Chem. Int. Edn Engl. 1988, 27, 851.
- 10. M. Witt, H. W. Roesky, D. Stalke, F. Pauer, T. Henkel and G. M. Sheldrick, J. Chem. Soc., Dalton Trans., in press.
- 11. M. Witt, H. W. Roesky and D. Stalke, paper in preparation.
- 12. M. Witt, H. W. Roesky, M. Noltemeyer and A. Schmidpeter, *New. J. Chem.*, in press.
- 13. D. Marsh, private communication.