Volume 29
Number 23
November 14, 1990

Inorganic Chemistry

Communications

Novel Approach to the Synthesis of Ring Systems Containing Phosphorus, Nitrogen, and Sulfur or Selenium

Inorganic ring systems are frequently used as precursors for polymers with inorganic backbones, which are of considerable interest because of their unusual physical properties.[1,2] Consequently, new procedures for the synthesis of inorganic heterocycles that may be of general application are important. The condensation reaction (eq 1) is a potentially versatile route to cyclic

$$\mathrm{X{-}A{=}N{-}SiMe_3} \xrightarrow{-\mathrm{Me_3SiX}} (1/n)(\mathrm{-A{=}N-})_n \qquad (1)$$

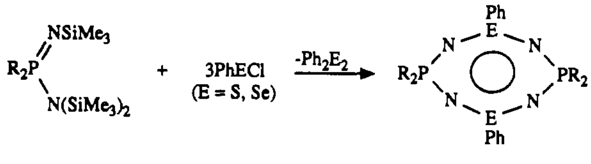
oligomers or linear polymers. Although this method has been used for the preparation of poly(organophosphazenes),[1] it has had limited success for the preparation of inorganic heterocycles.[3]

An alternative route to inorganic ring systems (or polymers) containing nitrogen, which takes advantage of the known susceptibility of N–S(Ph)[4] or N–Se(Ph)[5] bonds towards homolytic cleavage, is depicted in eq 2. As a test of this synthetic approach

$$\mathrm{A{-}N(SiMe_3)_2} +$$
$$\mathrm{2PhECl} \xrightarrow{-2\mathrm{Me_3SiCl}} \mathrm{A{-}N(EPh)_2} \xrightarrow{-\mathrm{Ph_2E_2}} (1/n)(\mathrm{-A{=}N-})_n \qquad (2)$$
$$\mathrm{E = S,\ Se}$$

we report here the preparation of eight-membered PNS and PNSe rings via reaction 2 and the X-ray structure of one of the products, $Ph_4P_2N_4S_2Ph_2$. These ring systems are potential precursors for polymers based on PNSN or PNSeN backbones.[6]

The reaction of **1a** or **1b** with 3 molar equiv of PhSCl or PhSeCl in methylene dichloride gives good yields of the eight-membered rings $R_4P_2N_4E_2Ph_2$ (**2a**, R = Ph, E = S; **2b**, R = Ph, E = Se; **2c**, R = Me, E = S) (eq 3). Benzenesulfenyl chloride (12.6 mmol) was added dropwise by syringe to a stirred solution of **1a**[7,8] (4.2 mmol) in CH_2Cl_2 (50 mL) at 0 °C. After 16 h the removal of solvent under vacuum followed by extraction of the solid residue with pentane gave Ph_2S_2 (60%). Recrystallization of the pentane-insoluble product from CH_2Cl_2 afforded colorless crystals of **2a**, mp 238–240 °C, in 65% yield.[9] The reaction was monitored by ^{31}P NMR spectroscopy, and the precursor of **2a** was observed at $\delta(^{31}P)$ +33.0 ppm. This resonance is tentatively assigned to the trisubstituted derivative, $Ph_2PN_2(SPh)_3$, but this intermediate could not be isolated due to its low thermal stability.



(3)

1a, R = Ph
1b, R = Me

2a, R = Ph, E = S
2b, R = Ph, E = Se
2c, R = Me, E = S

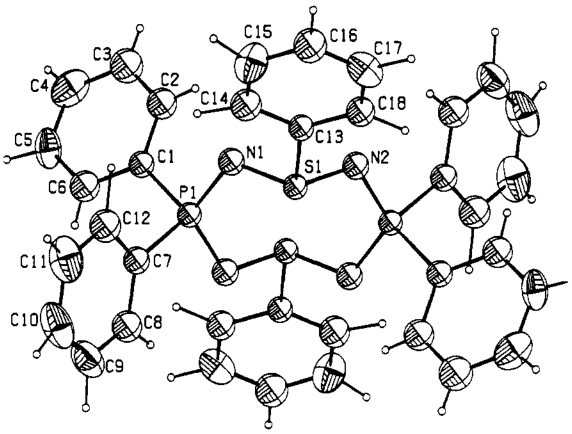


Figure 1. ORTEP drawing (50% probability ellipsoids) of 1,5-$Ph_4P_2N_4S_2Ph_2$ (**2a**). Selected bond lengths (Å) and bond angles (deg): S(1)–N(1) = 1.620 (4), S(1)–N(2) = 1.624 (5), P(1)–N(1) = 1.622 (5), P(1)–N(2a) = 1.614 (4), S(1)–C(13) = 1.793 (6), P(1)–C(1) = 1.814 (5), P(1)–C(7) = 1.806 (6); N(1)–S(1)–N(2) = 108.8 (2), N(1)–P(1)–N(2a) = 119.7 (2), S(1)–N(1)–P(1) = 117.4 (3), S(1)–N(2)–P(1a) = 117.1 (3).

Compound **2b** was obtained in a similar manner from the reaction of **1a** with PhSeCl in a 1:3 molar ratio. It was identified by comparison of IR and ^{31}P NMR spectra with those of an authentic sample prepared from **1a** and $PhSeCl_3$ [$\delta(^{31}P)$(in CH_2Cl_2) +33.2 ppm; cf. literature value of +33.6 ppm].[10] Ph_2Se_2 was isolated in 54% yield from reaction 3. The reaction of **1b** with 3 molar equiv of PhSCl in CH_2Cl_2 at 25 °C produced **2c**, mp 218–220 °C, in 25% yield after recrystallization from CH_2Cl_2,[11] and a quantitative yield of Ph_2S_2. The related compound

---

(1) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

(2) Zeldin, M.; Wynne, K. J.; Allcock, H. R., Eds. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988.

(3) The preparation of borazines via monomeric boron imides by this route required temperatures in excess of 500 °C: Paetzold, P.; von Plotho, C. *Chem. Ber.* **1982**, *115*, 2819.

(4) Barton, D. H. R.; Blair, I. A.; Magnus, P. D.; Norris, R. K. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1031.

(5) Back, T. G.; Kerr, R. G. *J. Chem. Soc., Chem. Commun.* **1987**, 134.

(6) The first examples of poly(thiophosphazenes) were reported recently, but poly(selenophosphazenes) are unknown: Dodge, J. A.; Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268.

(7) Chivers, T.; Dhathathreyan, K. S.; Liblong, S. W.; Parks, T. *Inorg. Chem.* **1988**, *27*, 1305.

(8) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1977**, *16*, 2519.

(9) Anal. Calcd for $C_{36}H_{30}N_4P_2S_2$ (**2a**): C, 67.07; H, 4.69; N, 8.69. Found: C, 66.70; H, 4.70; N, 8.64. $^{31}P\{^1H\}$ NMR (in CH_2Cl_2 at 25 °C): +29.3 ppm.

(10) Chivers, T.; Doxsee, D. D.; Fait, J. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1703.

(11) Anal. Calcd for $C_{16}H_{22}N_4P_2S_2$ (**2c**): C, 48.47; H, 5.59; N, 14.13. Found: C, 48.16; H, 5.61; N, 14.12. ^1H NMR (in $CDCl_3$): 7.9–7.8 and 7.55–7.35 (m, 10 H, C_6H_5), 1.75 (d, $^2J_{^1H-^{31}P}$ = 13.0 Hz, 12 H, CH_3). MS (EI, 70 eV): *m/e* 396 (M^+).

0020-1669/90/1329-4591$02.50/0 © 1990 American Chemical Society

$Ph_4P_2N_4S_2Me_2$ has been prepared from $Me_2S(NH)_2$ via a three-step process involving the use of the explosive reagent $Me_2S(NBr)_2$.[12]

In order to confirm the cyclic structure of the sulphur-containing products, an X-ray structural analysis of **2a** was carried out.[13] The molecular geometry and atomic numbering scheme are illustrated in Figure 1. The molecule is an eight-membered chair with the sulfur atoms displaced by 0.938 (5) Å on either side of the least-squares plane through P_2N_4. The exocyclic phenyl groups attached to the sulfur atoms occupy axial position with respect to their NSN planes [the angle between the S–C bond and NSN plane is 72.5 (3)°] but equatorial positions with respect to the P_2N_4 plane [the angle between the S–C bond and P_2N_4 plane is 11.8 (2) Å]. Similar ring conformations have been observed for 1,5-$Ph_4P_2N_4S_2Br_2$[14] and 1,5-$Ph_4P_2N_4Se_2Me_2$.[10] The S–N and P–N bond lengths in **2a** are equal within experimental error, and the average values are 1.622 (3) and 1.617 (4) Å, respectively, compared to 1.527 (6) and 1.621 (8) Å for the corresponding bonds in 1,5-$Ph_4P_2N_4S_2Br_2$.[14b] Thus, the replacement of Br by a Ph group results in a substantial lengthening of the S–N bond.

In view of the ready accessibility of both main-group and transition-metal reagents of the type $AN(SiMe_3)_2$,[15] the application of the organosulfur/selenium methodology represented by eq 2 is potentially capable of extension to a range of nitrogen-containing heterocycles wider than those from the condensation reaction (eq 1). The mild reaction conditions and the fact that the diaryl dichalcogenides can be recycled (after reaction with SO_2Cl_2) are attractive features of the new route to inorganic heterocycles exemplified by eq 3. The formation of eight-membered rings is in marked contrast to the reaction of $PhCN_2(SiMe_3)_3$ with 3 equiv of PhECl (E = S, Se), which produces the intensely colored azo compounds *trans*-PhENC(Ph)N=NC(Ph)NEPh[16a] via the resonance-stabilized radicals $PhC(NEPh)_2^{\bullet}$.[16b] The mechanistic implications of eq 3 are under investigation.

Acknowledgment. Financial support from the NSERC (Canada) is gratefully acknowledged.

Supplementary Material Available: Tables listing crystallographic parameters, atomic coordinates and thermal parameters for non-hydrogen atoms, bond distances, bond angles, and torsion angles (7 pages); a table of calculated and observed structure factors (13 pages). Ordering information is given on any current masthead page.

---

(12) Appel, R.; Eichenhofer, K. W. *Chem. Ber.* **1971**, *104*, 3859.

(13) Colorless crystals of **2a** were obtained by recrystallization from $CHCl_3$–pentane. Crystal data: $C_{36}H_{30}N_4P_2S_2$, **2a**, M = 644.73, monoclinic, $P2_1/n$, at 295 K, a = 10.563 (2) Å, b = 11.534 (1) Å, c = 13.031 (3) Å, β = 92.941 (9)°, V = 1585.5 (5) Å^3, Z = 2, D_c = 1.350 g cm^{-3}, $\lambda(\text{MoK}\bar{\alpha})$ = 0.710 73 Å, μ = 2.9 cm^{-1}, $F(000)$ = 672. Intensity data were collected on an Enraf-Nonius CAD-4F diffractometer operating in the $\omega-2\theta$ mode and interfaced to a Microvax 2000 computer. Crystal dimensions were 0.13 × 0.13 × 0.38 mm. The crystal structure was solved by standard Patterson methods and subsequent partial structure expansion and difference Fourier techniques. Anisotropic full-matrix least-squares refinement with 1873 observed reflections ($I \geq 2.5\sigma(I)$) (number of unique reflections 3105) and 259 parameters converged at R_F = 0.057.

(14) (a) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1046. (b) Marsh, R. E.; Slagle, K. M. *Inorg. Chem.* **1985**, *24*, 2114.

(15) Lappert, M. F.; Sanger, A. R.; Shrivasta, R. C.; Power, P. P. *Metal and Metalloidal Amides*; Horwood-Wiley: New York, 1979.

(16) (a) Chandrasekhar, V.; Chivers, T.; Fait, J. F.; Kumaravel, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 5373. (b) Chivers, T.; Kumaravel, S. S. Unpublished observations.

Department of Chemistry
The University of Calgary
Calgary, Alberta T2N 1N4,
Canada

Tristram Chivers*
Santhanathan S. Kumaravel

Laboratory of Polymer Chemistry
University of Groningen
Nijenborgh 16, 9747 AG
Groningen, The Netherlands

Auke Meetsma
Johan C. van de Grampel
Arie van der Lee

Received June 19, 1990

Bis(phenylimido) Complexes of Niobium and Tantalum Prepared by α-Hydrogen Abstraction Reactions

Transition-metal organoimido complexes[1] are involved in a number of industrial processes and synthetic methodologies in which the imido moiety is transferred to an organic substrate,[2] such as the ammoxidation of propylene[3] and the amination[4] and aziridination[5] of olefins. Imido ligands have also proven useful as ancillary groups in olefin and acetylene metathesis,[6] alkane activation,[7] and ring-opening metathesis polymerization[8] systems. Single metal sites coordinated by *more* than one imido ligand are presently restricted to the group 6–8 metals.[1] By analogy to the known bis(alkylidenes) $L_nM({=}CHR)_2$ of niobium and tantalum,[9] we have sought to synthesize their related bis(imido) $L_nM({=}NR)_2$ complexes. Herein, we demonstrate this analogy through the α-hydrogen abstraction preparation of bis(imides) of group 5 and verify a structural parallel to their bis(alkylidene) congeners.

Upon reaction of $Ta(NEt_2)_2Cl_3(OEt_2)$[10] with 2 equiv of LiNHAr in THF (room temperature, 36 h, Ar = 2,6-diisopropylphenyl), a yellow complex forms in high yield but is isolated only as an oily solid. By addition of pyridine to the THF reaction solution, yellow-orange crystals of compound **1** can be obtained in ca. 60% yield. The absence of a ν(N–H) mode in the IR spectrum of **1**, the lack of N*H* or ethyl resonances in its ^1H NMR spectrum, and its elemental analysis all support the formulation of **1** as the bis(imido) complex $Ta({=}NAr)_2Cl(py)_2$.[11] The analogous complex of niobium, orange $Nb({=}NAr)_2Cl(py)_2$ (**2**), is prepared from $[Nb(NEt_2)_2Cl_3]_2$[10] by a parallel procedure. Examining solutions of the initial yellow compound (which has not yet been induced to crystallize) led us to formulate this species as the THF adduct $Ta({=}NAr)_2Cl(THF)_2$. ^1H and ^{13}C NMR measurements of **1** and **2** reveal that each compound's phenylimido ligands lie in a molecular plane of symmetry and are equivalent, thereby requiring a C_{2v} molecule. Thus, both imido ligands must be either situated in the equatorial plane of a TBP or occuping its axial sites, with the chloride ligand necessarily equatorial in either case (although fluxionality could lead to a C_{2v} structure

---

(1) (a) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988.

(2) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.

(3) (a) Maatta, E. A.; Du, Y.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1990**, 756. (b) Maatta, E. A.; Du, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8249. (c) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *Ibid.* **1985**, *107*, 251. (d) Chan, D. M.-T.; Nugent, W. A. *Inorg. Chem.* **1985**, *24*, 1422.

(4) See, for example: (a) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628. (b) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420. (c) Sharpless, K. B.; Patrick, D. W.; Truesdale, L. K.; Biller, S. A. *Ibid.* **1975**, *97*, 2305.

(5) (a) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161. (b) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

(6) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *Ibid.* **1986**, *108*, 2771. (c) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *Ibid.* **1988**, *110*, 2686. (d) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (e) Kress, J.; Wesolek, M.; Le Ny, J.-P.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1039.

(7) (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *Ibid.* **1988**, *110*, 8731.

(8) (a) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169. (b) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907. (c) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(9) (a) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986; Vol. 1, pp 221–283. (b) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(10) Chao, Y.-W.; Polson, S.; Wigley, D. E. *Polyhedron*, in press.

(11) Analytical data for $Ta({=}NAr)_2Cl(py)_2$ (**1**) are as follows. ^1H NMR (C_6D_6): δ 9.23 (m, 4 H, H_o, py), 7.24 (d, 4 H, H_m, NAr), 6.96 (t, 2 H, H_p, NAr), 6.65 (m, 2 H, H_p, py), 6.28 (m, 4 H, H_m, py), 3.74 (spt, 4 H, C*H*Me$_2$), 1.04 (d, 24 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 153.7 (C_o, py), 153.6 (C_{ipso}, NAr), 142.8 (C_o, NAr), 138.8 (C_p, py), 124.4, 122.3, and 121.9 (C_m and C_p, NAr; C_m, py), 28.0 (*C*HMe$_2$), 24.0 (CH*Me*$_2$). Anal. Calcd for $C_{34}H_{44}ClN_4Ta$: C, 56.32; H, 6.12; N, 7.73. Found: C, 56.39; H, 6.15; N, 7.78. Complex **2** ($Nb({=}NAr)_2Cl(py)_2$) exhibits similar spectroscopic data.

0020-1669/90/1329-4592$02.50/0