metal–CO bond strengths[6,7] but is consistent with the observed reluctance of this species to undergo thermal CO substitution reactions.

In agreement with the observations that $CpMn(CO)_2THF$ is thermally sensitive and is readily substituted by a variety of ligands,[1] the Mn–THF bond was found to be relatively weak. In comparison, *cis*-cyclooctene and $Bu_2S$ form substantially stronger Mn–L bonds and the resulting complexes are correspondingly more stable. Complexes of both of these ligands can be isolated by displacement of THF from $CpMn(CO)_2THF$ and decompose only above room temperature.[2,8]

The rate constants $k_{obsd}$ for the coordination of L to $CpMn(CO)_2S$ displayed first-order dependences on the concentration of the incoming ligand. Plots of $k_{obsd}$ vs. [ligand] for *cis*-cyclooctene and $Bu_2S$ are shown in Figure 1. The rate constants are all very large, which demonstrates the reactivity of the $CpMn(CO)_2S$ intermediate toward donor molecules when weakly solvated by hydrocarbon solvents. Poliakoff et al.[9] obtained similar results upon examining the rates of reaction of $P(OMe)_3$ and $PPh_3$ with $CpMn(CO)_2S$ in *n*-heptane solution using time-resolved IR spectroscopy (Table I).

From the data in Table I, we expected the Mn–$SBu_2$ bond to be 4.2 ± 3.0 kcal/mol *stronger* than the Mn–*cis*-cyclooctene bond. To confirm this, we examined the equilibrium between the corresponding manganese complexes **1** and **2**.

$$\underset{\mathbf{1}}{CpMn(CO)_2(cis\text{-}C_8H_{14})} + SBu_2 \rightleftharpoons \underset{\mathbf{2}}{CpMn(CO)_2(SBu_2)} + cis\text{-}C_8H_{14}$$

Both of these complexes are known to undergo thermal substitution near 100 °C via clean first-order kinetics.[2,8] Since the equilibrium constant was expected to heavily favor the $SBu_2$ complex **2**, we ran the experiments under high concentrations of *cis*-cyclooctene, in either neat *cis*-cyclooctene (7.7 M) or 1.2 M solutions of *cis*-cyclooctene in heptane, with identical results.[10] The van't Hoff plot of the equilibrium data obtained between 80 and 120 °C gave $\Delta H = -2.9 \pm 1$ kcal/mol and $\Delta S = 3.6 \pm 2$ eu. This value for $\Delta H$ is very close to the $-4.2 \pm 3$ kcal/mol that we predicted on the basis of the individual bond strengths for the *cis*-cyclooctene complex **1** and the $SBu_2$ complex **2** determined by photoacoustic calorimetry. The degree to which these two very different techniques agree attests to the accuracy of the photoacoustic technique in determining metal–ligand bond dissociation energies.

An estimate of the strength of the heptane–Mn interaction can be obtained from consideration of information in the literature and our data. Angelici and Loewen[2] have studied the ligand substitution of the *cis*-cyclooctene complex **1** by $PPh_3$ in methylcyclohexane solution. Similarly, Butler and Sawai[8] have studied the ligand substitution of the $SBu_2$ complex **2** by $P(O\text{-}n\text{-}Bu)_3$ in methylcyclohexane solution. Both reactions proceed by purely dissociative pathways.

$$\underset{\mathbf{1}}{CpMn(CO)_2(cis\text{-}C_8H_{14})} + PPh_3 \rightarrow CpMn(CO)_2(PPh_3) + cis\text{-}C_8H_{14}$$

$$\Delta H^{\ddagger} = 34.9 \pm 0.7 \text{ kcal/mol};\ \Delta S^{\ddagger} = 27.5 \pm 2.0 \text{ eu}$$

$$\underset{\mathbf{2}}{CpMn(CO)_2(SBu_2)} + P(O\text{-}n\text{-}Bu)_3 \rightarrow CpMn(CO)_2(P(O\text{-}n\text{-}Bu)_3) + SBu_2$$

$$\Delta H^{\ddagger} = 36 \pm 1 \text{ kcal/mol};\ \Delta S^{\ddagger} = 22 \pm 1 \text{ eu}$$

In methylcyclohexane solution, the activation enthalpies for these reactions are respectively 10 and 7 kcal/mol *greater* than the corresponding Mn–L bond strengths in heptane. Assuming little difference between methylcyclohexane and heptane, this implies that the Mn–heptane interaction is close to 8 or 9 kcal/mol. This is similar to the 10 kcal/mol Cr–heptane interaction in $(CO)_5Cr$–heptane[5c] and the 9.6 kcal/mol W–ethane interaction in $(CO)_5W$–ethane.[11] The sum of Mn–heptane interaction (8–9 kcal/mol) and the solution-phase Mn–CO bond dissociation energy (46.7 kcal/mol) gives 55 kcal/mol as an estimate of the *gas-phase* Mn–CO bond dissociation energy in $CpMn(CO)_3$. Further experiments are necessary to confirm the magnitude of the Mn–heptane interaction.

**Acknowledgment.** We acknowledge the National Institutes of Health (GM-42704-01), the University of Southern California Faculty Research and Innovation Fund, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this research.

---

[6] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[7] Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905–3912.

[8] Butler, I. S.; Sawai, T. *Inorg. Chem.* **1975**, *14*, 2703.

[9] Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakoff, M. *Organometallics* **1987**, *6*, 2600–2605.

[10] Although differential vaporization of the ligands did not appear to be a problem, efforts were made to minimize the gas volume in the reaction vessel. The concentrations of the complexes were monitored by the intensity of the appropriate $\nu_{CO}$ bands. Identical equilibrium constants were obtained for the approach to equilibrium from either direction.

[11] Ishikawa, Y.; Brown, C. E.; Hackett, P. A.; Raynor, D. M. *Chem. Phys. Lett.* **1988**, *150*, 506–510.

---

## Poly(thiophosphazenes): New Inorganic Macromolecules with Backbones Composed of Phosphorus, Nitrogen, and Sulfur Atoms

Jeffrey A. Dodge, Ian Manners, and Harry R. Allcock*

*Department of Chemistry*
*The Pennsylvania State University*
*University Park, Pennsylvania 16802*

Gerhard Renner and Oskar Nuyken*

*Makromolekulare Chemie I, Universität Bayreuth*
*Universitätsstrasse 30, D-8580 Bayreuth, West Germany*

*Received November 3, 1989*

Macromolecules that possess backbones consisting entirely of inorganic elements are of considerable current interest from the viewpoint of both their unusual physical properties and their potential function as precursors to ceramic materials.[1-8] However, to date, relatively few well-characterized classes of these materials have been prepared.

Classical polyphosphazenes are a broad, well-established class of inorganic macromolecules with backbones of alternating phosphorus and nitrogen atoms. Their main method of synthesis involves the ring-opening polymerization of hexachlorocyclotriphosphazene (**1**) followed by replacement of the halogen atoms of **2** by organic, inorganic, or organometallic units. This has provided access to a wide variety of stable and useful materials.[9-11]

We are currently exploring the polymerization behavior of cyclic species analogous to **1** but containing skeletal heteroatoms in

---

[1] Allcock, H. R. *Chem. Eng. News* **1985**, *63*(11), 22.

[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] Kanatzidis, M. G.; Huang, S. *J. Am. Chem. Soc.* **1989**, *111*, 760–761.

[4] Seyferth, D.; Rees, W. S.; Haggerty, J. S.; Lightfoot, A. *Chem. Mater.* **1989**, *1*, 45.

[5] Bowden, M. J., Turner, R., Eds. *Electronic and Photonic Applications of Polymers*; Advances in Chemistry 218; American Chemical Society: Washington, DC, 1988.

[6] Hastings, G. W.; Ducheyne, P. *Macromolecular Biomaterials*, CRC Press: Boca Raton, FL, 1984.

[7] Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297.

[8] Mackenzie, J. D., Ulrich, D. R., Eds. *Ultrastructure Processing of Advanced Ceramics*; John Wiley and Sons: New York, 1988.

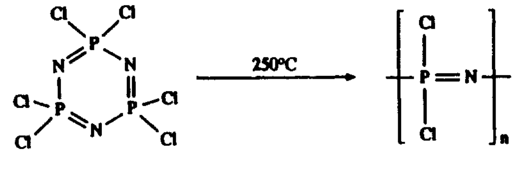
[9] Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic Press: New York, 1972.

[10] Allcock, H. R. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 147.

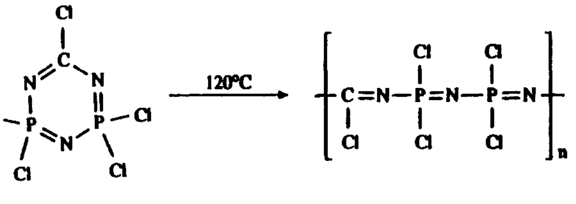
[11] Zeldin, M., Wynne, K. J., Allcock, H. R., Eds. *Inorganic and Organometallic Polymers*; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988; pp 250–282.

0002-7863/90/1512-1268$02.50/0

addition to phosphorus and nitrogen. In a recent communication we described the ring-opening polymerization of a cyclocarbophosphazene (**3**) which provided access to poly(carbophosphazenes), a new class of inorganic–organic macromolecules.[12] We now report the ring-opening polymerization of a compound (**5**) containing a skeletal sulfur atom in addition to phosphorus and nitrogen. This provides a synthetic route to a new class of inorganic macromolecules, the poly(thiophosphazenes).



**1** **2**

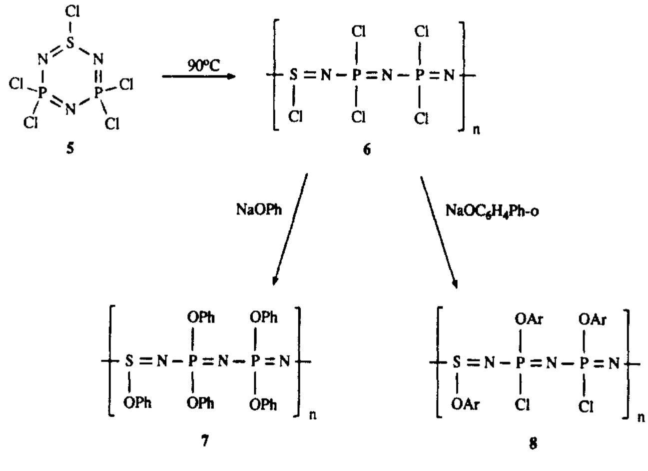


**3** **4**

The cyclothiophosphazene **5** was prepared as an air- and moisture-sensitive colorless liquid via the (3 + 3) cyclocondensation reaction of $Me_3SiN{=}S{=}NSiMe_3$[13] with $[Cl_3P{=}N{=}PCl_3]Cl$[14] in $CCl_4$. This reaction proceeds in 80–90% yield as deduced by $^{31}P$ NMR spectroscopy. Although the isolated yield is only 40–50%, this synthetic route is a considerable improvement over previously published procedures.[15] When species **5** was heated over a 4-h period at 90 °C in an evacuated Pyrex tube, a gradual increase in viscosity was noted. Analysis by $^{31}P$ NMR[16] showed that the products consisted of unreacted **5** (ca. 10%) and the poly(thiophosphazene) **6** (ca. 90%). The $^{31}P$ NMR spectrum of **6** comprised a singlet resonance at −4.6 ppm, which is significantly shifted to high field compared to that of **5** ($\delta$ = 24.5 ppm). Similar high-field shifts of the $^{31}P$ NMR resonance are observed in the formation of **2** ($\delta$ = −18.4 ppm) from **1** ($\delta$ = 19.9 ppm) and of **4** ($\delta$ = −3.7 ppm) from **3** ($\delta$ = 36.5 ppm).

Because of the sensitivity of **6** to moisture, attempts were made to replace the chlorine atoms by aryloxy groups. This methodology leads to hydrolytically stable polymers in the case of polyphosphazenes and poly(carbophosphazenes).[10,12] Thus, **6** was treated with excess sodium phenoxide (dioxane, 25 °C, 12 h), to afford a white, polymeric product **7**.[17,18] However, this polymer also proved to be sensitive to moisture, with significant decomposition noticeable after several hours in wet solvents. This sensitivity is almost certainly a consequence of the exposed sulfur–nitrogen multiple bonds in the polymer main chain. Therefore, attempts were made to replace the chlorine atoms of **6** by more sterically demanding aryloxy substituents which would be expected to provide significant protection of the polymer backbone from nucleophilic attack. Reaction of **6** with excess sodium *o*-phenylphenoxide (dioxane, 25 °C, 5 days) followed by sequential precipitation into water (twice) and hexanes (twice) yielded a white, film-forming polymeric material **8**.[19] The $^{31}P$ NMR spectrum of **8** was indicative of incomplete chlorine atom replacement and showed two broad, singlet resonances at −12.3 and −16.9 ppm of approximately equal intensity. These were assigned to phosphorus atoms that bear, in the former case, two chlorine substituents or one chlorine and one aryloxy substituent and, in the latter case, two aryloxy substituents. The presence of unreacted chlorine substituents was confirmed by elemental analysis, which indicated that approximately 65% of the halogen atoms of **6** had been replaced.[20] However, despite the lack of complete chlorine atom replacement, polymer **8** shows considerable stability toward hydrolysis.[21] The macromolecular nature of **8** was confirmed by gel permeation chromatography,[22] which indicated a weight-average molecular weight ($M_w$) of 3.1 × $10^5$ and a number-average molecular weight ($M_n$) of 1.0 × $10^5$.

Preliminary studies indicate that the sulfur–chlorine bond of **6** is considerably more reactive than the phosphorus–chlorine bonds toward nucleophilic substitution. Thus, reaction of polymer **6** with 1 equiv of sodium *o*-phenylphenoxide (dioxane, 15 °C, 2 h) yielded a single new product with a $^{31}P$ NMR singlet resonance at −7.4 ppm. This resonance is at only slightly higher field than that of **6** (−4.6 ppm), as would be expected for chlorine substitution at sulfur rather than phosphorus. In a model reaction, the cyclic trimer **5** reacted similarly, to give $N_3P_2S(OC_6H_4Ph\text{-}o\text{-})Cl_4$ **9** via exclusive substitution at sulfur.[23] This suggests that a range of regiospecific polymers with different substituents at sulfur and phosphorus may be accessible. Further studies on the synthesis and properties of this new class of macromolecules are in progress.



( OAr = $OC_6H_4Ph$-o )

**Acknowledgment.** This work was carried out at The Pennsylvania State University. We thank the U.S. Army Research Office (H.R.A., J.A.D. and I.M.), Bayer AG, and the FRG Ministry of Science and Technology (O.N. and G.R.) for financial support.

---

[12] Manners, I.; Renner, G.; Nuyken, O.; Allcock, H. R. *J. Am. Chem. Soc.* **1989**, *111*, 5478.

[13] Wannagat, U.; Kuckertz, H. *Angew. Chem.* **1962**, *74*, 117.

[14] Becke-Goehring, M.; Lehr, W. *Z. Anorg. Allg. Chem.* **1963**, *325*, 287.

[15] The cyclothiophosphazene **5** was isolated as a colorless oil after purification by vacuum distillation (bp 72 °C, 0.002 mmHg). A significant loss of product occurs due to polymerization in this process. In our hands, previously reported routes to **5** gave only very low (ca. 5–10%) yields of the isolated product. For alternative routes to **5**, see: Pohl, S.; Petersen, O.; Roesky, H. W. *Chem. Ber.* **1979**, *112*, 1545. Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 642.

[16] NMR spectra were recorded in dioxane ($^{31}P$) or $CDCl_3$ ($^1H$) on either a Bruker WP-360 or a JEOL FX-90 Q spectrometer. Chemical shifts are relative to 85% $H_3PO_4$ ($^{31}P$) or TMS ($^1H$).

[17] For **7**: $^{31}P$ NMR $\delta$ = −12.0 (s), $^1H$ NMR $\delta$ = 7.2 (br, s).

[18] In a model reaction, **5** was treated with excess NaOPh (dioxane, 25 °C, 12 h), to afford $N_3P_2S(OPh)_5$ as a moisture-sensitive oil: $^{31}P$ NMR $\delta$ = 1.9 ppm; MS calcd 601, found 508 ($M^+$ − OPh).

[19] The schematic representation of polymer **8** is oversimplified as both $PCl_2$ and $P(OAr)_2$ units are also present.

[20] For **8**: $^{31}P$ NMR $\delta$ = −12.3 and −16.9 (both br, s); $^1H$ NMR $\delta$ = 7.2 (br, s). Anal. Calcd for $[N_3P_2S(OC_6H_4Ph\text{-}o)_{3.25}Cl_{1.75}]_n$: C, 62.61; H, 3.95; N, 5.62; S, 4.28; Cl, 8.29. Found: C, 61.40; H, 3.85; N, 4.53; S, 3.62; Cl, 7.61. GPC: $M_w$ = 3.1 × $10^5$, $M_n$ = 1.0 × $10^5$.

[21] By way of comparison, poly(dichlorophosphazene) (**2**) reacts with $Na[OC_6H_4Ph\text{-}o]$ (THF, 150 °C, 14 days) to afford a hydrolytically stable polymer with 5% remaining chlorine atoms corresponding to 76% substitution: Mang, M. N.; Dembek, A. A.; Allcock, H. R.; Wynne, K. J. *Macromolecules* **1989**, *22*, 4179. Attempts to replace the unreacted chlorine atoms of **8** by reaction with nucleophiles such as trifluoroethoxide and phenoxide have been unsuccessful.

[22] GPC data were recorded in THF and calibrated against polystyrene. The values obtained for $M_w$ and $M_n$ are considered estimates.

[23] For **9**: $^{31}P$ NMR $\delta$ = 20.0. Preliminary studies have shown that the remaining chlorine atoms of **9** can be replaced via reaction with sodium trifluoroethoxide to afford $[N_3P_2S(OC_6H_4Ph\text{-}o)(OCH_2CF_3)_4]$ ($^{31}P$ NMR $\delta$ = 2.1; MS calcd 701, found 701).