product had the empirical formula $POCl_3 \cdot 2.5TMAO$. This compares with $SiCl_4 \cdot 3.3TMAO$, formed under similar conditions.[1] Then heating under vacuum brought the formula to $POCl_3 \cdot 1.68TMAO$ for the hard, brown residue. Very little of this dissolved in D_2O, giving only singlets for the ^{31}P NMR spectrum. The smallest of these (at $\delta = -0.6$ ppm) showed slight hydrolysis to D_3PO_4. Other small singlets at $\delta = 10.9$, 11.4, 21.0, and 38 ppm would not be P–F compounds—possibly impurities. The major feature was a broad singlet at $\delta = 24$ ppm, for the suspended solid, the P–Cl content of which evidently was protected against hydrolysis.

Rationale. The disproportionation of POF_3 as it is being liberated from one of the 1:1:1 complexes might begin with processes conjectured as

$$4POF_3 \rightarrow PF_6^- + 3POF_2^+ + O^{2-} \tag{3}$$

$$2POF_2^+ \rightarrow POF_3 + POF^{2+} \tag{4}$$

$$POF^{2+} + O^{2-} \rightarrow PO_2F \tag{5}$$

wherein (4) and (5) would be highly variable. When the PF unit is not seen in the NMR spectra, its P–F coupling might be lost in the breadth of the polymer peak; for PO_2F must be polymeric. Also, there may be other ways to employ O^{2-}.

Since PCl_6^- is far less stable than PF_6^-, $POCl_3$ cannot be expected to behave in the manner of (3). Instead, it would be reasonble to expect $POCl_3$ to react with TMAO more in the manner of its nearly isoelectronic analogue $SiCl_4$, as indeed it does.

Significance. We find here some analogy to prior reports of the disproportionation of POF_3 by various sources of the F^- ion. Lustig and Ruff[3] found that the low lattice energy of CsF makes F^- sufficiently available for an attack on POF_3 to make PF_6^- and $PF_2O_2^-$; and also of interest is the action of KF on $PSCl_3$ to form KCl, KPF_6, and KPF_2S_2. The present work shows that TMAO has enough electron-donor bonding power to displace F^- and even O^{2-} from POF_3, for action of these on other P sites; but it does not yet seem possible to determine just how many TMAO molecules form stabilizing attachments to O–P–F units.

The chemical versatility of TMAO is further demonstrated by other effects such as the oxidation of PF_3 to form POF_3 and the removal of HCl or BF_3 from the 1:1:1 complexes, for recovery of POF_3 as such. Indeed, the actual existence of the 1:1:1 complexes demonstrates the ability of TMAO to increase the electron-donor bonding power of a molecule to which it makes a dative bond.

---

(3) Lustig, M.; Ruff, J. K. *Inorg. Chem.* **1967**, *6*, 2115.

Contribution from the Institut für Anorganische
Chemie der Universität, Auf der Morgenstelle 18,
D-7400 Tübingen 1, West Germany

^{31}P and ^{29}Si Solid-State NMR Studies of a Phosphine-Functionalized Polysiloxane Framework

Ekkehard Lindner,* Armin Bader, and Hermann A. Mayer

Received August 27, 1990

Over the past few years, there has been an increasing interest in the preparation of immobilized homogeneous catalysts,[1-3] in chromatography,[4,5] and in fundamental studies in the field of surface chemistry.[6] These developments have spurred the synthesis of polymer-supported ligands and organometallic compounds. To that end, a great variety of organic resins and inorganic oxides have been used as base matrices. Among the latter class of supports, silica has gained outstanding importance due to its rigid structure and the ease of functionalization through its surface silanol groups.[7] However, phosphinated silicas obtained by treating even highly dispersed SiO_2 with reactive (chlorosilyl)alkylphosphines or (methoxysilyl)alkylphosphines suffer from great disadvantages, namely low ligand content and low surface loading. In order to overcome this drawback, phosphine-modified polysiloxane frameworks have been prepared by hydrolysis of (trimethoxysilyl)alkylphosphines ("sol-gel process").[8-12] Their cocondensation with x mol of tetraethoxysilane leads to solid polymers of the approximate stoichiometry $[SiO_{3/2}(CH_2)_nPR_2] \cdot xSiO_2$. Thus, a wide range of ligand densities may be realized. Such a "surface tailoring" is novel and represents a most promising technique for the preparation of supported organometallic species. It also opens up the possibility of studying their behavior as a function of the ligand density. Despite the preparative work that has been undertaken,[8-12] there is still a lack of detailed structural information. In this work, we present ^{31}P and ^{29}Si CP-MAS data for $[SiO_{3/2}(CH_2)_6P(Ph)CH_2CH_2OCH_3] \cdot 2SiO_2$ (**1**),[13] which contains a potentially bidentate ligand with oxygen and phosphorus donor atoms. This type of ligand has recently found outstanding applications in coordination chemistry and catalysis.[14] Cross-polarization magic-angle-spinning (CP-MAS) solid-state NMR spectroscopy is a powerful tool for the investigation of insoluble systems of this kind.[15-18]

Experimental Section

All manipulations were performed under argon by employing the usual Schlenk techniques. Ethanol was dried with sodium and stored under argon. The elemental analyses were carried out on a Carlo Erba analyzer, Model 1106. IR data were obtained on a Bruker IFS 48 FT-IR spectrometer. The CP-MAS solid-state NMR spectra were recorded on a Bruker MSL 200 multinuclear spectrometer with a wide-bore magnet (4.7 T) using samples of 200–300 mg in double-bearing rotors of ZrO_2. MAS was performed at a 4-kHz spinning rate. Frequencies and standards: ^{31}P, 81 MHz ($NH_4H_2PO_4$); ^{29}Si, 39.75 MHz (Q_8M_8[19]); recycle delay, 2 s. T_{SiH}, $T_{1\rho H}$ and I_0 values were calculated by using the Bruker software SIMFIT.

Reagents. $Si(OEt)_4$ and $(n\text{-}Bu)_2Sn(OAc)_2$ (Merck) were of analytical grade and were used without further purification. The ether–phosphine ligand $(MeO)_3Si(CH_2)_6P(Ph)CH_2CH_2OCH_3$ (**2**) was obtained according to a previously published procedure.[7]

Preparation of Ligand 1. Ethanol was added dropwise to a mixture of **2** (1.921 g, 5.16 mmol), $Si(OEt)_4$ (2.148 g, 10.31 mmol), and water (0.511 g, 28.36 mmol) until a homogeneous solution was formed. After addition of the catalyst $(n\text{-}Bu)_2Sn(OAc)_2$ (0.2 g) and stirring of the reaction medium for 24 h, the white precipitate was isolated and washed with ethanol and dichloromethane (three times each, 10 mL). Yield: 1.60 g (75%). IR: $\nu_{as}(SiO_2)$ 1100–1050 cm^{-1}. Anal. Calcd. for the idealized stoichiometry $[SiO_{3/2}(CH_2)_6P(Ph)CH_2CH_2OCH_3] \cdot 2SiO_2$: C,

---

(1) Pittman, C. U. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Chapter 55, p 553.

(2) Hartley, F. R. *Supported Metal Complexes*; D. Reidel Publishing Co.: Dordrecht, The Netherlands 1985.

(3) Lindner, E.; Bader, A.; Glaser, E.; Wegner, P. *J. Mol. Catal.* **1989**, *56*, 86.

(4) Pfleiderer, B.; Albert, K.; Bayer, E. *J. Chromatogr.* **1990**, *506*, 343.

(5) Bayer, E.; Albert, K.; Reiners, J.; Nieder, M.; Müller, D. *J. Chromatogr.* **1983**, *264*, 197.

(6) Lamb, H. H.; Gates, B. C.; Knözinger, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1127.

(7) Lindner, E.; Bader, A.; Glaser, E.; Pfleiderer, B.; Schumann, W.; Bayer, E. *J. Organomet. Chem.* **1988**, *355*, 45.

(8) Schubert, U.; Egger, C.; Rose, K.; Alt, C. *J. Mol. Catal.* **1989**, *55*, 330.

(9) Khatib, I. S.; Parish, R. V. *J. Organomet. Chem.* **1989**, *369*, 9.

(10) Parish, R. V.; Habibi, D.; Mohammadi, V. *J. Organomet. Chem.* **1989**, *369*, 17.

(11) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236.

(12) Kavan, V.; Čapka, M. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2100.

(13) Lindner, E.; Bader, A.; Mayer, H. A. *Z. Anorg. Allg. Chem.*, in press.

(14) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.

(15) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606.

(16) Pfleiderer, B.; Albert, K.; Bayer, E.; van de Ven, L.; de Haan, J.; Cramers, C. *J. Phys. Chem.* **1990**, *94*, 4189.

(17) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J. *J. Phys. Chem.* **1985**, *89*, 277.

(18) Harris, R. K. *Analyst* **1985**, *110*, 649.

(19) Lippmaa, E.; Samoson, A. *Bruker Rep.* **1982**, *1*, 6.

0020-1669/91/1330-3783$02.50/0

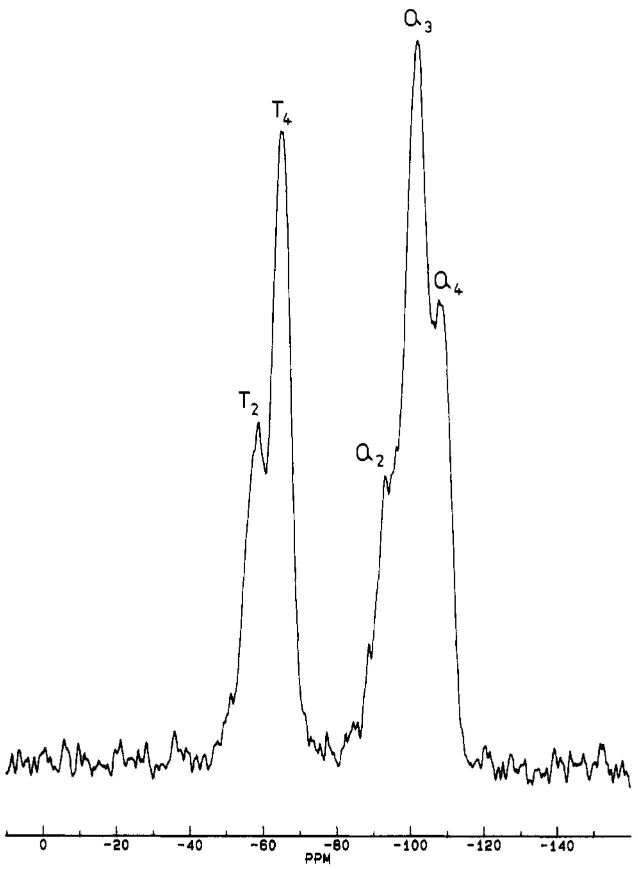

Figure 1. ^{29}Si CP-MAS NMR spectrum of $[SiO_{3/2}(CH_2)_6P(Ph)CH_2CH_2OCH_3]\cdot 2SiO_2$ (**1**).

42.50; H, 5.71. Found: C, 37.70; H, 5.80. The deviation of the C value is due to the loss of soluble oligomeric ligand during the washing process.

Reaction of the Polysiloxane 1 with $[RuCl_2(CO)_2]_n$.[13] $[RuCl_2(CO)_2]_n$ was made by passing CO through a boiling solution of $RuCl_3\cdot 3H_2O$ (0.55 g, 2.1 mmol) in 50 mL of 2-methoxyethanol. The completion of the reaction was indicated by a color change from deep red to yellow. After the solution was cooled to 20 °C, **1** (0.3 g, ca. 0.70 mmol phosphine) was suspended therein and stirred overnight. The pale yellow product was isolated by centrifugation and washed several times with ethanol and *n*-pentane.

Results and Discussion

The ^{31}P CP-MAS spectrum of **1** shows—in accord with the solution spectrum of the monomeric ligand **2**—a sharp singlet at −31.7 ppm. Its small line width ($\Delta\nu_{1/2}$ = 120 Hz) and the observation of only one resonance is consistent with a structure in which the phosphine-bearing C_6-alkyl chains are located at the outside of the polysiloxane matrix and in which there is no distribution of the ligands between surface and bulk. This spectroscopic evidence is supported by the high accessibility of all phosphorus atoms for even bulky reagents. Thus, treatment of **1** with a solution of $[RuCl_2(CO)_2]_n$ in 2-methoxyethanol at ambient conditions results in a quantitative complexation of all phosphine ligands to give surface-bound *all-trans*-$RuCl_2(CO)_2(PR_3)_2$ (PR_3 = **1**).[13] The formation of this complex is indicated by its ^{31}P CP-MAS resonance at 6.5 ppm; no free ligand could be detected in this sample.

Table I. Silyl Moieties Detected in **1** by ^{29}Si CP-MAS NMR Spectroscopy

structural type[a]	notation	$\delta(^{29}Si)$, ppm
$(\equiv SiO)_2SiR(OR')$	T_2	−58.4
$(\equiv SiO)_3SiR$	T_4	−64.7
$(\equiv SiO)_2Si(OR')_2$	Q_2	−91
$(\equiv SiO)_3Si(OR')$	Q_3	−101
$(\equiv SiO)_4Si$	Q_4	−110

[a] R = $(CH_2)_6P(Ph)CH_2CH_2OCH_3$; R' = H, Me, or Et.

Table II. Values of T_{SiH}, $T_{1\rho H}$, and I_0 Obtained for **1** by Contact Time Variation

species	T_{SiH}, ms	$T_{1\rho H}$, ms	I_0
T_2	0.63	4.05	1.6
T_4	0.73	3.63	3.3
Q_2	0.54	9.33	1.0
Q_3	0.79	6.71	2.8
Q_4	1.20	9.89	1.7[a]

[a] Value corresponding to sites containing ^{29}Si nuclei within a range of four single bonds from a proton.

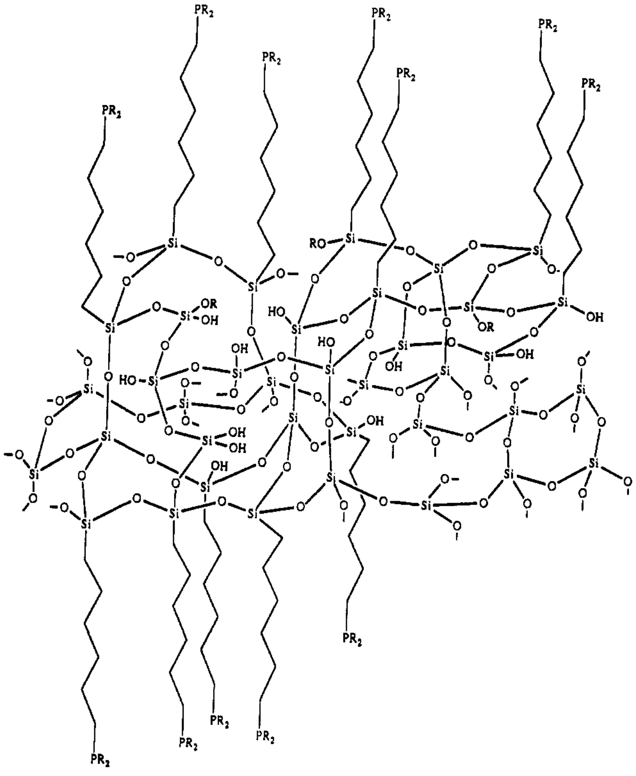

Figure 2. Suggested structure of the poly(phosphinoalkyl)siloxane **1**.

The ^{29}Si CP-MAS spectrum of **1** is depicted in Figure 1. It is typical of polysiloxanes obtained by cocondensation of $Si(OEt)_4$ and $(MeO)_3SiR$ (R = alkyl, phosphinoalkyl, etc.). The structural assignments are collected in Table I. Two separate groups of signals, due to the T and Q species,[4,16] can be distinguished in the spectrum, and—in comparison with modified silicas—there is a considerably higher amount of T species. The silicon atoms of T_2 and T_4 contain an ω-phosphinoalkyl substituent, and therefore a ligand is attached to these sites, whereas the groups Q_2, Q_3, and Q_4, which arise from $Si(OEt)_4$, are ligand-free. The amplitude (*I*) of each signal observed in the ^{29}Si CP-MAS spectrum (see Figure 1) is a function of the contact time T_c, the individual values of the ^{29}Si–^{1}H cross-polarization constant T_{SiH} and the ^{1}H spin-lattice relaxation time in the rotating frame $T_{1\rho H}$. The "real" intensity, I_0, which is a measure of the quantity of the corresponding silyl species, can be calculated from eq 1.[15,16]

$$I = I_0(1 - e^{-T_c/T_{SiH}})e^{-T_c/T_{1\rho H}} \qquad (1)$$

Table II compiles the parameters of eq 1 obtained for ligand **1** by means of a contact time variation under Hartmann–Hahn conditions. The ratio of the values of I_0 represents the relative amounts of each of the silyl species present in the sample.[16] The detection of silicon by ^{29}Si CP-MAS is, however, restricted to those nuclei that are near protons, typically within a range of four single bonds.[15-17,20] All T_2, T_4, Q_2, and Q_3 sites meet this condition very well and are thus accurately quantified. The quantification of Q_4 groups, however, is less reliable. This stems from the fact that

---

(20) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 1487.

the relaxation of Q_4 silicon atoms has to occur via adjacent proton-containing T, Q_2, or Q_3 moieties, which leads to rather long $^{29}Si-^{1}H$ distances. Hence, the Q_4 sites detected in **1** should be assigned to those which are directly bound to a T site or a Si–OH-containing moiety. Increasing amounts of $Si(OEt)_4$ used for the cocondensation with $(MeO)_3SiR$, combined with an incomplete hydrolysis of Si–OR residues, result in the occurrence of nondetectable Q_4 silicons. However, their numbers can be estimated from the difference of the Q:T ratio determined by CP-MAS and the Q:T ratio expected from the stoichiometry of the reaction. This reveals that in the case of **1** ca. 43% of all Q groups are Q_4 sites that are too far away from protons to be detected by CP-MAS and should therefore be predominantly bound to other Q_4 groups. Compound **1** contains considerable proportions of Q_2 and Q_3 groups (see Table II), and this indicates that the polycondensation reaction has not proceeded to full completion. The structural consequence of this is the occurrence of layers of partially opened siloxane rings, which in turn are interconnected to give a relatively open three-dimensional network. This is supported by the ability of the material to form swollen gels in alcohols. Figure 2 shows the proposed structure of the polysiloxane **1**. The relative numbers of the T and Q species present in this model reflect their ratios as determined above.

Acknowledgment. We wish to thank Dr. Bettina Pfleiderer for helpful discussions. We are grateful to the Bundesministerium für Forschung und Technologie, to Wacker-Chemie, Burghausen/Obb., Germany, and to the Verband der Chemischen Industrie e.V., Fonds der Chemischen Industrie, for financial support.

Registry No. **1**, 135339-91-2; **2**, 135339-89-8; $Si(OEt)_4$, 78-10-4; $(n\text{-}Bu)_2Sn(OAc)_2$, 1067-33-0; $RuCl_3$, 10049-08-8; $RuCl_2(CO)_2$ (homopolymer), 28986-72-3; 2-methoxyethanol, 109-86-4.

Contribution from the Department of Chemistry,
Miami University, Oxford, Ohio 45056

Complex Formation Reactions of the Chlorite Ion

István Fábián[†] and Gilbert Gordon*

Received March 13, 1991

Unique kinetic phenomena[1–4] and important practical applications[5,6] have generated great interest in the chemistry of chlorite ion. Previous studies in this field have extensively covered stoichiometric, kinetic, and mechanistic aspects of the oxidation–reduction reactions of ClO_2^-. In contrast, little is known about the coordination chemistry of chlorite ion.

The formation of only a few complexes with ClO_2^- has been confirmed. The preparation and the properties of the inert $Co(NH_3)_5ClO_2^{2+}$ complex was discussed by Thompson.[7] This species was shown to be stable in solid phase and undergo slow decomposition in acidic solution. Two labile complexes were reported with chlorine dioxide[8] and the uranyl ion.[9] The formation of these species was undoubtedly confirmed, but only rough estimates could be given for their stability constants. Other chlorito complexes were also postulated in redox reactions of chlorite ion but were not detected directly.

The lack of stability data for the chlorito complexes is mainly due to the inherent difficulties with finding suitable experimental conditions for the equilibrium studies. In order to avoid complications caused by the hydrolysis of the metal ions, precipitation of hydroxo species, formation of polynuclear complexes, etc., the experiments should be performed in acidic solutions. In the case of the most common di- and trivalent transition-metal ions, the pH should not exceed ~2.5. However, in the acidic pH range the chlorite ion is quite susceptible to decomposition reactions.[10]

The number of the appropriate methods for monitoring these reactions also appears to be somewhat limited. This is because the formation of relatively weak complexes is anticipated. Consequently, the pH effect of the complex formation cannot be measured with acceptable precision. The same problem is expected with other electrochemical methods, including potentiometry by using metal ion selective electrodes.

Spectrophotometry is one of the most frequently applied methods for studying the formation of weak complexes. However, in the case of chlorite ion, certain experimental difficulties must be anticipated. First of all, in the decomposition reactions of chlorite ion, chlorine dioxide is one of the products.[10] ClO_2 is characterized with a strong absorbance band in the near-UV–visible spectral region[11] (λ_{max} = 358.5 nm, ϵ_{max} = 1250 M^{-1} cm^{-1}), which overlaps the spectrum of the chlorite ion. It also may overlap the spectra of the ClO_2^- complexes. Accordingly, the decomposition reactions do not only compete with the complex formation but also may interfere with the spectrophotometric detection of the corresponding complex.

In the case of low oxidation state metal ions, possible redox reactions between the metal ion and ClO_2^- are an additional source of interference. Relatively fast redox reactions were reported between chlorite ion and several transition-metal ions and their complexes.[12–16] The rate of the electron-transfer process can be comparable, or even higher, than that of the complex formation reaction. Moreover, the redox reactions may generate strongly absorbing transient species, which obviously may complicate the evaluation of the data.

In order to avoid, or at least minimize, the effects of side reactions, the complex formation reactions should be monitored as soon as possible after mixing the reactants. Recent technical developments in fast kinetic methods make it possible to record the spectrum of the reacting systems a few milliseconds after triggering the reactions.[17] These techniques can effectively be applied for investigating both kinetic and equilibrium aspects of fast chemical processes. In this report, we present our stopped-flow–rapid-scan spectrophotometric (SF–RS) studies on the protolytic equilibria of the chlorite ion and the formation of the $CuClO_2^+$ complex.

Experimental Section

Chemicals. Reagent grade chemicals and deionized triply distilled water were used in all experiments. $NaClO_2$ was prepared from commercially available sodium chlorite (Olin, approximately 80% purity) according to the method described by Peintler et al.[18] In the final stage

---

[†] On leave from the Institute of Inorganic and Analytical Chemistry, Kossuth L. University, Debrecen, Hungary.

(1) Orbán, M.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 3907.
(2) Orbán, M.; DeKepper, P.; Epstein, I. R. *J. Phys. Chem.* **1982**, *86*, 431.
(3) Nagypál, I.; Bazsa, Gy.; Epstein, I. R. *J. Am. Chem. Soc.* **1986**, *108*, 3635.
(4) Nagypál, I.; Epstein, I. R. *J. Phys. Chem.* **1986**, *90*, 6285.
(5) Clapper, T. W.; Gale, W. A. In *Encyclopedia of Chemical Technology*, 2nd ed.; Kirk, R. E.; Othmer, D. F., Eds.; Wiley: New York, 1964; Vol. 5.
(6) Gordon, G.; Cooper, W. J.; Rice, R. G.; Pacey G. E. *Disinfectant Residual Measurement Methods*; AWWA Research Report; American Water Works Research Foundation: Denver, CO, 1987; and references therein.
(7) Thompson, R. C. *Inorg. Chem.* **1979**, *18*, 2379.
(8) Gordon, G.; Emmenegger, F. *J. Inorg. Nucl. Chem. Lett.* **1966**, *2*, 395.
(9) Gordon, G.; Kern, D. M. H. *Inorg. Chem.* **1964**, *3*, 1055.
(10) Gordon, G.; Kieffer, R. G.; Rosenblatt, D. H. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1972; Vol. 15, pp 201–286.
(11) Kieffer, R. G.; Gordon, G. *Inorg. Chem.* **1968**, *7*, 235.
(12) Khan, A. H.; Higginson, W. C. E. *J. Chem. Soc., Dalton Trans.* **1981**, 2537.
(13) Ondrus, M. G.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 985.
(14) Thompson, R. C.; Gordon, G. *Inorg. Chem.* **1966**, *5*, 562.
(15) Buchacek, R.; Gordon, G. *Inorg. Chem.* **1972**, *11*, 2154.
(16) Linn, D. E.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 3225.
(17) Robinson, B. H. In *Investigation of Rates and Mechanisms of Reactions, Part II*, 4th ed.; Bernasconi, C. F., Ed.; Wiley-Interscience: New York, 1986; pp 9–26.

0020-1669/91/1330-3785$02.50/0