eters for non-hydrogen atoms are given in Table IX.

Acknowledgment. We gratefully acknowledge financial support provided by the Office of Naval Research, Mechanics Division.

Supplementary Material Available: Tables of crystal data, positional and thermal parameters, anisotropic thermal parameters, and interatomic distances and angles (20 pages); listings of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

New Cyclic Phosphazenes with (Trimethylsilyl)methyl Side Groups: X-ray Crystal Structure of $[NP(CH_2SiMe_3)_2]_3$ and Its Conversion to $(NPMe_2)_3$[1]

Harry R. Allcock,* William D. Coggio, Masood Parvez, and Michael L. Turner

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

Received June 19, 1990

The synthesis of $[NP(CH_2SiMe_3)_2]_3$ has been achieved in almost quantitative yield via the reaction of Me_3SiCH_2Li with $(NPF_2)_3$ in tetrahydrofuran at 40 °C, followed by addition of a proton source. Treatment of $[NP(CH_2SiMe_3)_2]_3$ with $^nBu_4N^+F^-$ gave $(NPMe_2)_3$ in 60% yield. Partially substituted trimers of the formula $N_3P_3F_x(CH_2SiMe_3)_{6-x}$, where $x = 2$ and 4, were also prepared. The interaction of $(NPF_2)_3$ with Me_3SiCH_2Li involves a metal–hydrogen exchange side reaction to generate species such as $N_3P_3(CH_2SiMe_3)_5(CHSiMe_3)^-Li^+$, hence the need for subsequent protonation. Attempts to replace the fluorine atoms in *gem*-$N_3P_3F_4(CH_2SiMe_3)_2$ by treatment with $NaOCH_2CF_3$ led also to C–Si bond cleavage to generate *gem*-$N_3P_3(OCH_2CF_3)_4Me_2$. No C–Si bond cleavage occurred during the attempted preparation of *gem*-$N_3P_3(OCH_2CF_3)_2(CH_2SiMe_3)_4$, and none was detected when $[NP(CH_2SiMe_3)_2]_3$ was treated with $NaOCH_2CF_3$. The structure of $[NP(CH_2SiMe_3)_2]_3$ has been determined by single-crystal X-ray diffraction methods. Crystals were monoclinic with a $P2_1/n$ space group, with $a = 11.012$ (2) Å, $b = 19.851$ (5) Å, $c = 19.554$ (8) Å, $\beta = 90.51$ (2)°, $V = 4309.3$ Å^3, and $Z = 4$. A comparison is made with other alkyl- and (alkylsilyl)cyclotriphosphazenes.

The synthesis of phosphazene ring systems that bear organosilicon side groups is of interest from both mechanistic and practical points of view.[2-14] From a fundamental viewpoint a major problem is the development of reaction routes for the linkage of organosilicon units to the phosphorus atoms of phosphazene rings or chains. In our laboratory this has involved the study of a variety of reactions, including the interactions of chlorophosphazenes with aminosiloxane reagents[9] or Grignard reagents[4,5] or the reactions of phosphazenes having pendent organometallic sites with chloroorganosilanes.[8] Neilson and Wisian-Neilson[13-15] have also investigated a variant of this last route.

Our earlier work indicated that reactions of organosilyl Grignard reagents, such as Me_3SiCH_2MgCl, with chlorophosphazenes[4-7] provided an effective route for the replacement of *some* but not all of the chlorine atoms by organosilicon units. This method did not allow the preparation of species in which *all* the side groups were organosilicon units, because of interference by side reactions such as phosphorus–nitrogen bond cleavage.[16]

It is known from earlier studies[17-19] that the reactions between *fluoro*phosphazenes and organolithium reagents are cleaner than their counterpart reactions that utilize chlorophosphazenes. Side reactions such as phosphorus–nitrogen bond cleavage, metal–halogen exchange, or metal coordination to the skeletal nitrogen atoms play a smaller role in the chemistry of fluorophosphazenes. The fact that fluorine replacement is favored over side reactions in fluorophosphazene chemistry is attributed to the high electronegativity of the fluorine atoms.[17] For these reasons the present work involves an investigation of the reactions of hexafluorocyclotriphosphazene, $(NPF_2)_3$, with ((trimethylsilyl)methyl)lithium, Me_3SiCH_2Li. A major objective was the replacement of all six of the fluorine atoms by organosilicon units, together with an attempt to understand the mechanism of the substitution reaction.

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(16) Attempted reaction between excess $ClMgCH_2SiMe_3$ and $N_3P_3Cl_6$ at 66 °C for extended periods of time resulted in degradation of the phosphorus–nitrogen skeleton.[4,7] Attempts made in this work to react Me_3SiCH_3MgCl with $(NPF_2)_3$ did not result in any replacement of the fluorine atoms after refluxing for 24 h at 66 °C.

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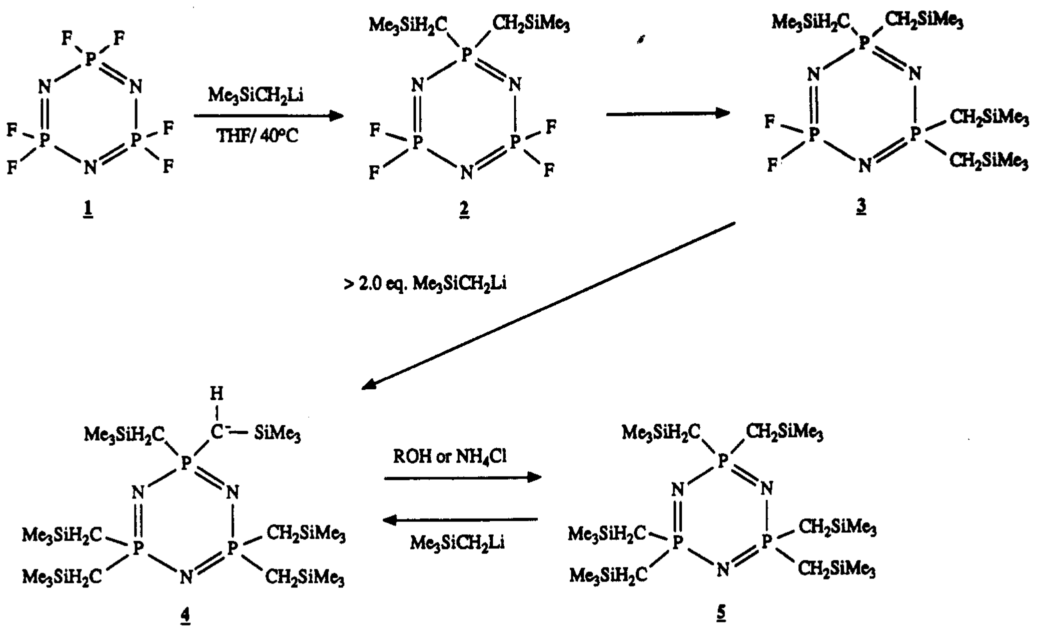
(18) Evans, T. L.; Patterson, D. B.; Suszko, P. R.; Allcock, H. R. *Macromolecules* **1981**, *14*, 218.

(19) (a) Paddock, N. L.; Ranganathan, T. N.; Todd, S. M. *Can. J. Chem.* **1971**, *49*, 164. (b) Paddock, N. L.; Ranganathan, T. N.; Todd, S. M. *Inorg. Chem.* **1973**, *12*, 316. (c) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201. (d) Ramachandran, K.; Allen, C. W. *J. Am. Chem. Soc.* **1982**, *104*, 2396.

0276-7333/91/2310-0677$02.50/0

Scheme I



From a practical viewpoint these reactions are important for the synthesis of high polymers that contain a phosphazene backbone and organosilicon side groups. Such species are of interest as membranes, low-temperature elastomers, and biomaterials. The (organosilyl)*cyclo*phosphazenes discussed here are possible "monomers" for ring-opening polymerization to macromolecules. Moreover, the reactions between $(NPF_2)_3$ and Me_3SiCH_2Li are models for the analogous interactions between the high polymer $[NPF_2]_n$ and the same organolithium reagent. The macromolecular reactions are considered in a separate publication.

Results and Discussion

Fluorine Replacement Reactions. The reaction between $(NPF_2)_3$ (1) and Me_3SiCH_2Li took place rapidly at 40 °C in tetrahydrofuran (THF). Fluorine replacement by CH_2SiMe_3 was geminal. The progress of the reaction and identification of products were followed by means of ^{31}P NMR spectroscopy and gas chromatography/mass spectrometry (GC/MS). The overall reaction pathway is summarized in Scheme I.

Formation of the fully substituted derivative $[NP(CH_2SiMe_3)_2]_3$ (5) was favored by higher reaction temperatures and shorter reaction times (<1.5 h). The yields of 5, as determined by ^{31}P NMR spectroscopy, were as high as 95% for reactions carried out in THF at 40 °C and as low as 30% for reactions carried out at −80 °C. Similar yields were obtained when diethyl ether was used as the reaction solvent in place of tetrahydrofuran.

The geminal pathway for the fluorine replacement process was identified by the following experiments. First, 1 molar equiv of Me_3SiCH_2Li in THF/pentane[20] was added to $(NPF_2)_3$ in THF. The ^{31}P NMR spectrum of this reaction mixture was consistent with the presence of a species such as $N_3P_3F_5(CH_2SiMe_3)$. The spectrum contained a doublet of triplets centered at 26 ppm (*P*FC) and a triplet of doublets centered at 4 ppm ($(PF_2)_2$; $^2J_{PP}$ = 53 Hz and J_{PF} = 800 Hz). Addition of a second equivalent of Me_3SiCH_2Li to the reaction mixture, followed by ^{31}P NMR analysis, showed that the *gem*-disubstituted product $N_3P_3F_4(CH_2SiMe_3)_2$ (2) had formed. Both of these compounds were identified further by GC/MS analysis. As discussed later, species 2 and its more highly substituted derivative 3 could be isolated, purified, and characterized from reactions in which a molar deficiency of Me_3SiCH_2Li was added to a solution of $(NPF_2)_3$ in THF. However, when exactly 6 equiv of Me_3SiCH_2Li was allowed to react with $(NPF_2)_3$, a mixture of *gem*-$N_3P_3F_2(CH_2SiMe_3)_4$ (3), $N_3P_3F(CH_2SiMe_3)_5$, and 5 were formed. This product mixture could be analyzed by ^{31}P NMR spectroscopy only after the reaction mixture was treated with a proton source such as methanol or NH_4Cl. The formation of these products was a consequence of a competing metal–hydrogen exchange process, discussed in the following section.

Metal–Hydrogen Exchange Reactions. As shown in Scheme I, the substitution process was complicated by a competing side reaction that involved metal–hydrogen exchange (deprotonation) at one or more of the methylene groups that connected silicon to skeletal phosphorus. This type of reaction has been reported before for species in which methyl groups are linked to phosphorus. For example, $(NPMe_2)_3$,[19a,b] $(NPPhMe)_n$,[14] and $(NPMe_2)_n$[15] undergo a metal–hydrogen exchange with methyl- or butyllithium to generate cyclic or polymeric phosphazenes with anionic methylene side groups. Subsequent reaction of these anionic sites with alkyl halides can result in the formation of novel alkylphosphazenes.[13,14,19a,b] However, if both phosphorus–alkyl and phosphorus–halogen bonds (i.e. $(NPMeF)_3$) are present in the molecule, then this exchange process can often result in detrimental side reactions such as phosphorus–nitrogen bond cleavage and ring-coupling reactions.[17] In the present system, these side reactions are retarded or prevented even though the initial deprotonation reaction takes place readily. Presumably this is a result of shielding by the bulky (trimethylsilyl)methyl side group. However, the existence of metal–hydrogen exchange species such as 4 in the reaction mixture necessitated the addition of a proton source in order to maximize the yield of 5.

Evidence that deprotonated species such as 4 were formed in this system was obtained mainly by ^{31}P NMR spectroscopy of the reaction mixtures. The two spectra shown in Figure 1 illustrate the changes that occur when $(NPF_2)_3$ in THF was added to an excess of Me_3SiCH_2Li

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(20) Me_3SiCH_2Li is available as a solution in pentane; therefore, pentane was present in all the reaction mixtures unless otherwise specified.

Table I. Analytical Data

compd	MS, m/z calcd	MS, m/z found	^{31}P NMR[a] signal	^{31}P NMR[a] shift, ppm	^{31}P NMR[a] J, Hz	elemental anal., % calcd	elemental anal., % found
$(NPF_2)_3$ (1)	249	249	PF_2	2.8 (t)	$J_{PF} = 840.0$		
gem-$N_3P_3F_2R_4$ (3, R = Me_3SiCH_2)	521[b]	521	$(PR_2)_2$	36.6 (d)	$^2J_{PP} = 31.3$	C, 36.82	37.01
			PF_2	1.8 (t, t)	$J_{PF} = 886.0$	H, 8.52	8.33
						N, 8.05	8.20
$N_3P_3R_5F$ (R = Me_3SiCH_2)	589[b]	589	$(PR_2)_2$	38.0 (d)	$^2J_{PP} = 32.0$	C, 40.70	40.10
			PFR	8.3 (d, t)	$J_{PF} = 904.0$	H, 9.41	9.36
						N, 7.12	6.90
$[NP(CH_2SiMe_3)_2]_3$ (5)	657[b]	657	$P(CH_2SiMe_3)_2$	22.6 (s)	$^2J_{PH} = 18.3$	C, 43.78	43.44
						H, 10.12	9.90
						N, 6.38	6.30

[a] ^{31}P NMR spectra were recorded in $CDCl_3$: s, singlet; d, doublet; t, triplet. [b] Fragments lost included methyl (m/z 15), $SiMe_3$ (m/z 73), and CH_2SiMe_3 (m/z 87).

in THF/pentane at 40 °C. Almost immediately the spectrum of the reaction mixture assumed the pattern shown in Figure 1a. No P–F coupling is evident (the P–F coupling of 800 Hz is absent), which suggests that all six fluorine atoms have been replaced by Me_3SiCH_2 units. However, the AB_2 character of the spectrum indicates that two different phosphorus environments are present in the molecule ($\delta_A = 32.2$ ppm, $\delta_B = 30.6$ ppm, $^2J_{PP} = 13.5$ Hz).

Addition of a small amount of methanol to this reaction mixture generated an exotherm and the conversion of the ^{31}P NMR spectrum to the singlet shown in Figure 1b. The proton-coupled ^{31}P NMR spectrum of this product was a pentet centered at 22.6 ppm ($^2J_{PH} = 18.3$ Hz). These results are compatible with the initial high-yield formation of the metal–hydrogen exchange product 4 and its conversion to species 5 following protonation. Full characterization data for 5 are listed in Table I.

The identification of 4 as an intermediate was also accomplished by the following experiments. First, hexakis((trimethylsilyl)methyl)cyclotriphosphazene (5) in THF-d_8 was allowed to react with 0.8 equiv of Me_3SiCH_2Li at 25 °C for 30 min. The ^{31}P NMR spectrum changed from that shown in Figure 1b to a spectrum similar to that shown in Figure 1a. A ^{13}C NMR spectrum of this species revealed the presence of a new methylene carbon environment, which appeared as a doublet upfield from the resonance associated with unreacted $P-CH_2SiMe_3$ units. This new resonance was assigned to deprotonated methylene group(s), in $P(CHSiMe_3)^-Li^+$ units. The upfield chemical shift of this carbon ($\delta = 18.3$ ppm, $J_{PC} = 80.0$ Hz) relative to the other methylene carbon atoms ($\delta = 28.4$ ppm, $J_{PC} = 82.1$ Hz) was consistent with the presence of a carbanion. Second, the same reaction mixture was then quenched with ND_4Cl to form a deuterio analogue of 5. The presence of a deuterium atom at an α-methylene carbon was confirmed by mass spectrometry and ^2H NMR spectroscopy. Thus, the ^{13}C NMR spectrum of the deuterium-labeled product lacked the anion site doublet at 18.3 ppm and the resonance at 28.4 ppm had broadened slightly due to C–D coupling. However, the most convincing evidence for the addition of a deuterium atom to a methylene carbon was the detection of a doublet in the ^2H NMR spectrum of this product at $\delta = 2.5$ ppm ($^2J_{PD} = 57.3$ Hz).

At what point in the overall reaction does metal–hydrogen exchange occur? Does it form at each step in the conversion of 1 to $N_3P_3F_5(CH_2SiMe_3)$, to 2, to 3, and to 5, or does it occur only for highly substituted species such as 5? Attempts were made to answer these questions by sequentially adding aliquots of Me_3SiCH_2Li to $(NPF_2)_3$ in THF and by monitoring the ^{31}P NMR spectrum at each step. No metal–hydrogen exchange was detected up to the point at which four fluorine atoms had been replaced by Me_3SiCH_2 units. Beyond that point, the presence of the deprotonated species 4 was detected easily from the appearance of a complex series of peaks between 35 and 25 ppm. The singlet spectrum, similar to that shown in Figure 1b, was generated, and the neutral products could be isolated only after addition of small amounts of methanol or NH_4Cl.

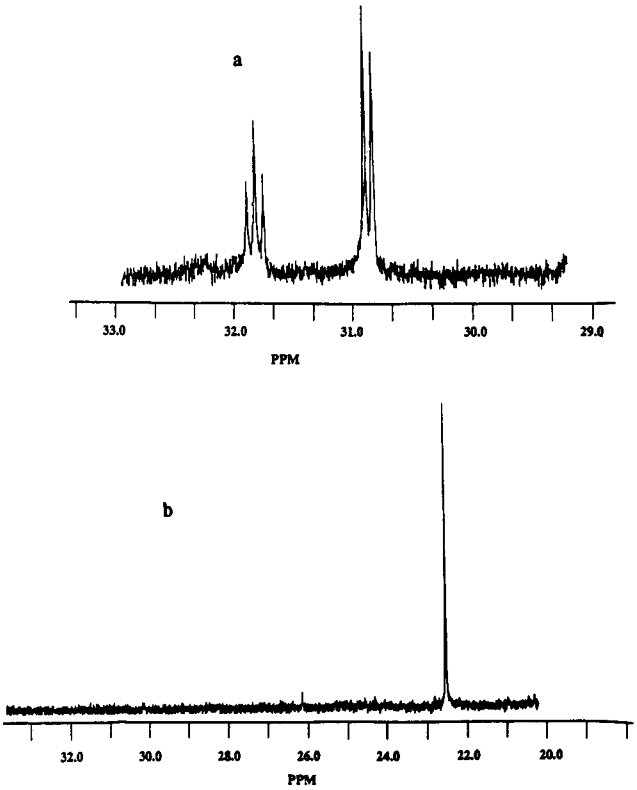

Figure 1. ^{31}P NMR spectra (121.5 MHz) of the reaction mixture obtained by the addition of $(NPF_2)_3$ to an excess of Me_3SiCH_2Li at 40 °C: (a) spectrum formed initially, which is indicative of metal–hydrogen exchange at a methylene unit (4); (b) spectrum formed after protonation of 4 by methanol to give $[NP(CH_2SiMe_3)_2]_3$ (5).

Replacement of Fluorine Atoms in 2 and 3 by Trifluoroethoxy Groups. Sodium trifluoroethoxide is a powerful nucleophile for the replacement of halogen side units in phosphazenes. Indeed, some of the earliest stable phosphazene trimers and high polymers were prepared by the route.[21] However, in the context of the present work, it was also known that C–Si bonds in (organosilyl)phosphazenes could be cleaved by sodium trifluoroethoxide in

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THF to convert, for example, a P–CH_2SiMe_3 group to a P–CH_3 unit.[4-7] The use of toluene as a solvent reduces this tendency for side-group bond cleavage. Thus, two questions were of interest in the present work. First, can the fluorine atoms in **2** or **3** be replaced by trifluoroethoxy groups without cleavage of the C–Si bonds? Second, could conditions be found to convert **5** to $(NPMe_2)_3$ by treatment with sodium trifluoroethoxide? The species $(NPMe_2)_3$ is difficult to prepare by alternative routes.

The compound *gem*-$N_3P_3F_4(CH_2SiMe_3)_2$ (**2**) was synthesized and was allowed to react in situ with excess $NaOCH_2CF_3$ in THF for 24 h at 66 °C. Replacement of all four fluorine atoms by the OCH_2CF_3 groups occurred readily but was accompanied by C–Si bond cleavage to give $N_3P_3(OCH_2CF_3)_4Me_2$ (**6**) (Scheme II, eq 1).

The species *gem*-$N_3P_3F_2(CH_2SiMe_3)_4$ (**3**) was treated similarly, but for 36 h at 66 °C. The reaction pattern was strikingly different. No C–Si bond cleavage occurred. Moreover, the reaction products consisted of unreacted **3** and *gem*-$N_3P_3(F)(OCH_2CF_3)(CH_2SiMe_3)_4$ (**7**), a product in which only one of the two fluorine atoms had been replaced (Scheme I, eq 2). It appears that the chemistry of compound **3** is strongly influenced by steric hindrance effects.

Finally, and surprisingly, it was found that species **5** underwent *no* reaction with $NaOCH_2CF_3$ in THF at 66 °C during reaction times as long as 72 h (Scheme II, eq 3). Thus, steric shielding in species **5** appears to confer a special stability not found in other (alkylsilyl)phosphazenes.

Conversion of 5 to $(NPMe_2)_3$. Following the failure of **5** to react with $NaOCH_2CF_3$, an attempt was made to induce C–Si bond cleavage with less hindered nucleophiles such as $^nBu_4N^+F^-$. The cleavage of C–Si bonds by fluoride ions has been well-documented. Other workers have used this approach to cleave trimethylsilyl groups from (trimethylsilyl)acetylene derivatives of cyclic phosphazenes.[22] It was found that crude **5** mixed to a paste with $^nBu_4N^+F^-$ and heated in a sublimator at 60 °C and 0.2 mmHg generated $(NPMe_2)_3$ (Scheme II, eq 4). The overall yield starting from $(NPF_2)_3$ was 50%. This simple, two-step synthesis represents a marked improvement over other multistep alternatives such as the equilibration of $(NPMe_2)_4$ at 350 °C for 96 h.[23]

Thermolysis. Some cyclophosphazenes undergo ring-opening polymerization when heated.[10,21,24,25] Others do not polymerize but participate in small-molecular ring-expansion reactions.[26-28] A third group undergoes condensation reactions.[29] Neither **3** nor **5** underwent any detectable reaction when heated at 250 °C for 96 h. Even when 2% of $(NPCl_2)_3$ (which polymerizes at this temperature) was added as a potential initiator, no change in **5** could be detected. This unusual stability can probably be attributed to the severe steric influence of the Me_3SiCH_2

Table II. Bond Lengths for $[NP(CH_2SiMe_3)_2]_3$ (Å)

P(1)–N(1)	1.592 (5)	Si(2)–C(7)	1.78 (1)
P(1)–N(3)	1.588 (5)	Si(2)–C(8)	1.77 (1)
P(1)–C(1)	1.795 (6)	Si(3)–C(9)	1.89 (1)
P(1)–C(5)	1.801 (7)	Si(3)–C(10)	1.82 (1)
P(2)–N(1)	1.616 (5)	Si(3)–C(11)	1.83 (1)
P(2)–N(2)	1.605 (5)	Si(3)–C(12)	1.83 (1)
P(2)–C(9)	1.790 (7)	Si(4)–C(13)	1.85 (1)
P(2)–C(13)	1.812 (7)	Si(4)–C(14)	1.78 (1)
P(3)–N(2)	1.612 (5)	Si(4)–C(15)	1.87 (1)
P(3)–N(3)	1.589 (5)	Si(4)–C(16)	1.75 (1)
P(3)–C(17)	1.772 (8)	Si(5)–C(17)	1.90 (1)
P(3)–C(21)	1.843 (8)	Si(5)–C(18)	1.90 (1)
Si(1)–C(1)	1.88 (1)	Si(5)–C(19)	1.85 (1)
Si(1)–C(2)	1.85 (1)	Si(5)–C(20)	1.79 (1)
Si(1)–C(3)	1.85 (1)	Si(6)–C(21)	1.81 (1)
Si(1)–C(4)	1.84 (1)	Si(6)–C(22)	1.81 (1)
Si(2)–C(5)	1.88 (1)	Si(6)–C(23)	1.84 (1)
Si(2)–C(6)	1.85 (1)	Si(6)–C(24)	1.69 (1)

Table III. Bond Angles for $[NP(CH_2SiMe_3)_2]_3$ (deg)

N(2)–P(1)–N(3)	116.5 (3)	C(2)–Si(1)–C(4)	109.1 (5)
N(1)–P(1)–C(1)	108.3 (3)	C(3)–Si(1)–C(4)	107.9 (4)
N(1)–P(1)–C(5)	109.5 (3)	C(5)–Si(2)–C(6)	109.3 (5)
N(3)–P(1)–C(1)	108.4 (3)	C(5)–Si(2)–C(7)	107.6 (5)
N(3)–P(1)–C(5)	107.6 (3)	C(5)–Si(2)–C(8)	116.1 (4)
C(1)–P(1)–C(5)	106.0 (3)	C(6)–Si(2)–C(7)	105.2 (6)
N(1)–P(2)–N(2)	116.4 (3)	C(6)–Si(2)–C(8)	109.5 (6)
N(1)–P(2)–C(9)	108.9 (3)	C(7)–Si(2)–C(8)	108.6 (7)
N(1)–P(2)–C(13)	108.2 (3)	C(9)–Si(3)–C(10)	112.2 (4)
N(2)–P(2)–C(9)	107.7 (3)	C(9)–Si(3)–C(11)	107.1 (4)
N(2)–P(2)–C(13)	109.5 (3)	C(9)–Si(3)–C(12)	114.6 (4)
C(9)–P(2)–C(13)	105.7 (3)	C(10)–Si(3)–C(11)	108.9 (5)
N(2)–P(3)–N(3)	116.4 (3)	C(10)–Si(3)–C(12)	105.7 (5)
N(2)–P(3)–C(17)	110.3 (2)	C(11)–Si(3)–C(12)	108.3 (5)
N(2)–P(3)–C(21)	107.8 (4)	C(13)–Si(4)–C(14)	110.8 (5)
N(3)–P(3)–C(17)	108.5 (3)	C(13)–Si(4)–C(15)	107.0 (4)
N(3)–P(3)–C(21)	108.8 (3)	C(13)–Si(4)–C(16)	116.2 (5)
C(17)–P(3)–C(21)	104.3 (4)	C(14)–Si(4)–C(15)	109.3 (6)
C(1)–Si(1)–C(2)	113.1 (4)	C(14)–Si(4)–C(16)	101 (1)
C(1)–Si(1)–C(3)	110.3 (3)	C(15)–Si(4)–C(16)	112.2 (6)
C(1)–Si(1)–C(4)	106.3 (4)	C(17)–Si(5)–C(18)	108.6 (4)
C(2)–Si(1)–C(3)	110.0 (5)	C(17)–Si(5)–C(19)	111.5 (4)
C(17)–Si(5)–C(20)	108.3 (5)	P(1)–N(1)–P(2)	122.5 (3)
C(18)–Si(5)–C(19)	108.9 (4)	P(2)–N(2)–P(3)	122.6 (3)
C(18)–Si(6)–C(22)	108.9 (5)	P(1)–N(3)–P(3)	122.9 (3)
C(19)–Si(5)–C(20)	110.9 (5)	P(1)–C(1)–Si(1)	120.9 (4)
C(21)–Si(6)–C(22)	108.9 (5)	P(1)–C(5)–Si(2)	122.2 (4)
C(21)–Si(6)–C(23)	108.7 (7)	P(2)–C(9)–Si(3)	120.4 (4)
C(21)–Si(6)–C(24)	120.7 (5)	P(2)–C(13)–Si(4)	122.1 (4)
C(22)–Si(6)–C(23)	102.8 (8)	P(3)–C(17)–Si(5)	118.6 (4)
C(22)–Si(6)–C(24)	115.2 (7)	P(3)–C(21)–Si(6)	121.1 (5)
C(23)–Si(6)–C(24)	98.0 (1)		

Table IV. Bond Lengths (Å)

compd	P–N	P–C	C–Si	Si–Me	P–Cl	ref
5	1.600	1.802	1.872	1.84		
$(NPMe_2)_3$	1.594	1.793				30
$(NPCl_2)_3$	1.67				1.99	21
gem-$N_3P_3Cl_4R_2$ (R = CH_2SiMe_3)	1.629	1.781	1.894	1.856	2.0	5
	1.57[a]					

[a] The value represents the length found at the phosphorus atom to which chlorine atoms are bonded.

Table V. Bond Angles (deg)

compd	NPN	PNP	NPC	CPC	NPCl	ClPCl
5	116.5	122.6	108.3	106.4	106.4	
$(NPMe_2)_3$	117.9	122.5	108.9	102.6		
$(NPCl_2)_3$	117.0	123.0				105.5
gem-$N_3P_3Cl_4R_2$ (R = CH_2SiMe_3)	113.1	122.4	107.5	107.9	107.3	100.3
	119.6[a]	120.0[a]				

[a] Values represent angles found at the phosphorus atom to which chlorine atoms are bonded.

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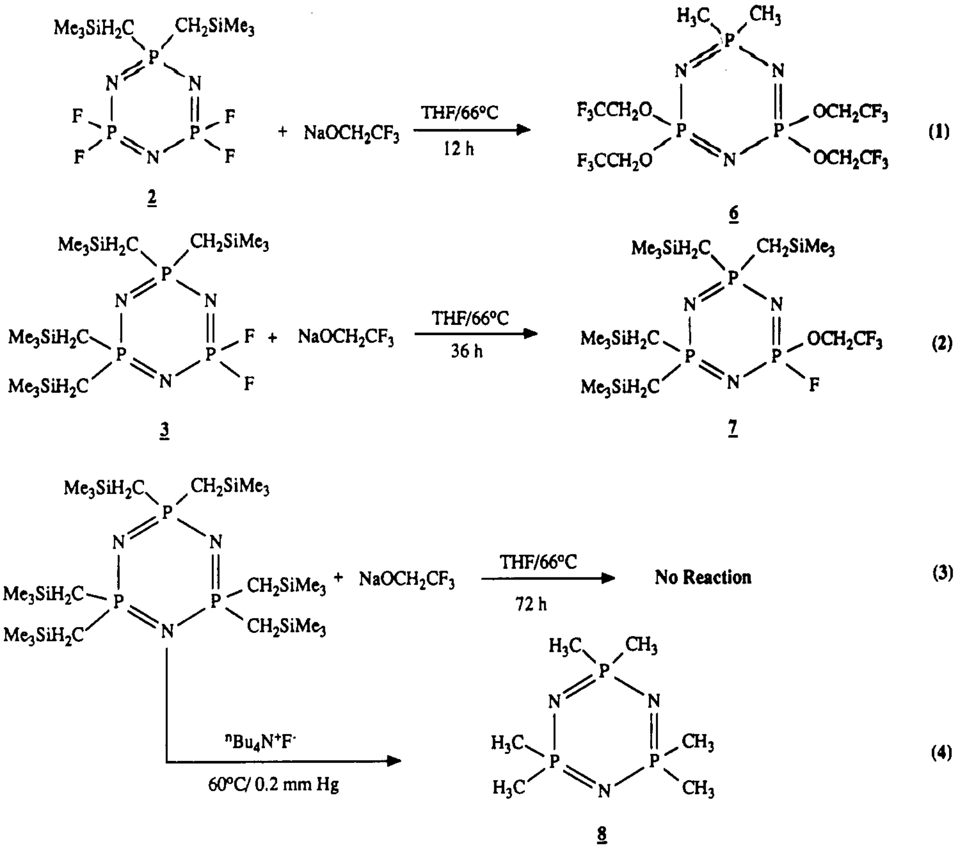
Scheme II



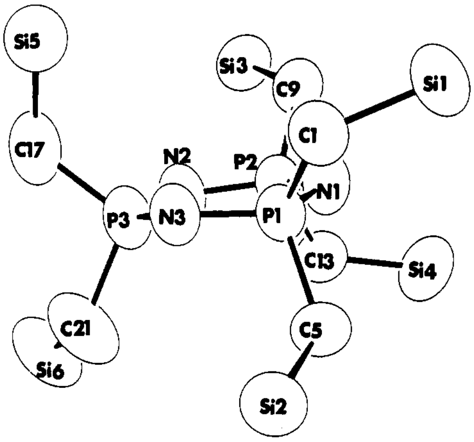


Figure 2. ORTEP structure of 5 with methyl groups omitted for clarity.

Table VI. Summary of Crystal Data and Collection Parameters

formula	$C_{22}H_{66}N_3P_3Si_6$
mw	658.25
cryst size, mm	0.37 × 0.54 × 0.43
space group	$P2_1/n$
a, Å	11.102 (2)
b, Å	19.851 (5)
c, Å	19.554 (8)
β, deg	90.51 (2)
V, Å^3	4309.3
Z	4
D(calcd), g/cm^3	1.015
radiation	Mo Kα
θ limits, deg	2–23
μ, cm^{-1}	3.151
λ, Å	0.71073
T, K	293
scan method	$\omega/2\theta$
ω-scan width, deg	1.00 + 0.35 tan θ
cryst decay	none
min transmissn coeff	0.9711
max transmissn coeff	0.9993
no. of unique data measd	4028
no. of data used [$I > 3\sigma(I)$]	3582
data:param ratio	11
R; R_w $(=(\sum w\Delta^2/\sum wF_o^2)^{1/2})$	0.073; 0.116
$(\Delta/\sigma)_{max}$ in last cycle	<0.2
$\Delta\rho$ in final ΔF map, e Å^{-3}	0.37, −0.04
final p param in weighting scheme	0.120
error in weights	1.737

side groups, which would both shield the skeleton and thermodynamically favor rings over chains because of side-group steric repulsion.[30] Further studies on the thermal behavior of these and high-polymeric counterparts are planned.

X-ray Structure of $[NP(CH_2SiMe_3)_2]_3$ (5). Compound 5 was analyzed by single-crystal X-ray diffraction techniques with a view to making comparisons between structure 5 and those of related alkyl- and (alkylsilyl)-phosphazenes reported previously.[3,5,6,10,31] The structure is shown in Figure 2. The structure of 5, solved from a data set collected at 25 °C, revealed some thermal disorder in the methyl groups, and this was partly responsible for the relatively high R factor of 7.3%. However, additional data collected at −80 °C were identical with those collected at room temperature. Hence, no further refinement was carried out. The bond lengths and angles of 5 were compared with those in $(NPCl_2)_3$, $(NPMe_2)_3$, and *gem*-$N_3P_3(CH_2SiMe_3)_2Cl_4$ and are listed in Tables II–V, respectively. The crystal data and collection parameters are listed in Table VI.

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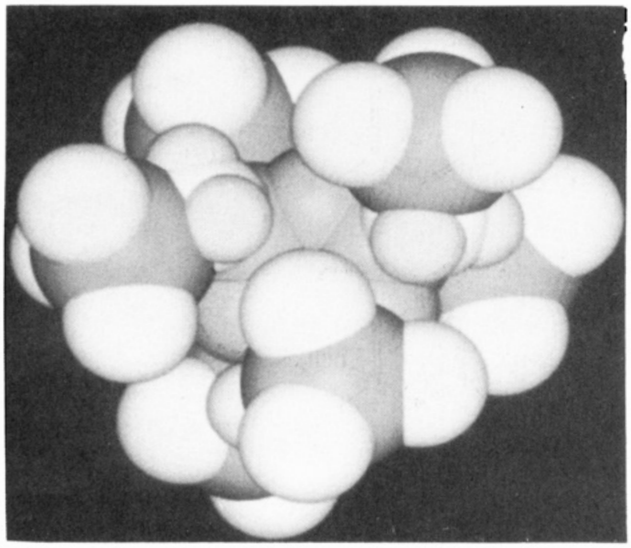

Figure 3. Computer-generated space-filling model of **5**. The model was generated from X-ray crystal structure data with use of the Sybil molecular mechanics program.

The phosphazene ring in **2** had a distorted chair conformation ($\chi^2 = 790$) for the least-squares-plane analysis through the phosphazene ring. A plane passed through atoms P(2), P(3), N(1), N(2), and N(3), while atom P(1) deviated from the plane by 0.18 Å.

The bond distances are listed in Table II. The phosphazene ring bond lengths ranged from 1.586 Å (P(3)–N(3)) to 1.615 Å (P(2)–N(1)). These values are consistent with those reported for analogous cyclotriphosphazenes (see Table IV). The P–C and C–Si bond lengths are similar to those in other alkyl- and (alkylsilyl)cyclotriphosphazenes.

The level of steric crowding of the CH_2SiMe_3 groups around the phosphazene ring is illustrated in Figure 2. The disposition of these groups generates a protective sheath of Si–Me units that serves as a barrier against attack by bulky reagents on the skeletal phosphorus atoms. This may explain the unreactivity of **5** toward $NaOCH_2CF_3$ and perhaps the resistance of **5** to undergo ring-opening polymerization reactions. However, it is clear from the computer-generated space-filling model[32] (Figure 3) that the methylene hydrogen atoms are exposed, and this undoubtedly explains why metal–hydrogen exchange occurs at these sites.

The bond angles in **5** are listed in Table III and are compared to those in related compounds in Table V. The phosphazene ring in **5** appears to be only slightly less strained than the ring in *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$. For example, the N–P(R_2)–N bond angle in **5** (116.5°) is 3° wider than the corresponding N–P(R_2)–N angle in *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (113.5°). This difference, although significant, is not enough to explain why *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ polymerizes when heated but **5** does not. More reasonable explanations include side-group steric hindrance effects and the absence of ionizable P–Cl or P–F initiation sites in **5**.

Experimental Section

Equipment. ^{31}P (36.2 MHz) and ^{13}C (22.5 MHz) NMR spectra were obtained with use of a JEOL FX 90Q spectrometer: references were relative to external 85% H_3PO_4 and $SiMe_4$, respectively. High-field ^{31}P NMR (120.5 MHz) and ^1H NMR (300.3 MHz) spectra were obtained with the use of a Bruker AM 300 spectrometer. ^2H NMR spectra (30.7 MHz) were obtained by use of a Bruker WP200 instrument and were referenced to C_6D_6 at 7.2 ppm. All heteronuclear NMR spectra were proton-decoupled unless otherwise specified. Infrared spectra were recorded by means of a Perkin-Elmer 1710 FTIR spectrophotometer interfaced with a Perkin-Elmer 3600 data station. Gas chromatography was carried out by means of a Varian 3700 unit with a flame ionization detector. A Supelco OV-101 column with injector and detector temperatures set at 270 °C was used. An initial temperature of 40 °C and a heating rate of 10 °C/min were employed. Typical sample sizes were between 1 and 3 μL in CH_2Cl_2. Retention times were in the range of 4–12 min. X-ray crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer controlled by a PDP 11/44 computer. Additional details of the X-ray analysis are available in Table VI and in the supplementary material.

Materials. Hexachlorocyclotriphosphazene was provided by Ethyl Corp. It was recrystallized from hexane and sublimed (30 °C, 0.05 mmHg) before use. All solvents were distilled from sodium–benzophenone ketyl. Hexafluorocyclotriphosphazene (**1**) was prepared by a method reported previously.[33] 2,2,2-Trifluoroethanol (Halocarbon) was distilled from anhydrous BaO. ((Trimethylsilyl)methyl)lithium, a 1.0 M solution in pentane, was obtained from Aldrich and was used as received. Me_3SiCH_2Li can be isolated as a solid by vacuum removal of pentane. It was stored in a nitrogen-filled glovebox in a sealed flask. *Caution!* $Me_3SiCH_2Li(s)$ is *extremely pyrophoric* and will ignite spontaneously even in dry air. Caution should be exercised when using this compound. All reactions with Me_3SiCH_2Li were carried out by use of dry glassware and solvents. Me_3SiCH_2Li, as a 1.0 M solution in pentane, was stored at 5 °C and was warmed to 25 °C before use to ensure a reproducible concentration. Because of the air sensitivity of many of these reagents, all manipulations were carried out with use of standard Schlenk-line techniques.

Synthesis of [NP(CH_2SiMe_3)$_2$]$_3$ (5). In a three-neck, round-bottomed flask was placed dry THF (50 mL) and Me_3SiCH_2Li (130 mL, 130 mmol) in pentane. The solution was warmed to 40 °C. $(NPF_2)_3$ (**1**; 5.0 g, 120 equiv of P–F bonds) was dissolved in dry THF (30 mL), and this solution was transferred to an addition funnel under nitrogen. The solution of **1** was added to the warmed solution of Me_3SiCH_2Li, and the mixture was stirred for 90 min. The reaction mixture turned light yellow. A ^{31}P NMR spectrum of the mixture showed a complex series of peaks between 35 and 25 ppm. Addition of NH_4Cl or MeOH (*Caution!*) to the solution in an NMR tube produced an exotherm: the ^{31}P NMR spectrum of this sample gave a major singlet at 22.6 ppm and a smaller doublet at 36 ppm from *gem*-$N_3P_3F_2(CH_2SiMe_3)_4$. The reaction mixture was then treated with 30 mL of MeOH (*Caution!* An exotherm will result.) and was stirred for 5 min to quench the anion **4** and any excess Me_3SiCH_2Li. The pentane was removed under reduced pressure; the remaining solution was poured into water at 4 °C, and this mixture was extracted twice with diethyl ether. The organic layers were combined and were dried over $MgSO_4$. Removal of solvent left an oil that sublimed at 80 °C (0.5 mmHg) to give crude, oily crystals, which were then recrystallized from warm EtOH–THF (9:1). ^1H NMR ($CDCl_3$): $\delta = 1.1$ ppm (d, PCH_2, $^2J_{PH} = 18.0$ Hz); $\delta = 0.04$ ppm (s, $SiCH_3$). ^{13}C NMR ($CDCl_3$): $\delta = 28.4$ ppm (d, PCH_2, $J_{PC} = 82.1$ Hz); $\delta = 0.3$ ppm (s, $SiCH_3$). See Table I for additional characterization data.

Reaction of 5 with Me_3SiCH_2Li for NMR Studies. This reaction was carried out in a nitrogen-filled glovebox. Solid $Me_3SiCH_2Li(s)$ was obtained by removal of pentane at reduced pressure from a standard 1.0 M solution. *Caution!* See warning given earlier. Freshly sublimed and dried **5** (30 mg, 0.046 mmol) was dissolved in dry THF-d_8 (3 mL). To this solution was added 3.6 mg (0.8 equiv) of $Me_3SiCH_3Li(s)$. The reaction mixture was stirred for 30 min at 25 °C. A portion of the mixture was placed in a 5-mm NMR tube, which was capped and sealed with Teflon tape. ^{31}P, ^{13}C, and ^1H NMR spectra were obtained by use of a Bruker WP360 instrument operating at fields of 145.8, 90.3, and 360 MHz, respectively. To the remaining solution was added dry ND_4Cl (dried by heating under vacuum at 40 °C for 8 h), and the

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[32] Figure 3 was generated from the Sybil molecular mechanics program. The data were derived from the positional parameters (Table VII, supplementary material) obtained from the X-ray data set.

[33] Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 75.

mixture was stirred until the solvent had evaporated. The residue was removed from the glovebox and dissolved in hexane, and the solution was filtered to remove the salts. Removal of the hexane left a solid that was analyzed further by mass and NMR spectroscopy. The addition of the ^{2}H atom to a methylene carbon was confirmed by mass spectroscopy (m/z = 658 ($N_3P_3(CH_2SiMe_3)_5CHDSiMe_3$)) and ^{2}H NMR (THF, C_6D_6 lock; 2.6 ppm, d, J_{PCD} = 57.3 Hz).

Synthesis of *gem*-$N_3P_3(CH_2SiMe_3)_4F_2$ (3). Hexafluorocyclotriphosphazene (1; 2.0 g, 8.0 mmol) was dissolved in dry THF, and the solution was warmed to 40 °C. ((Trimethylsilyl)methyl)lithium (1.0 M solution in pentane, 35.0 mmol, 4.1 equiv) was added slowly to the stirred solution of 1. The reaction was monitored by ^{31}P NMR spectroscopy until no further change was detected. The pentane was removed under reduced pressure, and the remaining solution was poured into water. The solution was extracted twice with CH_2Cl_2, and the organic layers were combined and dried over $MgSO_4$. Filtration, followed by solvent removal, produced a light yellow oil. The crude mixture was purified by column chromatography on silica gel and eluted with hexane–CH_2Cl_2 (3:1); isolated yield 2.1 g (51%). ^{1}H NMR ($CDCl_3$): δ = 1.2 ppm (d, PCH_2, $^2J_{PH}$ = 15.4 Hz); δ = 0.03 ppm (s, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ = 27.0 ppm (d, PCH_2, J_{PC} = 84.8 Hz); δ = 0.3 ppm (s, $SiCH_3$). Additional characterization data are listed in Table I.

Synthesis of $N_3P_3(CH_2SiMe_3)_5F$. This reaction was carried out in a manner similar to the preparation of 3. Thus, hexafluorocyclotriphosphazene (1; 2.0 g, 8.0 mmol) was dissolved in dry THF and the solution was warmed to 40 °C. ((Trimethylsilyl)methyl)lithium (1.0 M solution in pentane, 44.0 mmol, 5.1 equiv) was added to the stirred solution of 1. The reaction was terminated when no further change was detected by ^{31}P NMR spectroscopy. After solvent removal and extraction with CH_2Cl_2, the crude product was found to contain a mixture of tetra-, penta-, and hexasubstituted trimers, as determined by GC retention times. The mixture was purified by column chromatography on silica gel and was eluted with hexane–CH_2Cl_2 (3:1); isolated yield 1.2 g (21%) of $N_3P_3(CH_2SiMe_3)_5F$. ^{1}H NMR ($CDCl_3$): δ = 1.1 ppm (d, PCH_2, $^2J_{PH}$ = 13.5 Hz); δ = 0.1 ppm (s, $SiCH_3$). ^{13}C NMR ($CDCl_3$): δ = 27.5 ppm (d, PCH_2, J_{PC} = 81.5 Hz); δ = 0.6 ppm (s, $SiCH_3$). See Table I for additional characterization data.

Synthesis of $(NPMe_2)_3$ by C–Si Bond Cleavage.[34] Crude 5 (2.0 g, 0.30 mmol) was placed in a sublimator and was mixed with $^nBu_4N^+F^-\cdot 3H_2O$. The solid mixture was heated under vacuum (0.2 mmHg). $(NPMe_2)_3$ had sublimed onto the cold finger after 4–6 h. The sublimation was continued for an additional 6 h, and the contents of the sublimator were stirred occasionally. $(NPMe_2)_3$ was collected from the cold finger and was recrystallized from hot heptane to remove traces of $^nBu_4N^+F^-$ that had cosublimed with the product: isolated yield 0.41 g (60% yield); mp 188–190 °C. ^{1}H NMR ($CDCl_3$): δ = 1.4 ppm (d, PCH_3, $^2J_{PH}$ = 12.3 Hz). ^{13}C NMR ($CDCl_3$): δ = 23.4 ppm (d, PCH_3, J_{PC} = 94.1 Hz). ^{31}P NMR ($CDCl_3$): δ = 24.4 ppm (s, $^2J_{PH}$ = 12.3 Hz).

Acknowledgment. We thank the Air Force Office of Scientific Research for the support of this work. We also thank A. J. Benesi and L. M. Jackman for help with NMR experiments. The assistance of D. C. Ngo with the computer-generated space-filling model is also gratefully acknowledged.

Supplementary Material Available: Positional parameters (Table VII), general displacement parameter expressions (Table VIII), an ORTEP diagram, including methyl groups (Figure 4), and a table of least-squares planes for 5 (6 pages); a listing of structure factor amplitudes (41 pages). Ordering information is given on any current masthead page.

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(34) C–Si bond cleavage by $^nBu_4N^+F^-$ was also found to be effective when carried out in solution. However, it was found that yields improved significantly if the reaction was carried out in the solid state.

Displacement of Hard Bases from a Soft Center by a Soft Ligand: Reaction of $Ir(CO)(OH)(SO_4)L_2$ (L = PPh_3, $P(p\text{-tolyl})_3$) with CO and the Crystal Structure of $[Ir(CO)_3(PPh_3)_2{}^+][HSO_4{}^-]\cdot{}^1/_3H_2O$

Sherri L. Randall, Jeffrey S. Thompson, Lisa A. Buttrey, Joseph W. Ziller,
Melvyn Rowen Churchill,* and Jim D. Atwood*

*Departments of Chemistry, University at Buffalo, State University of New York,
Buffalo, New York 14214, and University of California, Irvine, California 92717*

Received March 13, 1990

The iridium(III) complexes $Ir(CO)(OH)(SO_4)L_2$, L = PPh_3, $P(p\text{-tolyl})_3$, have been prepared and shown to react with CO, yielding the iridium(I) species $[Ir(CO)_3L_2{}^+][HSO_4{}^-]$ (L = PPh_3, $P(p\text{-tolyl})_3$) and CO_2. The species $[Ir(CO)_3(PPh_3)_2{}^+][HSO_4{}^-]\cdot{}^1/_3H_2O$ crystallizes in the centrosymmetric rhombohedral space group $R\bar{3}$ [C_{3i}^2; No. 148]. Cell parameters (for the hexagonal setting) are a = 40.938 (7) Å, c = 11.850 (2) Å, V = 17 199 Å^3, and Z =18. Diffraction data (Mo K$\bar{\alpha}$, 2θ = 4.0–45.0°) were collected on a Syntex P2$_1$ diffractometer, and the structure was refined to R_F = 6.1% for all 4772 unique data (R_F = 4.2% for those 3673 data with $|F_o| > 6.0\sigma(|F_o|)$).

In many respects classical coordination chemistry ("Werner chemistry") and organometallic chemistry have followed divergent paths. Coordination complexes typically contain ligands with oxygen and nitrogen donor atoms surrounding the metal in an octahedral configuration, and the reactivity is dominated by the d-electron configuration of the metal. Organometallic complexes typically contain carbon and phosphorus donor atoms (with π-acceptor capabilities), and the 18-electron rule controls both the number of coordinated ligands and the reactivity. In recent years there has been a growth of interest in organometallic complexes containing oxygen (especially alkoxy) and nitrogen ligands, but these complexes are organometallic in most of their characteristics.[1]

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* To whom correspondence should be addressed at the State University of New York.

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