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Synthesis and Reactions of 2,4-Di-*tert*-butyl-3-chloro-1λ^6-thia-2,4-diaza-3-phosphetidine 1,1-Dioxide, a Heterocycle Containing Nitrogen, Sulfur, and Tricoordinate Phosphorus

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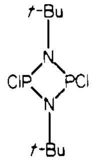
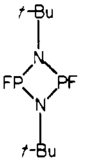
A new four-membered nitrogen–sulfur–phosphorus ring of composition $O_2S(t\text{-BuN})_2PCl$ has been prepared by the action of PCl_3 on the sulfamide $(t\text{-BuNH})_2SO_2$ in the presence of Et_3N and characterized by elemental analysis and NMR, IR, and mass spectroscopy. Reaction of the title compound with SbF_3 and Me_3SiNMe_2 afforded the 3-fluoro and 3-(dimethylamino) derivatives, $O_2S(t\text{-BuN})_2PF$ and $O_2S(t\text{-BuN})_2PNMe_2$, respectively, and treatment with sodium in octane produced the diphosphine $[O_2S(t\text{-BuN})_2P]_2$. Treatment of the thiadiazaphosphetidine ring with $Fe_2(CO)_9$ afforded the phosphorus–iron-bonded complex $O_2S(t\text{-BuN})_2P(Cl)Fe(CO)_4$.

Introduction

Following the discovery of the diazadiphosphetidines **1A**[3,4] and **1B**,[5] numerous publications have appeared concerning the stereochemistry,[6] ligative behavior,[7] and cognate chemistry[8] of this class of compound. The present paper is concerned with the synthesis of a four-membered nitrogen–sulfur–phosphorus ring system, which is related to the dihalodiphosphetidines by replacing a PX by an SO_2 moiety. This particular four-membered (thiadiazaphosphetidine) ring system has, in fact, been known for a number of years. For example, Becke-Goehring and co-workers[9] prepared the pentacoordinate phosphorus compounds **2**–**5**.


1A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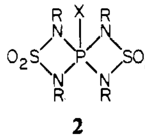
More recently, it has been shown that the reaction of *N*,*N*′-dimethyl- or *N*,*N*′-diethylsulfamide with PCl_3 in the presence of tertiary amines leads to apparently polymeric materials of composition $[O_2S(NMe)_2PCl]_n$ and to ring-opened products, respectively.[10]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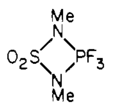
X = F, Cl
R = Me, Ph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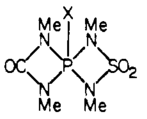
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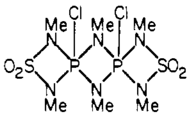
X = F, Cl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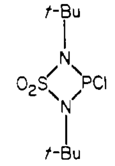
Since it is known from, e.g., diazadiphosphetidine chemistry, that sterically bulky nitrogen substituents stabilize the four-membered ring, we decided to investigate the reaction of *N*,*N*′-di-*tert*-butylsulfamide with PCl_3 in an effort to prepare **6**.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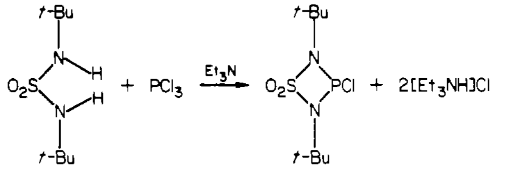
Results and Discussion

2,4-Di-*tert*-butyl-3-chloro-1λ^6-thia-2,4-diaza-3-phosphetidine 1,1-dioxide (**6**) can be prepared by the action of PCl_3 on the sulfamide $(t\text{-BuNH})_2SO_2$ in the presence of Et_3N (eq 1). The monomeric nature of **6** is indicated by the mass spectrum which exhibits a parent peak at *m*/*e* 273. There was no evidence for species possessing higher mass.



6
(1)

The significance of **6** is that it represents the first example of a four-membered nitrogen–sulfur–phosphorus(III) ring. As pointed out in the Introduction, only pentacoordinate phos-

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(1) University of Texas at Austin.
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(3) Scherer, O. J.; Klusmann, P. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 752.
(4) Other diazadiphosphetidines, $(RNPCl)_2$, particularly where R = Me and Ph, had been claimed much earlier, See: Michaelis, A.; Schroeter, G. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 690. Abel, E. W.; Armitage, D. A.; Willey, G. R. *J. Chem. Soc.* **1965**, 57. However, these claims were disputed subsequently. See: Goldschmidt, S.; Krauss, H. L. *Liebigs Ann. Chem.* **1955**, *595*, 193. Jefferson, R.; Nixon, J. F.; Painter, T. M. *J. Chem. Soc. D* **1969**, 622.
(5) Nixon, J. F.: Wilkins, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1970**, *25B*, 649.
(6) Muir, K. W.; Nixon, J. F. *J. Chem. Soc. D* **1971**, 1405. Muir, K. W.; *J. Chem. Soc., Dalton Trans.* **1975**, 259.
(7) (a) Hawker, P. N.; Jenkins, L. S.; Willey, G. R. *J. Organomet. Chem.* **1976**, *118*, C44. (b) Zeiss, W.; Feldt, C. H. *Ibid.* **1977**, *127*, C5. (c) Jenkins, L. S.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1979**, 777. (d) Burckett-St. Laurent, J. C. T. R.; Hosseini, J. S.; Sinclair, J.; Nixon, J. F. *Inorg. Chim. Acta* **1980**, *44*, L17.
(8) See, for example: Davies, A. R.; Dronsfield, A. T.; Haszeldine, R. N.; Taylor, D. R. *J. Chem. Soc., Perkin Trans. 1* **1973**, 379. Bowden, F. L.; Dronsfield, A. T.; Haszeldine, R. N.; Taylor, D. R. *Ibid.* **1973**, 516. Jefferson, R.; Nixon, J. F.; Painter, T. M.; Keat, R.; Stobbs, L. *J. Chem. Soc., Dalton Trans.* **1973**, 1414. Bulloch, G.; Keat, R. *Ibid.* **1974**, 2010; **1976**, 1113. Niecke, E.; Flick, W.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 309. Scherer, O. J.; Glassel, W. *Chem. Ber.* **1977**, *110*, 3874. Bulloch, G.; Keat, R.; Thompson, D. G. *J. Chem. Soc., Dalton Trans.* **1977**, 99. Harvey, D. A.; Keat, R.; Keith, A. N.; Muir, K. W.; Rycroft, D. S. *Inorg. Chim. Acta* **1979**, *34*, L201.
(9) Becke-Goehring, M.; Wald, H.-J.; Weber, H. *Naturwissenschaften* **1968**, *55*, 491. Becke-Goehring, M.; Weber, H. *Z. Anorg. Allg. Chem.* **1969**, *365*, 185. Becke-Goehring, M.; Wald, H.-J. *Ibid.* **1969**, *371*, 88. Becke-Goehring, M.; Schwind, H. *Ibid.* **1970**, *372*, 285.
(10) Roesky, H. W.; Mehrotra, S. K.; Platte, C.; Amirzadeh-Asl, D.; Roth, B. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1130.

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Table I. Summary of NMR Data for Thiadiazaphosphetidines

compd	chem shifts, ppm[a] ^{1}H	^{13}C	^{19}F	^{31}P	coupling const, Hz
$O_2S(t\text{-BuN})_2PCl$ (6)	1.42	29.75 (*Me*$_3$C), 58.49 (Me$_3$*C*)		107.43	$^2J_{PNC} = 2.96$, $^3J_{PNCC} = 5.88$
$O_2S(t\text{-BuN})_2PF$ (8)	1.46	30.12 (*Me*$_3$C), 57.71 (Me$_3$*C*)	−58.76	89.46	$^2J_{PNC} = 5.0$, $^3J_{PNCC} = 4.8$, $^1J_{PF} = 1227.5$
$O_2S(t\text{-BuN})_2PNMe_2$ (9)	1.32 Me$_3$C (80 °C) 2.65 Me$_2$N (80 °C) (−40 °C)	29.49 (*Me*$_3$C) 55.23 (Me$_3$*C*) 30.13 (N*Me*)		68.44	$^2J_{PNC} = 8.2$, $^3J_{PNCC} = 4.4$ $J_{PNCH} = 9$ $J_{PNCH'} = 15$, $J_{PNCH} = 3$
$[O_2S(t\text{-BuN})_2P]_2$ (12)	1.43	29.93 (*Me*$_3$C), 57.37 (Me$_3$*C*)		76.87	$^2J_{PNC} = \sim 0$, $^3J_{PNCC} = 3.4$
$O_2S(t\text{-BuN})_2P(Cl)Fe(CO)_4$ (15)	1.49[b]	29.34 (*Me*$_3$C),[c] 60.26 (Me$_3$*C*),[c] 212.21 (*C*O)[c]		125.30	$^2J_{PNC} = \sim 0$, $^3J_{PNCC} = 4.4$, $^2J_{PFeC} = 8.83$

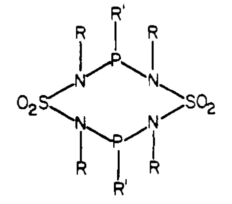
[a] See Experimental Section for statement of references used. [b] Chemical shift measured relative to internal C_6H_6 (7.24 ppm). [c] Chemical shift measured relative to internal pentane (13.70 ppm for Me groups).

Table II. Analytical and Infrared Spectroscopic Data for Thiadiazaphosphetidines

compd	% C calcd	% C found	% H calcd	% H found	% N calcd	% N found	% Cl calcd	% Cl found	IR[a] SO_2 vib[b]	IR[a] NSN vib
$O_2S(t\text{-BuN})_2PCl$ (6)	35.5	35.3	6.7	6.8	10.3	10.3	13.0	14.5	565, 1178, 1330	893
$O_2S(t\text{-BuN})_2PF$ (8)[c]									570, 1170, 1295	902
$O_2S(t\text{-BuN})_2PNMe_2$ (9)	42.7	42.9	8.6	8.9	14.9	14.8			570, 1168, 1300	890
$[O_2S(t\text{-BuN})_2P]_2$ (12)	40.5	39.7	7.7	8.3	11.8	11.4			570, 1170, 1315	905
$O_2S(t\text{-BuN})_2P(Cl)Fe(CO)_4$ (15)	32.7	32.6	4.1	4.4	6.4	6.5	8.1	8.2	528, 1177, 1326	892

[a] In cm^{-1}. [b] Assigned by analogy to the sulfamide $(t\text{-BuNH})_2SO_2$, which exhibits these vibrations at 531, 1140, and 1306 cm^{-1}. [c] Analysis impossible due to rapid hydrolysis; see text.

phorus compounds featuring this ring system had been described previously.[9] The succesful synthesis of **6** can be attributed to the steric demands of the *tert*-butyl groups since the attempted syntheses of the methyl or ethyl analogues of **6** resulted in production of apparently polymeric substances of composition $[O_2S(NMe)_2PCl]_n$ or ring-opened products.[10] Replacement of PCl_3 by the phosphinous chloride $MePCl_2$ or $PhPCl_2$ resulted in the production of eight-membered ring compounds (**7**).[10]

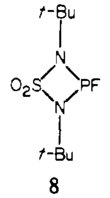


7

R′ = Me, Ph
R = Me, Et

The geometry of **6**, by analogy with that of the diazadiphosphetidine **1A**,[6] is expected to feature a slightly puckered four-membered ring with both nitrogens possessing essentially trigonal-planar geometries. Moreover, since the SO_2 moiety of **7** is arranged with the O–S–O planes perpendicular to the N–S–N planes,[10] a similar structural feature may be assumed for **6**. With these assumptions it is obvious that **6** can exist in only one conformation. Accordingly, only one peak was detectable in the ^{31}P NMR spectrum (Table I).

Treatment of **6** with SbF_3 and a catalytic amount of SbF_5 affords **8** in ~69% yield. Conventional elemental analysis (Table II) of **8** proved to be very difficult due to the moisture sensitivity of the compound. Accordingly, the characterization of **8** was based on NMR and mass spectroscopy. For example, a parent peak is apparent in the mass spectrum of **8** at *m/e* 256. Moreover, the presence of a PF (rather than, e.g., a PF_3) moiety is established by the ^{31}P and ^{19}F NMR spectra of **8**, both of which consist of doublets at anticipated chemical shift values (Table I).



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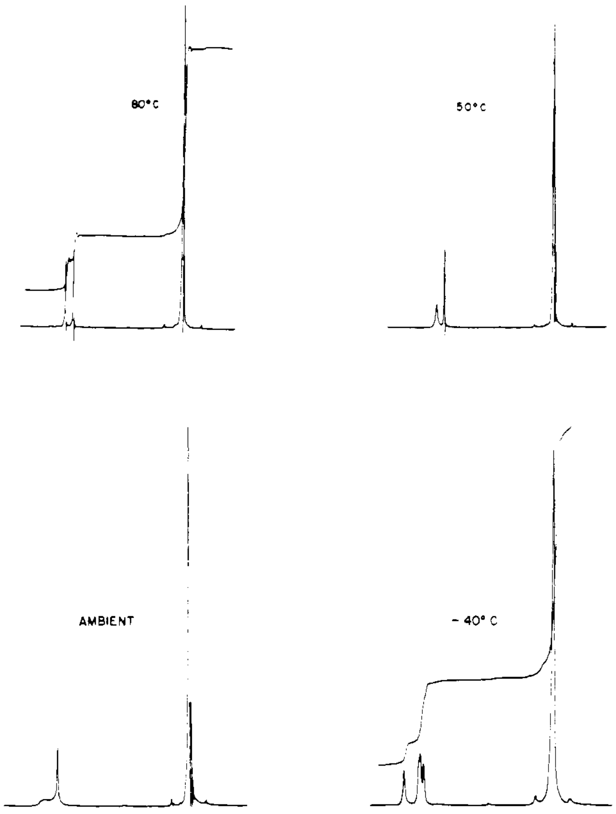
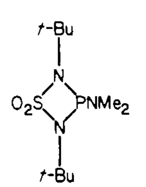


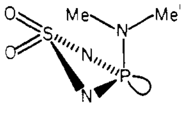
Figure 1. ^1H NMR spectra of $O_2S(t\text{-BuN})_2PNMe_2$ (**9**) at various temperatures.

The metathetical reaction of **6** with Me_3SiNMe_2 affords **9** in virtually quantitative yield. Compound **9** is a fluxional



9

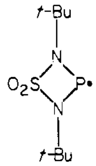
molecule. Below −40 °C two *N*-methyl signals are apparent in the ^1H NMR spectrum (Figure 1). Coalescence occurs at ~40 °C, and above this temperature averaging of the two methyl environments becomes rapid on the NMR time scale. The foregoing observations can be accommodated by postulating **10** as the ground-state structure. In this conformation



10

one of the exocyclic *N*-methyl groups (Me′) is situated syn to the phosphorus lone pair, while the other, (Me) lies across the PN_2S ring. Assignment of the larger PNCH coupling to Me′ (Table I) is consistent with previous observations on aminophosphines[11] and with more general trends concerning the influence of a syn lone pair of electrons on coupling constants.[12] A parallel may be drawn between **10** and the ground-state structure which has been suggested[13] for R_2N-substituted diazaphospholanes. We note that other suggestions have been made[14] for the geometry of the exocyclic R_2N moiety in diazaphospholanes. However, we favor **10** because it corresponds to the "bisected" geometry of acyclic aminophosphines[15] in which the nitrogen and phosphorus lone pairs are mutually orthogonal.

Lappert, Goldwhite, and co-workers[16] have shown that the treatment of phosphinous chlorides with sodium or electron-rich olefins leads to the production of stable radicals, $R_2P\cdot$, provided the bulk of the R groups is sufficient to impart kinetic stabilization. We were therefore prompted to treat **6** with sodium in octane in an attempt to generate **11**. However, **11** is not sufficiently long-lived to permit its isolation or spectroscopic identification, and the reaction results in the production of the diphosphine **12** which is the dimer of **11**.



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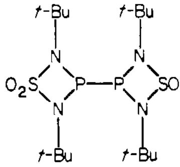
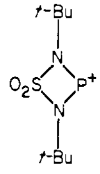


12

The conformational behavior of diphosphines is a matter of current interest. On one hand, it has been found that the gauche ground-state preference of tetraalkyldiphosphines increases as the steric bulk of the alkyl group is increased from Me to *t*-Bu.[17] On the other hand, we have found recently that bulky aryl groups such as mesityl favor the adoption of the anti conformation.[18] In the case of **12**, the ^1H NMR signal for the *t*-Bu groups remains a singlet down to −90 °C. In all likelihood, P–P rotation is still rapid on the NMR time scale at this temperature; however, our observations are also consistent with an anti ground-state geometry.

The treatment of haloaminophosphines with halide ion abstractors has been shown[19] to result in amino-substituted phosphenium ions, R_2P^+. We therefore attempted to prepare **13** via the following routes: (1) the reaction of **6** with Al_2Cl_6,



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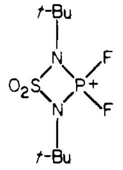
(2) the reaction of **6** with $NaBPh_4$, (3) the reaction of **6** with $AgBF_4$, and (4) the reaction of **8** with SbF_5. Reactions 1 and 2 do not proceed, reaction 3 affords $O_2S(t\text{-BuN})_2PF$ (**8**) and unidentified products, while reaction 4 produces the phosphonium cation **14**,[20] together with unidentified products.



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Reaction 4 implies the net transfer of F^+ from SbF_5 to **8**.[21] While the mechanism of this reaction is unknown, it can be

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[11] Cowley, A. H.; Dewar, M. J. S.; Jackson, W. R.; Jennings, W. B. *J. Am. Chem. Soc.* **1970**, *92*, 5206.

[12] Jennings, W. B.; Boyd, D. R.; Watson, C. G.; Becker, E. D.; Bradley, R. B.; Jerina, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 8501.

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[14] Gray, G. A.; Albright, T. A. *J. Am. Chem. Soc.* **1977**, *99*, 3243.

[15] For a summary of our theoretical and experimental work in this area, see: Cowley, A. H.; Mitchell, D. J.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1979**, *101*, 5224 and references therein.

[16] Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Chem. Commun.* **1976**, 623.

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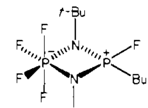
[18] Baxter, S. G.; Cowley, A. H.; Davis, R. E.; Riley, P. E. *J. Am. Chem. Soc.*, in press.

[19] Fleming, S.; Lupton, M. K.; Jekot, K. *Inorg. Chem.* **1972**, *11*, 2534. Hutchins, R. O.; Maryanoff, B. E. *J. Org. Chem.* **1972**, *37*, 3475. Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3046. Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Ibid.* **1977**, *16*, 994. Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784. Cowley, A. H.; Cushner, M. C.; Lattman, M.; McKee, M. L.; Szobota, J. S.; Wilburn, J. C. *Pure Appl. Chem.* **1980**, *52*, 789.

[20] Unfortunately, it was not possible to isolate a salt of **14** in a pure state. The structure most similar to **14** is that of the zwitterion

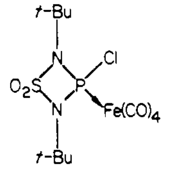


For the four-coordinate phosphorus moiety, $\delta_P = +68.5$, $\delta_F = -72.6$, and $J_{PF} = 1228$ Hz. See: Schlak, O.; Schmutzler, R.; Shiebel, H.-M.; Wazeer, M. I. M.; Harris, R. K. *J. Chem. Soc., Dalton Trans.* **1974**, 2153.

[21] This type of reaction has been observed previously in our laboratory. For example, $(Me_2N)_2PF$ reacts with AsF_5 to produce the phosphonium cation $[(Me_2N)_2PF_2]^+$. The ^{31}P NMR spectrum of this cation consists of a triplet at +20.79 ppm with $J_{PF} = 1055.9$ Hz, and the ^{19}F spectrum consists of a doublet at −85.5 ppm with the same J_{PF}. See: Pagel, D. M.A. Thesis, University of Texas at Austin, 1980.

speculated that two steps are involved. Presumably, the first step involves oxidative fluorination of **8** to the trifluorophosphorane, and the second step is fluoride ion abstraction from the latter.

From the reaction of **6** with $Fe_2(CO)_9$, it is possible to isolate



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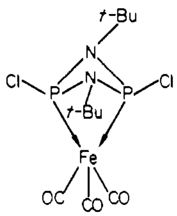
15 in almost quantitative yield. This compound is formulated as the P-bonded complex for the following reasons: (i) there is a significant change in the ^{31}P NMR chemical shift upon coordination (Table I), (ii) coupling between ^{31}P and the carbonyl carbons is detectable and is of appropriate magnitude for $^2J_{PFeC}$, and (iii) ^{13}C NMR spectroscopy indicates that the *t*-Bu groups are isochronous.

It is interesting to contrast the behavior of **1A** and **6** toward $Fe_2(CO)_9$. The diazadiphosphetidine **1A** can act in a chelating (**16**) or bridging (**17**) capacity.[7a,c]



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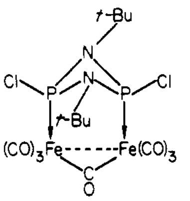

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Finally, we note that although the phosphorus atom of **6** can behave as a donor toward an $Fe(CO)_4$ moiety, it is not sufficiently active to react with elemental sulfur or MeI.

Experimental Section

Materials and General Procedures. *N*,*N*′-Di-*tert*-butylsulfamide, $O_2S(t\text{-BuNH})_2$, was prepared according to the method of Bermann and Van Wazer.[22] The physical properties of $O_2S(t\text{-BuNH})_2$ corresponded to those reported by Stowell.[23] (Dimethylamino)trimethylsilane was synthesized by the literature method,[24] and $Fe_2(CO)_9$ was prepared by UV irradiation of $Fe(CO)_5$ in pentane. All other reagents were procured commercially and used without subsequent purification. All solvents were carefully dried prior to use.

Virtually all the materials described herein are moisture sensitive. Accordingly, it was necessary to perform all operations in vacuo or under an inert atmosphere.

Elemental analyses were carried out by Canadian Microanalytical Service, Ltd., Vancouver, B.C., Canada. The analytical data are summarized in Table II.

Spectroscopic Measurements. The ^1H and ^{19}F NMR spectra were recorded on Varian A-60 and EM-390 instruments operating at spectrometer frequencies of 60 and 84.96 MHz, respectively. The variable-temperature ^1H NMR experiments were conducted on a Varian HA 100 spectrometer. Except where indicated in Table I, the ^1H and ^{19}F chemical shifts were measured with respect to internal CH_2Cl_2 (5.28 ppm relative to Me_4Si) and external CCl_3F, respectively. The ^{13}C and ^{31}P NMR spectra were measured in the FT mode on a Bruker WH-90 instrument operating at spectrometer frequencies of 22.6 and 36.43 MHz, respectively. Dichloromethane (54.2 ppm relative to Me_4Si) was employed as the internal reference for the ^{13}C spectra, and 85% H_3PO_4 was used as the external reference for the ^{31}P spectra. The NMR data are summarized in Table I.

IR spectra of Nujol mulls were recorded on a Perkin-Elmer 137 spectrophotometer using NaCl plates. Selected IR data are summarized in Table I. The mass spectra were determined on a CEC 21-491 spectrometer at an ionizing voltage of 70 eV.

Preparation of $O_2S(t\text{-BuN})_2PCl$ (6). A 20% excess of the required amount of Et_3N was added to a solution of 6.0 g (28.8 mmol) of $O_2S(t\text{-BuNH})_2$ in ~60 mL of diethyl ether. To this solution was added slowly with constant stirring a solution of 3.8 g (27.7 mmol) of PCl_3 in 15 mL of Et_2O. An exothermic reaction was observed. After the addition was complete, the mixture was refluxed for approximately 4 h. Filtration, removal of solvent, and subsequent vacuum distillation (bp 86–91 °C (0.5 torr)) gave an oil which solidified immediately upon cooling. The yield of the product after distillation was 5.0 g (18.3 mmol, 64.7% yield). The white solid, mp 61–64 °C, can also be purified by sublimation in vacuo or by recrystallization from a mixture of dichloromethane and pentane at low temperatures.

Preparation of $O_2S(t\text{-BuN})_2PF$ (8). A mixture of 6.44 g (24.4 mmol) of $O_2S(t\text{-BuN})_2PCl$, a 20% excess of SbF_3, and a catalytic amount of SbF_5 in ~60 mL of dichloromethane was refluxed for approximately 6 h. Filtration and removal of solvent gave a white solid product which contained some impurities. Purification was achieved by vacuum distillation at 81 °C (0.5 torr). A white crystalline solid, mp 53–55 °C, was formed on cooling. The yield was 69% (4.3 g, 16.78 mmol).

Preparation of $O_2S(t\text{-BuN})_2PNMe_2$ (9). A solution of 2.0 g (7.33 mmol) of $O_2S(t\text{-BuN})_2PCl$ (**6**) and 0.94 g (8.02 mmol) of Me_3SiNMe_2 in ~40 mL of CH_2Cl_2 was stirred at −20 °C for 2 h. The temperature of the reaction mixture was raised slowly, initially to room temperature and then to reflux. The refluxing was continued for 2 h. Removal of solvent and subsequent vacuum distillation (86–87 °C (0.5 torr)) gave the pure white, waxy solid product in 96% yield (1.98 g, 7.04 mmol).

Preparation of $[O_2S(t\text{-BuN})_2P]_2$ (12). A mixture of 3.48 g (12.8 mmol) of $O_2S(t\text{-BuN})_2PCl$ (**6**) and 0.43 g (18.7 mmol) of Na in 40 mL of octane was heated under reflux for 3 h. A black solid separated out from the reaction mixture as the sodium reacted. Filtration and removal of the solvent gave 2.34 g (4.95 mmol) of yellowish solid **12**.

Attempted Preparation of $[O_2S(t\text{-BuN})_2P]^+$ (13). (a) Attempted Reaction of $O_2S(t\text{-BuN})_2PCl$ (6) with Al_2Cl_6. Aluminum trichloride (1.5 g, 1.13 mmol) was added to a stirred solution of 3.1 g (1.14 mmol) of $O_2S(t\text{-BuN})_2PCl$ (**6**) at −80 °C. The suspended solid dissolved slowly; however, ^{31}P NMR spectroscopic assay of the solution revealed only the presence of unreacted **6**.

(b) Attempted Reaction of $O_2S(t\text{-BuN})_2PCl$ (6) with $NaBPh_4$. Sodium tetraphenylborate (2.495 g, 7.29 mmol) was added to a solution of **6** (1.99 g, 7.30 mmol) in ~30 mL of CH_2Cl_2 at −80 °C. The mixture was stirred for 2 h at this temperature, allowed to warm to room temperature, and stirred for an additional 4 h. ^{31}P NMR spectroscopic assay of the solution indicated that no reaction had occurred.

(c) Reaction of $O_2S(t\text{-BuN})_2PCl$ (6) with $AgBF_4$. Silver tetrafluoroborate (2.31 g, 1.19 mmol) was added to a stirred solution of 2.3 g (0.84 mmol) of $O_2S(t\text{-BuN})_2PCl$ (**6**) in ~20 mL of CH_2Cl_2 at −80 °C. An evolution of gas was observed at low temperatures. The ^{31}P NMR spectrum of the solution at room temperature revealed the presence of $O_2S(t\text{-BuN})_2PF$ (**8**) together with some unidentified signals.

(d) Reaction of $O_2S(t\text{-BuN})_2PF$ (8) with SbF_5. Antimony pentafluoride (3.6 g, 1.66 mmol) was added to a vigorously stirred solution of 4.23 g (1.65 mmol) of $O_2S(t\text{-BuN})_2PF$ (**8**) in ~20 mL of CH_2Cl_2 at −80 °C. The ^{31}P spectrum of the solution was measured after approximately 3 h of stirring and found to consist of several peaks. The color of the solution changed from colorless to black during this time. After 2 days, the ^{31}P (triplet centered at 35.64 ppm with J_{PF} = 1191 Hz) and the ^{19}F (doublet centered at −81.7 ppm with same coupling constant; SbF_6^- broad signal at −109.7 ppm) spectra of the reaction mixture showed the presence of the difluorophosphonium cation $[O_2S(t\text{-BuN})_2PF_2]^+$.[20]

Preparation of $O_2S(t\text{-BuN})_2P(Cl)Fe(CO)_4$ (15). A mixture of 1.95 g (7.15 mmol) of $O_2S(t\text{-BuN})_2PCl$ and 2.2 g (6.05 mmol) of Fe_2CO_9 in ~30 mL of pentane was heated under reflux for 4–5 h. The suspended solid went into solution slowly, accompanied by the evolution of gas and a change of color of the reaction mixture from yellow to brown. After the solvent was stripped, the product was evacuated for 4 h and then recrystallized from pentane at low temperatures. Yellow needles of **15** (mp 123–124 °C) were obtained in virtually quantitative yield.

Attempted Reaction of $O_2S(t\text{-BuN})_2PCl$ (6) with MeI. A solution of 1.2 g (0.44 mmol) of $O_2S(t\text{-BuN})_2PCl$ (**6**) and ~15 mL of MeI

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was heated under reflux for approximately 5 h. The solution remained clear during this period. ^{31}P NMR spectroscopy indicated the presence of only unchanged starting material.

Attempted Reaction of $O_2S(t\text{-}BuN)_2PCl$ (6) with Elemental Sulfur. A mixture of 2.63 g (0.96 mmol) of $O_2S(t\text{-}BuN)_2PCl$ (6) and an excess of elemental sulfur was refluxed in benzene for approximately 5 h. When the mixture was allowed to stand overnight, yellow crystals of elemental sulfur deposited from the solution. NMR spectroscopic examination of the filtrate revealed only the presence of unchanged starting material.

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Registry No. **6**, 76037-02-0; **8**, 76037-03-1; **9**, 76037-04-2; **12**, 76037-05-3; **14**, 76037-06-4; **15**, 76037-10-0; $O_2S(t\text{-}BuNH)_2$, 13952-67-5; PCl_3, 7719-12-2; SbF_3, 7783-56-4; Me_3SiNMe_2, 2083-91-2; $AgBF_4$, 14104-20-2; SbF_5, 7783-70-2; Fe_2CO_9, 15321-51-4.

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Synthesis and Molecular Structure of Two Cyclotriphosphazenes with Phosphorus–Iron Bonds

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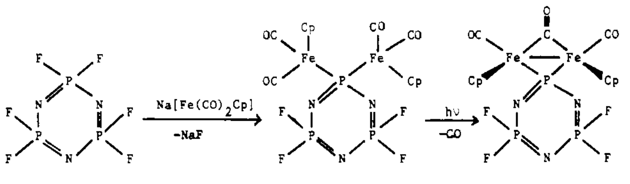
Hexafluorocyclotriphosphazene (I), $(NPF_2)_3$, reacts with sodium dicarbonylcyclopentadienylferrate to form photolytically unstable 1,1-bis(dicarbonylcyclopentadienyliron)-3,3,5,5-tetrafluorocyclotriphosphazene (II). This compound decarbonylates to 1,1-[μ-carbonyl-bis(carbonylcyclopentadienyliron)(*Fe–Fe*)]-3,3,5,5-tetrafluorocyclotriphosphazene (III) on exposure to light. Compounds II and III are the first phosphazenes known that contain direct phosphorus–metal side group bonds. In addition, III is the first phosphazene with a three-membered spirocyclic ring at phosphorus. Compounds II and III are forerunners of a potentially important class of new compounds based on other transition-metal systems. Spectroscopic evidence and X-ray crystallographic analyses were used to confirm the two structures. Compound II crystallizes in a triclinic unit cell of $P\bar{1}$ symmetry with lattice constants of a = 9.035 (3) Å, b = 14.287 (15) Å, c = 8.613 (4) Å, α = 104.04 (4)°, β = 110.44 (1)°, and γ = 96.56 (2)°; ρ_{calcd} = 1.9 g/cm^3 for Z = 2. Least-squares refinement gave R_1 = 0.056 and R$_2$ = 0.066 for 3906 observed reflections with $I \geq 3\sigma(I)$. The distance between the iron atoms in II is 3.922 (1) Å, and the Fe–P–Fe angle is 119.12 (3)°. Compound III crystallizes in a triclinic unit cell of $P\bar{1}$ symmetry with lattice constants of a = 9.116 (14) Å, b = 14.219 (9) Å, c = 7.735 (17) Å, α = 90.48 (3)°, β = 113.93 (4)°, and γ = 92.83 (2)°; ρ_{calcd} = 1.9 g/cm^3 for Z = 2. Least-squares refinement gave R_1 = 0.0498 and R_2 = 0.0524 for 2634 observed reflections with $I \geq 3\sigma(I)$. The Fe–Fe bond distance in III is 2.593 (1) Å and the Fe–P–Fe bond angle is 72.77 (3)°. The N–P–N bond angles at the phosphorus that is bonded to the iron atoms are 109.18 (11) and 110.09 (16)° for compounds II and III, respectively. In both compounds, an alternation of longer and shorter bonds exists for the P–N bonds located at increasing distance from the iron atoms.

Halophosphazenes, both polymeric and cyclic, are known to react with a wide range of nucleophiles including alkoxides, aryl oxides, amines, and organolithium or Grignard reagents[1] to yield *organo*phosphazenes of the type $[NP(OR)_2]_{3,4,n}$, $[NP(NHR)_2]_{3,4,n}$, or $(NPR_2)_{3,4,n}$. However few examples of phosphazene–transition-metal compounds have been reported,[2-7] and in most of these cases the phosphazene component served as a coordination ligand for the transition metal.

In this paper, we extend the known reactions of halophosphazenes into a new and important area—the synthesis of the first compounds that contain a metal-to-phosphorus covalent bond. This has been accomplished by the interaction of halophosphazenes with transition-metal carbonyl anions. Here we report the interaction of one of the most nucleophilic transition-metal carbonyl anions,[8] $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, with $(NPF_2)_3$ (I). This has led to the isolation of two cyclophosphazenes that possess iron–phosphorus covalent bonds. These compounds have the structures shown in II and III.



I II III

Species II and III are of interest because (a) they are the first members of a potentially large group of transition-metal-linked cyclophosphazenes, (b) such compounds are expected to provide new information about the bonding within the phosphazene ring, and (c) these cyclic derivatives are models for the synthesis of the related phosphazene high-polymer derivatives. Polyphosphazenes of this type may be important because of their potential value in the development of new polymeric electrical conductors and because of their potential utility in polymer-supported catalyst systems. Work on these applied aspects is under way.

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