organolithium reagents yielding partially and fully substituted phosphazenes.[5]

Experimental Section

Materials.—Reagent grade tetrahydrofuran used in these experiments was refluxed with calcium hydride, distilled, and stored over calcium hydride. Triphenyltin chloride and tri-*n*-butyltin chloride were obtained from Metal and Thermit Corp. and used as received. The hexachlorocyclotriphosphazene was prepared from the NH_4Cl–PCl_5 reaction in monochlorobenzene; mp 111–112° (lit.[4] mp 114°). Mol wt: calcd, 348; found, 350 in benzene. *Anal.* Calcd for $[PNCl_2]_3$: N, 12.06; P, 26.72; Cl, 61.20. Found: N, 12.03; P, 26.85; Cl, 61.04. The infrared spectrum is consistent with that of hexachlorocyclotriphosphazene reported in the literature. Triphenylstannyllithium and tri-*n*-butylstannyllithium were prepared by the method of Gilman, *et al.*[3,6]

Analyses.—Elemental analyses and molecular weight determinations were carried out by Galbraith Microanalytical Laboratories, Inc., Knoxville, Tenn. The infrared spectra (listed in Table I) were obtained with a Beckman IR-10 spectrophotometer. The spectra of liquids were determined on thin films supported by KBr plates. The spectra of solids were determined using KBr pellets. Melting points were obtained using Pyrex capillaries on a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. The ^1H nmr spectra were recorded with a Varian Model A-60A nuclear magnetic resonance spectrometer.

TABLE I

INFRARED SPECTRAL DATA (CM^{-1})[a]

$(C_6H_5)_3SnSn(C_6H_5)_3$, KBr disk

3060 (m), 3000 (w), 2920 (w), 1870 (w), 1820 (w), 1730 (w), 1640 (w), 1575 (w), 1160 (w), 1075 (s), 1025 (m), 1000 (s), 970 (vw), 730 (vs), 700 (vs), 675 (vw), 660 (w), 445 (s)

$(n\text{-}C_4H_9)_3SnSn(n\text{-}C_4H_9)_3$, neat

2835 (b, vs), 1450 (vs), 1420 (sh), 1380 (m), 1340 (sh), 1290 (sh), 1255 (s), 1200–970 (vb, vs), 960 (sh), 860 (s), 790 (vs), 655 (vs), 640 (m), 580 (vs), 485 (vs)

[a] Key: v, very; s, strong; m, medium; b, broad; w, weak.

Reaction of Triphenylstannyllithium with Hexachlorocyclotriphosphazene.—Triphenyltin chloride (22.5 mmol) was dissolved in 30 ml of dry tetrahydrofuran and the solution was added to 0.53 g (76 mg-atoms) of lithium metal cut into small pieces and suspended in 2 ml of dry tetrahydrofuran. The reaction mixture was stirred for 6 hr at room temperature under a dry nitrogen atmosphere. The insoluble matter was removed by passing the contents through a glass wool plug. The solution was transferred to a 100-ml, three-necked, round-bottomed flask equipped with a reflux condenser and a nitrogen inlet tube. A solution of hexachlorocyclotriphosphazene (3.28 mmol) in 40 ml of dry tetrahydrofuran was slowly added to the green solution of $(C_6H_5)_3SnLi$. After being stirred for 12 hr at room temperature, the mixture was refluxed for another 8 hr. Tetrahydrofuran was stripped off under vacuum leaving a tan solid in the flask. The solid was boiled with 60 ml of ether. The ether solution yielded 0.34 g of a white solid which melted at 190–220°. The infrared and ^1H nmr spectra of this solid were similar to those of the solid obtained from benzene solution and later identified as hexaphenyldistannane. The ether-insoluble solid was boiled with 50 ml of petroleum ether (bp 30–60°). A white solid (0.03 g) melting at 230–231° was recovered from the solution. This solid was identified as hexaphenyldistannane by its infrared spectrum and melting point. Recrystallization of the petroleum ether insoluble solid residue from hot benzene gave 5.22 g of a white, crystalline solid, mp 235–236° (lit.[7] mp 232°). Mol wt: calcd, 699; found, 690 in benzene. *Anal.* Calcd for $(C_6H_5)_3SnSn(C_6H_5)_3$: C, 61.77; H, 4.29; Sn, 33.94. Found: C, 61.52; H, 4.41; Sn, 33.67.

The ^1H nmr spectrum in completely deuterated chloroform showed a complex peak at 2.63 ppm (tetramethylsilane used as internal standard) which falls in the aromatic region. The total yield of hexaphenyldistannane was 5.59 g or 71% of theory.

The benzene-soluble solid was extracted with boiling tetrahydrofuran. Evaporation of the solvent yielded 1.17 g of a solid shown by its chloride content and its flame color to contain mostly lithium chloride.

The small amounts of a white residue insoluble in boiling tetrahydrofuran did not yield to further attempts at separation and identification.

Reaction of Tri-*n*-butylstannyllithium with Hexachlorocyclotriphosphazene.—Tri-*n*-butyltin chloride (20.0 mmol) was added to lithium metal (100 mg-atoms) cut into very small pieces and suspended in 2 ml of tetrahydrofuran. A dry nitrogen atmosphere was maintained. The reaction was initiated by adding a tiny crystal of iodine and warming the reaction mixture. Forty milliliters of tetrahydrofuran was slowly added to the reaction flask. The contents was stirred for 4 hr at room temperature and the reaction mixture was occasionally warmed. The insoluble matter was removed by passing the contents through a glass wool plug. The yellow solution containing $(n\text{-}C_4H_9)_3SnLi$ was transferred to a 100-ml, three-necked, round-bottomed flask fitted with a reflux condenser and nitrogen-inlet tube. Hexachlorocyclotriphosphazene (2.57 mmol) dissolved in 30 ml of tetrahydrofuran was slowly added to the yellow solution of the lithium salt. The reaction mixture was continuously stirred overnight and then refluxed for 8 hr. The white solid was then filtered, washed with tetrahydrofuran, and dried; yield 0.05 g. This solid was identified as LiCl by its chloride content and flame test.

Tetrahydrofuran was removed from the filtrate under vacuum leaving a greasy, yellowish residue, together with some liquid. The residue was extracted with 60 ml of boiling ether. Evaporation of the ether gave 3.3 g of a colorless liquid. Fractionation of this liquid at 0.2 mm and at a bath temperature of 150° yielded 0.61 g of a colorless liquid distilling at 106–108°. The infrared and H nmr spectra of this liquid were similar to those of the liquid obtained as the second fraction and identified as hexa-*n*-butyldistannane. The poor analytical data obtained for this material, however, indicate that this material was impure.

The bath temperature was raised to 230°. A liquid distilling at 152–154° (0.025 mm) was collected; yield 2.29 g, 49%. The boiling point reported in the literature for hexa-*n*-butyldistannane is 156–160° (0.025 mm).[8] Mol wt: calcd, 579; found, 560 in benzene (vapor phase osmometry). *Anal.* Calcd for $(n\text{-}C_4H_9)_3SnSn(n\text{-}C_4H_9)_3$: C, 49.70; H, 9.31; Sn, 40.97. Found: C, 47.89; H, 9.36; Sn, 42.93. The general observation that, in the combustion method, analysis for carbon in organotin compounds commonly gives low results because of the retention of some CO_2 by the SnO_2 residue accounts for the rather low carbon and rather high tin analyses obtained for hexa-*n*-butyldistannane.[9]

The ether-insoluble residue was extracted several times with boiling tetrahydrofuran. Evaporation of tetrahydrofuran yielded 0.88 g of a white solid identified as lithium chloride by its chloride analysis and flame test.

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[5] T. Moeller and F. Tsang, *Chem. Ind. (London)*, 361 (1962).

[6] H. Gilman, F. K. Cartledge, and S.-Y. Sim, *J. Organometal. Chem.*, **1**, 8 (1963).

[7] W. P. Neumann and B. Schneider, *Angew. Chem.*, **76**, 891 (1964).

[8] G. A. Baum and W. J. Considine, *J. Org. Chem.*, **29**, 1267 (1964).

[9] O. H. Johnson, *et al.*, *J. Amer. Chem. Soc.*, **77**, 5857 (1955).

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Preparation and Characterization of Oxobis(fluorosulfato)cerium(IV) and Trifluoro(fluorosulfato)cerium(IV)

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Peroxydisulfuryl difluoride has been reported to react with transition metal carbonates yielding oxyfluorosulfates in the higher oxidation state.[1] Bromine(I) fluorosulfate has been reported as an efficient fluoro-

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[1] R. Dev and G. H. Cady, *Inorg. Chem.*, **10**, 2354 (1971).

sulfonating and oxidizing agent.[2-5] Peroxydisulfuryl difluoride has now been found to react with cerium(III) carbonate to form oxobis(fluorosulfato)cerium(IV), while peroxydisulfuryl difluoride and bromine(I) fluorosulfate each react with cerium(III) fluoride giving trifluoro(fluorosulfato)cerium(IV).

Experimental Section

Materials.—Peroxydisulfuryl difluoride was prepared by the reaction of fluorine with sulfur trioxide[6] and purified by prolonged pumping of the crude product held at −78°. Infrared analysis and vapor density measurements indicated that the product was substantially pure. Bromine(I) fluorosulfate was prepared by the method of Aubke and Gillespie.[7]

Cerium(III) carbonate was prepared by dissolving Ce_2O_3 in dilute HCl and precipitating $Ce_2(CO_3)_3 \cdot 5H_2O$ by the addition of sodium bicarbonate solution. The pentahydrate was made anhydrous by heating it to 100–110° in an oven and subsequently drying under dynamic vacuum at about 70° for several hours. Cerium(III) fluoride was used as received from the American Potash and Chemical Corp. without further purification.

Infrared spectra of the solid compounds were obtained using Nujol mulls held between silver chloride disks. Spectra of the gaseous products were obtained with a 10-cm Pyrex glass cell fitted with silver chloride windows and a cold finger. The instrument used was a Beckman IR-10 spectrometer.

Reaction of Peroxydisulfuryl Difluoride with Cerium(III) Carbonate.—Cerium(III) carbonate, 0.0693 g, was placed in a 100-ml glass reaction vessel fitted with a Fischer-Porter LabCrest valve closed with a Teflon stopper. After evacuating and cooling the vessel to −183°, an excess of peroxydisulfuryl difluoride was added by distillation. The vessel was then brought slowly to room temperature and allowed to stand overnight. The volatile products were removed by pumping and were shown by a combination of distillation and infrared spectroscopic techniques to be CO_2, $S_2O_6F_2$, $S_2O_5F_2$, O_2, and a trace of SiF_4. After pumping to constant weight at room temperature, the vessel contained 0.1028 g of an orange solid. The calculated weight for $CeO(SO_3F)_2$ was 0.1067 g.

For analysis, a weighed sample of the solid was digested at 100° in an excess of a solution 0.1 *M* in NaOH and 0.1 *M* in Na_2CO_3. The cerium carbonate which precipitated was removed by filtration. The filtrate was then neutralized and treated with oxalic acid. Any cerium oxalate which precipitated was removed and combined with the carbonate. After igniting at about 800°, the resulting CeO_2 was weighed. Sulfur was determined by weighing as $BaSO_4$ and fluorine was determined using a distillation technique similar to that of Willard and Winter[8] followed by titration with 0.1 *N* $Th(NO_3)_4$. A fluoride ion selective electrode was used to observe the end point. *Anal.* Calcd for $CeO(SO_3F)_2$: Ce, 39.6; S, 10.7; F, 18.1. Found: Ce, 39.8; S, 10.5; F, 16.5.

Reaction of Peroxydisulfuryl Difluoride with Cerium(III) Fluoride.—Cerium(III) fluoride, 0.1882 g, was placed in a 100-ml glass vessel like that described in the previous paragraph. An excess of peroxydisulfuryl difluoride, 0.8223 g, was condensed onto the CeF_3, while the vessel was held at −183°. The reaction vessel was then placed behind a safety shield and brought to room temperature. A visible reaction took place. After the vessel had stood for 16 hr to allow all of the cerium(III) fluoride to react, the volatile materials were removed by pumping until the remaining yellowish brown solid had a constant weight of 0.2810 g. The theoretical weight for CeF_3SO_3F was 0.2830 g.

Reaction of Bromine(I) Fluorosulfate with Cerium(III) Fluoride.—Cerium(III) fluoride, 0.1547 g or 0.785 mmol, was placed in a vessel similar to that described above. Bromine(I) fluorosulfate, 1.4663 g or 8.20 mmol, was condensed onto the CeF_3 while the vessel was held at −183°. The reaction vessel was slowly warmed to room temperature behind a safety shield. The reaction proceeded to completion at room temperature when left overnight.

TABLE I

IR SPECTRA OF $CeO(SO_3F)_2$ AND $CeF_3(SO_3F)$

KSO_3F[a]	$CeF_3(SO_3F)$	$CeO(SO_3F)_2$	Assignments[b]
1280 s	1270 vs, br	1346 vs 1224 vs, br	ν_4(e) SO_3 asym st
1080 s	1112 s, br	1160 s, br 1045	ν_1(a) SO_3 sym st
750 s	841 s 725 m, br	873 s 720 m, br 652 m	ν_2(a) S–F st
590 s	598 w 583 m	604 s 579 s	ν_5(e) SO_3 asym def
570 sh	560 s	564 s	ν_3(a) SO_3 sym def
408 vw	420 m, vbr	416 w	ν_6(e) S–F def
138 m, br			Lattice vib

[a] Reported in ref 9. [b] Assignments are tentative and are based on those found in ref 9: s, strong; m, medium; v, very; w, weak; br, broad; sh, shoulder; def, deformation; sym, symmetric; asym, asymmetric; st, stretch; vib, vibration.

There was no oxygen found among the volatile products. The vessel was held at room temperature and pumped to constant weight. A yellowish brown crystalline solid having a weight of 0.2342 g remained. The expected weight for $CeF_3(SO_3F)$ was 0.2326 g. This product had the same properties as that of the previous paragraph. *Anal.* Calcd for CeF_3SO_3F: Ce, 47.3; S, 10.8; F, 25.7. Found: Ce, 46.8; S, 10.4; F, 26.1.

Infrared Spectra (Nujol Mulls).—The infrared spectrum of $CeF_3(SO_3F)$ is much simpler than that of $CeO(SO_3F)_2$. The region of the $CeO(SO_3F)_2$ spectrum between 1400 and 1000 cm^{-1} consists of a strong broad absorption centered at about 1250 cm^{-1} with some fine structure superimposed on it. The spectrum of $CeF_3(SO_3F)$ also has a strong broad peak in the S–O stretching region, but this band takes up only the region from about 1400 to 1150 cm^{-1} and is centered at about 1265 cm^{-1}. It has much less fine structure than that of $CeO(SO_3F)_2$. The location of the S–F stretching peak is at 873 and 841 cm^{-1} in the $CeO(SO_3F)_2$ and $CeF_3(SO_3F)$ spectra, respectively. The $CeO(SO_3F)_2$ spectrum also has more peaks than does the $CeF_3(So_3F)$ spectrum in the region 725–560 cm^{-1}. The peaks are listed in Table I along with the spectrum of KSO_3F and assignments reported by Gobeau and Milne.[9] From splitting of the E modes (ν_4 and ν_5) in the spectrum for $CeO(SO_3F)_2$ and an apparent lack of splitting for $CeF_3(SO_3F)$, it seems that the SO_3F groups in the former compound have lost the C_{3v} symmetry they possess in $Ca(SO_3F)_2$[9] whereas the symmetry seems to have been retained in $CeF_3(SO_3F)$. This, together with the higher frequency of the S–F stretching mode of $CeO(SO_3F)_2$ relative to that of $CeF_3(SO_3F)$, may mean that the former is a more covalent material than the latter.[9-12]

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(2) D. D. DesMarteau, *Inorg. Chem.*, **7**, 434 (1968).
(3) J. E. Roberts and G. H. Cady, *J. Amer. Chem. Soc.*, **82**, 352 (1960).
(4) W. P. Gilbreath and G. H. Cady, *Inorg. Chem.*, **2**, 496 (1963).
(5) B. L. Earl, B. K. Hill, and J. M. Shreeve, *ibid.*, **5**, 2184 (1966).
(6) F. B. Dudley and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 513 (1957).
(7) F. Aubke and R. J. Gillespie, *Inorg. Chem.*, **7**, 599 (1968).
(8) H. H. Willard and O. B. Winter, *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).
(9) J. Gobeau and J. B. Milne, *Can. J. Chem.*, **45**, 2321 (1967).
(10) D. A. Edwards, M. J. Stiff, and A. A. Woolf, *Inorg. Nucl. Chem. Lett.*, **3**, 426 (1967).
(11) D. W. Sharpe, *J. Chem. Soc.*, 3761 (1956).
(12) R. J. Gillespie and W. A. Whitla, *Can. J. Chem.*, **47**, 4153 (1969).

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Reaction of Bromine(I) Fluorosulfate with Gold and with Platinum

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The reaction of bromine(I) fluorosulfate with gold and platinum was discovered almost accidentally.