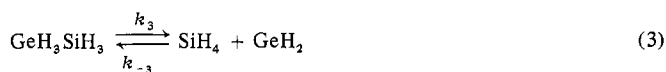


position route of Si-P bond rupture in  $\text{SiH}_3\text{PH}_2$  to yield  $\text{SiH}_3$  and  $\text{PH}_2$  radicals.

The results from the pyrolyses of  $\text{GeH}_3\text{SiH}_3$  in the presence of a 10/1 excess of  $\text{CH}_3\text{SiH}_3$  and  $\text{CH}_3\text{SiD}_3$  (stable at  $500^\circ$ )<sup>11</sup> clearly demonstrate that  $\text{GeH}_3\text{SiH}_3$  decomposed by eq 3 and possibly by eq 4. The absence of molecular hydrogen elim-



inates primary formation of H atoms by Si-H or Ge-H rupture. The fact that  $\text{SiH}_3\text{D}$  was not formed in the pyrolysis with  $\text{CH}_3\text{SiD}_3$  eliminates initial homolytic Si-Ge rupture to form  $\text{SiH}_3$  and  $\text{GeH}_3$  radicals. The low yield of  $\text{GeH}_4$  argues similarly.

The fact that no silylene ( $\text{SiH}_2$ ) insertion products were found under conditions where this diradical has been chemically trapped<sup>1,2,12</sup> suggests that step 4 is less significant than expected from the  $\text{SiH}_4/\text{GeH}_4$  product ratio.

The homogeneity of these reactions (decomposition and insertion) is uncertain at this time. However, the thermal reactions of  $\text{SiH}_3\text{PH}_2$  and  $\text{GeH}_3\text{SiH}_3$  follow the same mechanism as that of the homogeneous<sup>13</sup> thermal decomposition of  $\text{Si}_2\text{H}_6$  (eq 5 and 6). The alkali metal salt catalyzed de-



composition of  $\text{Si}_2\text{H}_6$  in  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$ <sup>14</sup> and the Pyrex-catalyzed thermolysis of  $\text{P}_2\text{H}_4$ <sup>15</sup> both appear to follow an intermolecular exchange not observed in the thermal reactions of  $\text{SiH}_3\text{PH}_2$  and  $\text{GeH}_3\text{SiH}_3$  with deuteriosilanes. Thus, it appears that the pyrolyses of  $\text{SiH}_3\text{PH}_2$  and  $\text{GeH}_3\text{SiH}_3$  are homogeneous over a silicon mirror. In our further discussion, we assume that these decompositions were homogeneous.

It is interesting to note that while 1,2-hydrogen shifts in  $\text{SiH}_3\text{PH}_2$  take place with similar rates ( $k_1 \approx k_2$ ),  $\text{GeH}_3\text{SiH}_3$  decomposes primarily by one route ( $k_3 \gg k_4$ ). These results can be understood if one assumes that the forward and reverse (insertion) reactions are reversible, which should be the case. We then have that

$$k_i = K_i k_{-i} \quad (7)$$

where  $K_i$  is the equilibrium constant. Since entropies of formation for silicon compounds are fairly additive,<sup>16</sup> one has that

$$\log K_i/K_j = (\Delta H_j^\circ - \Delta H_i^\circ)/2.3RT$$

where  $\Delta H_i^\circ$  is the heat of reaction for the  $i$ th reaction. Although the heats of formation of  $\text{GeH}_2$  and PH are not known, one can estimate that  $K_3/K_4$  is probably  $10^4$  or greater while  $K_1$  and  $K_2$  are probably of the same order of magnitude. Therefore, in  $\text{GeH}_3\text{SiH}_3$ , even with  $k_{-4} > k_{-3}$ ,  $K_3 \gg K_4$  so that  $k_3 \gg k_4$ . In  $\text{SiH}_3\text{PH}_2$ ,  $K_1/K_2$  and  $k_{-1}/k_{-2}$  are both small numbers so that  $k_1/k_2$  is also a small number.

Data from competitive  $\text{GeH}_2$  insertions into  $\text{Ge}_2\text{H}_6$  vs.  $(\text{CH}_3)_3\text{SiH}$  compared to  $\text{SiH}_2$  insertions into  $(\text{CH}_3)_3\text{SiH}$  vs.

$(\text{CH}_3)_3\text{GeH}$ <sup>17</sup> suggest that  $\text{GeH}_2$  insertions are greatly favored into Ge-H bonds vs. Si-H bonds. This observation is consistent with the results from this study. In the pyrolysis of  $\text{GeH}_3\text{SiH}_3$  in the presence of  $\text{CH}_3\text{GeH}_3$  in a 8/1 gas phase excess, the product ratio of  $\text{CH}_3\text{Ge}_2\text{H}_5$  to  $\text{SiGe}_2\text{H}_8$  (presumed to be mainly  $\text{SiH}_3\text{Ge}_2\text{H}_5$ ) was on the order of 7/1 which would be due to  $\text{GeH}_2$  insertion into the Ge-H bonds of  $\text{CH}_3\text{GeH}_3$  and  $\text{SiH}_3\text{GeH}_3$ . In the pyrolysis of  $\text{GeH}_3\text{SiH}_3$  in the presence of  $\text{CH}_3\text{SiD}_3$  in a 10/1 gas phase excess, the products  $\text{CH}_3\text{SiGeD}_3\text{H}_2$  (presumed to be  $\text{CH}_3\text{SiD}_2\text{GeH}_2\text{D}$ ) and  $\text{SiGe}_2\text{H}_8$  (presumed to be mainly  $\text{SiH}_3\text{Ge}_2\text{H}_5$ ) were obtained in similar quantities. These products were due to  $\text{GeH}_2$  insertions into the Ge-H bond in  $\text{GeH}_3\text{SiH}_3$  and the Si-D bond in  $\text{CH}_3\text{SiD}_3$ .

**Registry No.**  $\text{GeH}_3\text{SiH}_3$ , 13768-63-3;  $\text{SiH}_3\text{PH}_2$ , 14616-47-8; PH, 13967-14-1.

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Contribution from the Savannah River Laboratory, E. I. du Pont de Nemours and Company, Inc., Aiken, South Carolina 29801

### Quadrivalent Actinide Tetrakis(hexafluoroacetylpyrazolide) Compounds<sup>1</sup>

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Pyrazole ( $\text{HN}_2\text{C}_3\text{H}_3$  or HPz) can react to form polymeric compounds with transition metal ions, lanthanide ions, or actinide ions.<sup>3-5</sup> The probable structure of a polymeric metal pyrazolide (Figure 1a) is stabilized by the resonance both in the pyrazolide ligand and its chelate-type bonding with metal ions. The polymeric metal ion pyrazolides are quite insoluble and inert to dilute acids and bases.

Mahler, at the Du Pont Experimental Station, discovered that hexafluoroacetone (hfa) and some other perhaloketones will react with polymeric pyrazolides to yield compounds with a stability comparable to that of chelates.<sup>5</sup> These compounds are formed by hfa adding between the 1 nitrogen of pyrazole and the metal ion and breaking half the pyrazolide-metal ion bonds (Figure 1b). Mahler prepared and characterized hexafluoroacetylpyrazolide (hfaPz) compounds with 16 metal ions including  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$ . The work reported in this paper includes the synthesis and study of tetrakis(hexafluoroacetylpyrazolide) compounds of  $\text{U}^{4+}$ ,  $\text{Np}^{4+}$ , and  $\text{Pu}^{4+}$  and the tetrakis(hexafluoroacetyl-3-methylpyrazolide), (hfa-3-MePz)<sub>4</sub>, compounds of  $\text{Th}^{4+}$ ,

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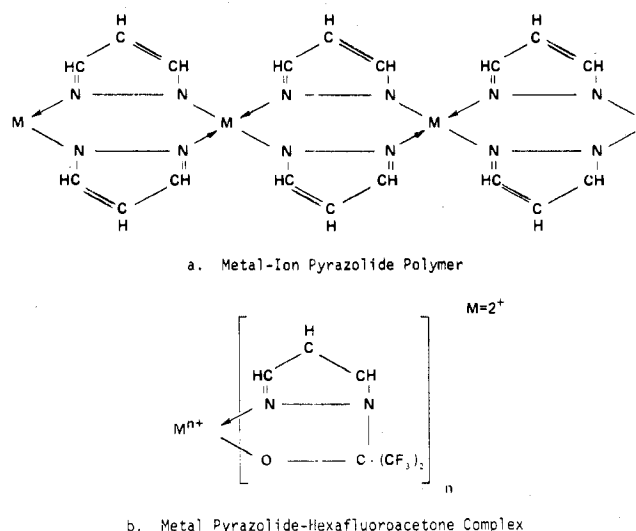
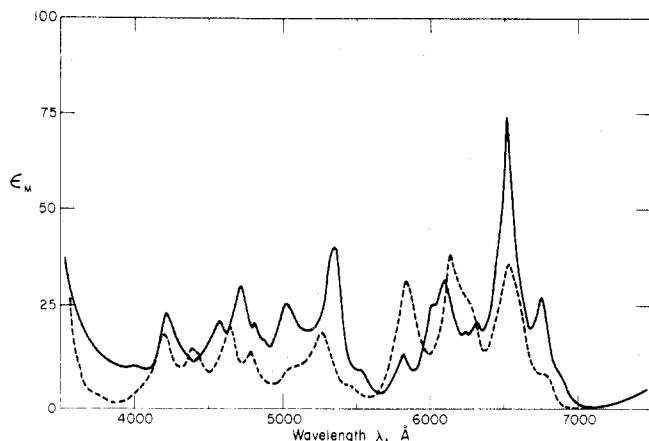


Figure 1. Probable molecular structures.

Figure 2. Absorption spectra of  $[U(\text{hfaPz})_4]_2$  (—) and  $U(\text{hfa-3-MePz})_4$  (---) in  $C_7H_8$  solution.

$U^{4+}$ ,  $Np^{4+}$ , and  $Pu^{4+}$ . The preparation, characterization, and physical properties of these compounds are described.

### Experimental Section

**Reagents.** Pyrazole was recrystallized from benzene and vacuum dried. 3-Methylpyrazole was used as received. Hexafluoroacetone solutions in methanol were prepared by dissolving gaseous hfa in anhydrous methanol. Quadrivalent actinide ions were introduced into the reactions via their bis(tetraethylammonium) hexachloroactinide(IV) compounds.<sup>6</sup> Solvents were of reagent grade and were further purified by passage through a column of 4-Å molecular sieve.

**Preparation of Compounds.** All compounds were prepared in an inert atmosphere glove box; dissolved and/or occluded air was removed from solvents and reagents under vacuum. A typical preparation illustrative of the synthesis is that of  $U(\text{hfaPz})_4$ .

A toluene solution of potassium pyrazolide was prepared by allowing stoichiometric quantities of metallic potassium and pyrazole to react in toluene (~1 g of Pz/50 ml of  $C_7H_8$ ) at room temperature. The potassium was added in two portions over a period of 0.5 hr to minimize the vigor of its reaction with HPz. After 2–3 hr, the unreacted potassium was removed from the solution, solid  $[(C_2H_5)_4N]_2UCl_6$  (1 mmol/2.5 mmol of KPz) was added, and the solution was stirred overnight. The solvent was filtered or decanted from the solids, and 2.2 M hfa- $CH_3OH$  in  $CH_3OH$  (~4 mmol of hfa/mmol of Pz) was stirred with solids for 1–3 hr, during which the solution became dark green. The undissolved solids were removed by filtration, and the solution was vacuum evaporated to about half its volume. Crystals of the purple  $U(\text{hfaPz})_4$  appeared on standing. A second crop of crystals could normally be obtained by further evaporation.  $U(\text{hfaPz})_4$  was purified by recrystallization from ben-

zene or toluene. The yield was about 50%, based upon the amount of metal ion.

The preparation of  $U(\text{hfa-3-MePz})_4$  compounds followed the same procedure as that of  $U(\text{hfaPz})_4$  compounds. Repeated attempts to prepare 3,5-dimethylpyrazole-hexafluoroacetyl compounds with actinide(IV) ions resulted only in oils of indefinite composition.

**Properties.** The hfaPz and hfa-3-MePz compounds of actinide(IV) ions are crystalline, air-stable solids, which are insoluble in water, very weakly soluble in petroleum ether, and sparingly soluble in toluene or benzene.  $U(\text{hfaPz})_4$  and  $U(\text{hfa-3-MePz})_4$  both sublime at ~140° in a diffusion pump vacuum; the hfa-3-MePz compounds are soluble in toluene to about 10 g/l., and the hfaPz compounds are soluble to about 2 g/l.

**Analytical Measurements.** Metal ion analyses were performed as before;<sup>6</sup> carbon, hydrogen, and nitrogen contents were measured with an F&M Model 185 CHN Analyzer. Powder X-ray diffraction data and absorption and infrared (solid compounds in KBr mixture) spectra were obtained as before.<sup>6</sup> Magnetic susceptibility measurements were performed with a Foner vibrating-sample magnetometer;<sup>7</sup> gas chromatographic experiments were done with a Varian Aerograph Model 204 instrument with a hydrogen flame detector. The injection port temperature was 237°, the detector temperature was 230°, and the helium flow was 80  $cm^3/min$ . Gas chromatographic tests explored column temperatures from 140 to 210° on a SE-30 (10 wt %) column. Molecular weights of the thorium and uranium compounds in benzene solution were measured by osmometer by Galbraith Laboratories, Inc.

### Results and Discussion

Elemental analyses (Table I) are in acceptable agreement with the assumed formulas for tetrakis(hexafluoroacetylpyrazolide)actinide(IV) and tetrakis(hexafluoroacetyl-3-methylpyrazolide)actinide(IV) chelates. X-Ray diffraction patterns of powdered samples showed that the four  $M(\text{hfaPz})_4$  compounds have identical structure and the four  $M(\text{hfa-3-MePz})_4$  compounds have identical powder patterns that are different from those of the  $M(\text{hfaPz})_4$  compounds. Volz, Zalkin, and Templeton<sup>8</sup> have determined the structure of  $Th(\text{hfaPz})_4$  by single-crystal X-ray diffraction and found the  $Th^{4+}$  ion to be eight-coordinate, at the center of a distorted Archimedean antiprism formed by four nitrogen atoms from pyrazole 2 nitrogens and four oxygen atoms from hfa. Comparison of the infrared spectra of  $Th(IV)$ ,  $U(IV)$ , and  $Cu(II)$  chelates of Pz, 3-MePz, and hfa showed that the only major effect was the absence of the strong hfa C=O stretching fundamental at 1809  $cm^{-1}$  and the appearance of a C—O stretching band at 1065  $cm^{-1}$  in the infrared spectra of the compounds. Since the C=O stretching frequency was not observed, possible resonance forms can make only a minor contribution.

The presence of actinide(IV) hexafluoroacetylpyrazolide compounds as dimer species while actinide(IV) hexafluoroacetyl-3-methylpyrazolide compounds are monomers is unexpected, since the crystal structure<sup>8</sup> shows no indication of a dimerization and attempts to separate  $Th(\text{hfaPz})_4$  from  $Th(\text{hfa-3-MePz})_4$  by gas chromatography were unsuccessful. However, the differences in the absorption spectra of  $U(\text{hfaPz})_4$  and  $U(\text{hfa-3-MePz})_4$  in toluene solution (Figure 2) are consistent with a major difference in the species in solution and can be taken to support the molecular weight measurements. There is no obvious point for dimerization between actinide(IV) hexafluoroacetylpyrazolide molecules, although the absence of dimerization in the actinide(IV) hexafluoroacetyl-3-methylpyrazolide compounds suggests that the pyrazole moiety is involved.

The results of magnetic susceptibility measurements (Table

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Table I. Elemental Analysis of hfaPz<sup>a</sup> and hfa-3-MePz<sup>b</sup> Compounds of Actinide (IV) Ions

Compd	Color	% metal		% carbon		% hydrogen		% nitrogen		Mol wt <sup>c</sup>
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Th(hfaPz) <sub>4</sub>	White	19.93	20.4	24.74	24.82	1.03	0.94	9.62	10.43	2000
U(hfaPz) <sub>4</sub>	Purple	20.27	20.4	24.61	24.77	1.03	1.02	9.57	9.83	2260
Np(hfaPz) <sub>4</sub>	Green	20.34	19.6							
Pu(hfaPz) <sub>4</sub>	Light red	20.41	19.4							
Th(hfa-3-MePz) <sub>4</sub>	White	19.01		27.42	26.99	1.64	1.34	9.22	9.58	1165
U(hfa-3-MePz) <sub>4</sub>	Blue-green	19.41	18.8	27.40	27.62	1.63	1.66	9.14	8.99	1260
Np(hfa-3-MePz) <sub>4</sub>	Green	19.34	20.7							
Pu(hfa-3-MePz) <sub>4</sub>	Green	19.48	18.3							

<sup>a</sup> hfaPz is N<sub>2</sub>C<sub>3</sub>H<sub>2</sub>OC(CF<sub>3</sub>)<sub>2</sub>. <sup>b</sup> hfa-3-MePz is CH<sub>3</sub>N<sub>2</sub>C<sub>3</sub>HOC(CF<sub>3</sub>)<sub>2</sub>. <sup>c</sup> Benzene solution.

Table II. Magnetic Susceptibilities of Tetrakis(hexafluoroacetylpyrazole)actinide(IV) and Tetrakis(hexafluoroacetyl-3-methylpyrazole)actinide(IV) Compounds

Compd	Temp, range, °K	Θ, <sup>a</sup> °K	C, <sup>a</sup> emu-°K/mol	μ <sub>eff</sub> , BM	χ, emu/mol
U(hfaPz) <sub>4</sub>	2.9-46		TIP <sup>b</sup>		(1.19 ± 0.05) × 10 <sup>-2</sup>
Np(hfaPz) <sub>4</sub>	2.5-7.5	0.91	0.54	2.04	
	10-45	6.0	1.0	2.8	
Pu(hfaPz) <sub>4</sub>	2.5-20		TIP		(8.1 ± 0.8) × 10 <sup>-3</sup>
U(hfa-3-MePz) <sub>4</sub>	2.8-40		TIP		(2.0 ± 0.03) × 10 <sup>-2</sup>
Np(hfa-3-MePz) <sub>4</sub>	2.6-25	1.93	0.50	1.99	
	25-45	16	0.8	2.5	
Pu(hfa-3-MePz) <sub>4</sub>	2.6-50		TIP		(6.2 ± 0.8) × 10 <sup>-3</sup>

<sup>a</sup> Constants from the Curie-Weiss expression  $\chi = C/(T + \Theta)$ .

<sup>b</sup> Temperature-independent paramagnetism.

II) are consistent with a site of low symmetry for the actinide(IV) ions. U<sup>4+</sup> and Pu<sup>4+</sup> compounds show only temperature-independent paramagnetism (TIP), and Np<sup>4+</sup> compounds have a strong temperature-dependent paramagnetism. The expected magnetic behavior can be derived by a descent in symmetry from a cubic class crystal field model<sup>9,10</sup> and the crystal structure.<sup>8</sup>

In this model, the U<sup>4+</sup> ion would have singlets for its lowest crystal field levels, the Pu<sup>4+</sup> ion will have a singlet level lowest for any crystal field symmetry, and the Np<sup>4+</sup> compounds can only have Kramers doublets for crystal field levels. Singlet levels can have only TIP paramagnetism, and doublet levels will show temperature-dependent paramagnetism, in agreement with the magnetic susceptibility measurements. The persistence of TIP to 40-45°K for the U<sup>4+</sup> compounds suggests a crystal field splitting on the order of several hundred reciprocal centimeters. The Np<sup>4+</sup> ion would have a Γ<sub>8</sub> quartet level for a lowest crystal field level in cubic symmetry; the low site symmetry in these compounds will split the Γ<sub>8</sub> level into Γ<sub>6</sub> and Γ<sub>7</sub> doublets. The higher transition temperature for Np(hfa-3-MePz)<sub>4</sub> compared to that of Np(hfaPz)<sub>4</sub> suggests a stronger crystal field for the hfa-3-MePz chelates.

**Registry No.** Pu(hfaPz)<sub>4</sub>, 40804-50-0; U(hfaPz)<sub>4</sub>, 40904-28-7; Np(hfaPz)<sub>4</sub>, 40904-27-6; Pu(hfa-3-MePz)<sub>4</sub>, 40904-26-5; Th(hfa-3-MePz)<sub>4</sub>, 40904-25-4; U(hfa-3-MePz)<sub>4</sub>, 40904-24-3; Np(hfa-3-MePz)<sub>4</sub>, 40904-23-2; 3-methylpyrazole, potassium salt, 40802-35-5; hexafluoroacetone, 684-16-2; potassium pyrazolide, 40802-36-6.

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pounds and advice on their preparation; to Karl Volz, Allan Zalkin, and D. H. Templeton of the Lawrence Berkeley Laboratory, University of California, for communicating the results of their single-crystal X-ray study in advance of publication; and to Sandra Slates, formerly of the Savannah River Laboratory, for assistance in gas chromatography experiments.

Contribution from the Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands

### Sulfur Dioxide and Carbon Disulfide Complexes of Osmium(II)

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In a previous communication<sup>1,2</sup> we described the isolation of the complex OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub> (PCy<sub>3</sub> = tricyclohexylphosphine), a monomeric coordinately unsaturated molecule. This complex forms with pyridine (py) the compound OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub>(py). We now report the reaction of OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub> with sulfur dioxide and carbon disulfide and present complete spectroscopic data on the prepared complexes. The reactions with these small molecules have not been studied in osmium metal chemistry.

### Experimental Section

**Materials.** OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub> was prepared as previously described.<sup>1,2</sup> All other reagents were analytical grade.

**Preparation of OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)·C<sub>6</sub>H<sub>6</sub>.** Sulfur dioxide was passed through a solution of OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub> (0.3 mmol) in 15 ml of benzene for 4 hr at room temperature. After evaporating the solution to 5 ml in a nitrogen atmosphere, the yellow precipitate was filtered off, washed with benzene, and dried *in vacuo*, mp (dec pt) 164°. *Anal.* Calcd for C<sub>43</sub>H<sub>73</sub>ClS<sub>2</sub>O<sub>3</sub>Os: C, 53.93; H, 7.68; Cl, 3.70; S, 3.35. Found: C, 53.98; H, 7.53; Cl, 3.66; S, 3.37.

**Preparation of α-OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub>(CS<sub>2</sub>).** OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub> (0.4 mmol) was added to 10 ml of carbon disulfide in an atmosphere of nitrogen. After evaporating the solution to 2 ml the yellow-brown crystals were filtered off and dried *in vacuo*, dec pt 140°. *Anal.* Calcd for C<sub>38</sub>H<sub>67</sub>ClS<sub>2</sub>P<sub>2</sub>OOs: C, 51.19; H, 7.57; Cl, 3.98; S, 7.19. Found: C, 49.96; H, 7.29; Cl, 4.55; S, 7.02.

**Preparation of β-Os(CO)Cl(PCy<sub>3</sub>)<sub>2</sub>(HCS<sub>2</sub>).** Carbon disulfide (25 ml) was added to a solution of OsH(CO)Cl(PCy<sub>3</sub>)<sub>2</sub> (0.6 mmol) in 40 ml of benzene in an atmosphere of nitrogen. After evaporating the solution to 5 ml, the brown crystals were collected, washed with benzene, and dried *in vacuo*, dec pt 194°. *Anal.* Calcd for C<sub>38</sub>H<sub>67</sub>ClS<sub>2</sub>P<sub>2</sub>OOs: C, 51.19; H, 7.57; Cl, 3.98; S, 6.67. Found: C, 50.94; H, 7.47; Cl, 4.05; S, 6.67.

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