There are errors in the NMR parameters reported[1] since the authors did not take into account the high symmetry of the cadmium.

The cadmium occupies one of the $\bar{3}$ ($C_{3i}$) special positions in the rhombohedral space group $R\bar{3}$, on the 3-fold xis of the unit cell.[2] This *requires* that the NMR shift tensor be axially symmetric ($\sigma_{11} = \sigma_{22}$) with one axis of the tensor ($\sigma_{33}$) aligned along the 3-fold axis.[3] The directions of the $x$ and $y$ axes are not uniquely defined when axial symmetry is present; any pair of orthogonal axes that are also orthogonal to the $z$ axis will serve.[4] The symmetry also requires that the NMR chemical shifts determined by rotations about the rhombohedral $a$, $b$, and $c$ axes be identical. The fact that Kennedy, Ellis, and Jakobsen found that $\sigma_{33}$ was 2.4° away from the 3-fold axis and that $\sigma_{11} = 414$ ppm while $\sigma_{22} = 385$ ppm actually represents a measure of the various errors associated with the experiment rather than any real differences in the $\sigma_{11}$ and $\sigma_{22}$ parameters.

The NMR measurements in this particular case can be greatly simplified by choosing an alignment based on hexagonal rather than rhombohedral axes.[5] In the hexagonal setting, the $z$ axis of the tensor is coincident with the $c$ axis of the hexagonal unit cell, and the $x$ and $y$ components of the tensor are perpendicular to it. Thus only two measurements are necessary to obtain the tensor components, the chemical shifts when the $c$ axis is parallel to the applied field and when it is perpendicular to it.

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# A New Synthesis of Xenon Oxytetrafluoride, $XeOF_4$

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There has been continued interest in xenon fluorides to increase the knowledge of the bonding and reactivity of noble gas compounds. Reported syntheses of xenon fluorides and oxyfluorides can be less than safe and in some instances very hazardous. For example, one common preparation of $XeOF_4$ involves partial hydrolysis of $XeF_6$ in either a static or dynamic system. The dynamic method, a controlled hydrolysis, involves a complex setup to monitor the decrease in the $XeF_6$ concentration in a flow loop while air is bled into the system.[1] The static method, accomplished by reacting $XeF_6$ with either $SiO_2$ or $H_2O$, can be quite dangerous due to inadvertent formation of highly explosive $XeO_3$.[2] Another method uses $SeO_2F_2$ as an oxygen source but suffers from the high toxicity and difficult preparation of $SeO_2F_2$.[3] Recently, Christe and Wilson reported that $XeOF_4$ can be prepared in high yields from readily available reagents through the reaction of $XeF_6$ with $NaNO_3$.[4] However, if an excess of $NaNO_3$ is used, $XeOF_4$ further reacts with $NaNO_3$ to give $XeO_2F_2$.[5] We report a new synthetic method for preparing $XeOF_4$ in nearly quantitative yield that reduces the problem of $XeO_3$ formation.

## Experimental Section

***Caution!*** The reaction of $XeF_6$ or $XeOF_4$ with an excess of $P(O)F_3$ can lead to the formation of explosive $XeO_3$. Care must be used when performing this procedure to ensure that an excess of $P(O)F_3$ is not used. Small amounts of all reagents should be used in order to minimize risk of explosions and damage, and appropriate safety precautions should be taken. Xenon hexafluoride is a potent oxidizer that readily hydrolyzes to explosive $XeO_3$.

**Materials and Apparatus.** Xenon (Matheson Corp.) was used as received. Xenon hexafluoride, $XeF_6$, was prepared by the method of Chernick and Malm from Xe and excess $F_2$ in the presence of NaF followed by vacuum pyrolysis of the adduct $NaXeF_7$.[6] Phosphoryl fluoride, $P(O)F_3$, was prepared by the reaction of $SbF_3$ and $P(O)Cl_3$ and purified by vacuum distillation.[7] Volatile materials were manipulated in a stainless steel vacuum line equipped with Kel-F and stainless steel traps, Autoclave Engineers valves, and MKS and Helicoid pressure gauges. Prior to use, the vacuum line was thoroughly passivated with $ClF_3$ and $XeF_6$ followed by overnight evacuation. Nonvolatile materials were handled in a dry He atmosphere glovebox. Infrared spectra of volatile materials were recorded on a Perkin-Elmer 1500 FTIR spectrometer using a 10-cm stainless steel cell fitted with AgCl windows.

**Preparation of $XeOF_4$.** Xenon hexafluoride (1.2 g, 4.9 mmol) followed by 0.52 g (4.9 mmol) of $P(O)F_3$ at −196 °C was condensed into a Kel-F reaction tube. The reaction vessel was allowed to warm slowly to room temperature, and within 5 min the solid $XeF_6$ began to evolve gas and liquefy. After 2 h at room temperature, the contents of the reactor were vacuum-transferred to a 30-mL stainless steel cylinder containing dried NaF to remove $PF_5$. After several hours at room temperature in contact with NaF, the volatile material was removed from the cylinder and identified as pure $XeOF_4$ (1.1 g, 4.9 mmol) by its infrared spectrum[8] and room-temperature vapor pressure.[1] The NaF scrubber retained 0.59 g (4.7 mmol) of complexed $PF_5$. Alternately, the $PF_5$ may be more rapidly removed by vacuum distillation from the mixture using a trap held at −55 °C.

## Results and Discussion

The reaction of $P(O)F_3$ and $XeF_6$ provides a very convenient, high-yield, fast synthesis of $XeOF_4$. The oxygenating agent ($P(O)F_3$) is easily prepared in quantity from readily available materials, is anhydrous as prepared, and is easily handled in vacuum systems, allowing for precise and accurate measurement of small quantities. The only byproduct of the reaction ($PF_5$) is easily separated from $XeOF_4$ on the basis of either its greater volatility or its stronger Lewis acidity (toward NaF). It is not necessary to use a large excess of $XeF_6$ to avoid formation of significant amounts of treacherous $XeO_3$, since $XeOF_4$ reacts much more slowly with $P(O)F_3$ than does $XeF_6$. This was demonstrated by the reaction of $P(O)F_3$ with $XeOF_4$ in a 1:1 ratio. After this reaction was allowed to proceed for 4 days followed by removal of volatiles (unreacted $XeOF_4$, $P(O)F_3$, and $PF_5$), only a small amount of white solid (less than 0.05 g) was recovered. During an attempt to identify this material, an explosion occurred and the material, on the basis of its detonability and lack of volatility, was presumed to be either $XeO_2F_2$ or $XeO_3$. Explosions can be avoided if $P(O)F_3$ and $XeF_6$ are reacted in a ratio close to 1:1 and a short reaction time is used. Separation of the resulting products is simple. When the reaction is performed in the prescribed manner, the products are all gases or volatile liquids and fractional condensation through two traps kept at −55 and −196 °C cleanly separates $XeOF_4$ from $PF_5$ and $P(O)F_3$ and gives spectroscopically pure $XeOF_4$ in quantitative yield. If a slight excess of $XeF_6$ is used, purification may be accomplished by placing the contents of the reaction over NaF to complex $PF_5$ and $XeF_6$.

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**Registry No.** $XeOF_4$, 13774-85-1; $P(O)F_3$, 13478-20-1; $XeF_6$, 13693-09-9.

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# The Novel Redox Reaction and Thiolato Ligand Transfer between $Cp_2Ti(SCMe_3)_2$ and $CpCo(CO)_2$. Preparation and Structure of $[CpCo(\mu\text{-}SCMe_3)]_2$

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## Introduction

Dimers of the type $[CpM(CO)_xSR]_2$ are an important class of molecules containing bridging thiolato ligands.[2] There are several geometric isomers possible for such complexes.[2,3] Briefly, the Cp rings can be cis or trans with respect to the M–M vector and the R groups can be axial or equatorial with respect to a nonplanar $M_2S_2$ "butterfly" ring.[4] Only a few complexes of the type $[CpCoSR]_2$ have been prepared, where R = $CH_3$,[5] Ph,[5] $CF_3$,[6] and $C_6F_5$;[6] however, they are unstable for R = Ph and $CF_3$. We report here the preparation and structural characterization of $[CpCoSCMe_3]_2$, the product of an unusual redox reaction between $CpCo(CO)_2$ and $CpTi(SCMe_3)_2$.

## Results

UV irradiation of a solution of $CpCo(CO)_2$ and $Cp_2Ti(SCMe_3)_2$ in hexanes caused a color change from red to green and the precipitation of a red solid. The latter was identified as $[Cp_2TiSCMe_3]_2$ by elemental analysis, mass spectroscopy, and its NMR spectrum.[7] Green crystals of $[CpCoSCMe_3]_2$ were isolated from the hexane solution and characterized by elemental analysis, mass spectroscopy, and its VT $^1H$ NMR spectra. The NMR spectrum shows one peak for the Cp protons and a broad peak for the Me protons. Heating the sample causes the broad peak to sharpen, while cooling causes the peak to broaden even more, pass through a coalescence temperature, and reemerge as two sharp peaks of equal intensity at low temperature.[8]

On the basis of the NMR data, one would predict a structure for $[CpCoSCMe_3]_2$ wherein the Cp rings are mutually cis and the $CMe_3$ groups axial and equatorial with respect to the $Co_2S_2$ ring. The first X-ray structure of a cobalt complex of this type is depicted in Figure 1, and it confirms the assignment. The crystallographic data, atomic coordinates, and selected structural

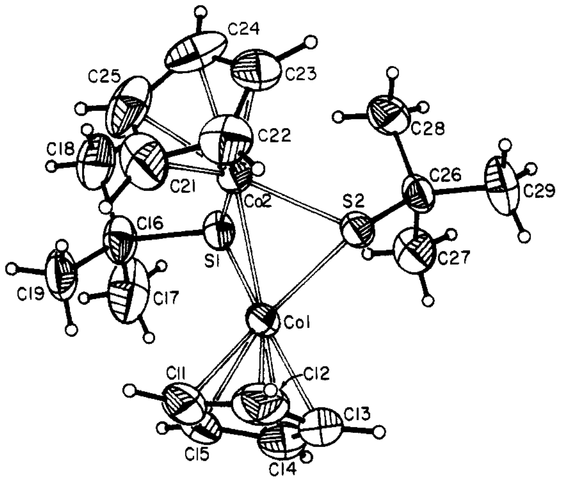

Figure 1. ORTEP view of $[CpCoSCMe_3]_2$ showing the numbering scheme.

Table I. Crystallographic Data for $[CpCoSCMe_3]_2$

| | |
|---|---|
| chem formula: $C_{18}H_{28}Co_2S_2$ | $Z = 4$ |
| fw = 456.64 | $T = 20 \pm 1$ °C |
| space group: $P2_1/n$ | $\lambda = 0.71073$ Å |
| $a = 14.770$ (3) Å | $\rho_{calcd} = 1.539$ g cm$^{-3}$ |
| $b = 9.145$ (1) Å | $\mu$(Mo K$\alpha$) = 2.72 mm$^{-1}$ |
| $c = 15.483$ (2) Å | $R_1 = 0.037$ |
| $\beta = 109.51$ (1)° | $R_2 = 0.047$ |
| $V = 1971.4$ (5) Å$^3$ | |

Table II. Positional Parameters ($\times 10^4$) and Isotropic Thermal Parameters (Å$^2 \times 10^3$) for $[CpCoSCMe_3]_2$

| atom | *x* | *y* | *z* | *U* |
|---|---|---|---|---|
| Co(1) | 1812 (1) | 2108 (1) | 4729 (1) | 30 (1) |
| Co(2) | 2350 (1) | −128 (1) | 5649 (1) | 27 (1) |
| S(1) | 3240 (1) | 1126 (1) | 5035 (1) | 30 (1) |
| S(2) | 1247 (1) | −92 (1) | 4286 (1) | 27 (1) |
| C(11) | 1563 (4) | 3797 (5) | 5516 (3) | 61 (2) |
| C(12) | 698 (3) | 3146 (5) | 5016 (3) | 56 (2) |
| C(13) | 584 (3) | 3298 (4) | 4082 (3) | 47 (1) |
| C(14) | 1359 (3) | 4050 (4) | 3997 (3) | 53 (1) |
| C(15) | 1990 (4) | 4341 (4) | 4895 (4) | 59 (2) |
| C(16) | 4295 (3) | 2113 (5) | 5848 (3) | 42 (1) |
| C(17) | 4632 (4) | 3157 (7) | 5248 (3) | 75 (2) |
| C(18) | 5058 (3) | 967 (6) | 6275 (3) | 55 (1) |
| C(19) | 4047 (3) | 2956 (5) | 6589 (3) | 51 (1) |
| C(21) | 2254 (4) | 112 (5) | 6956 (3) | 57 (2) |
| C(22) | 1524 (3) | −793 (5) | 6419 (3) | 44 (1) |
| C(23) | 1960 (3) | −2011 (4) | 6160 (3) | 44 (1) |
| C(24) | 2943 (3) | −1866 (5) | 6525 (3) | 55 (2) |
| C(25) | 3132 (3) | −538 (6) | 7009 (3) | 59 (2) |
| C(26) | 1570 (2) | −1017 (4) | 3335 (2) | 32 (1) |
| C(27) | 1872 (3) | 89 (5) | 2764 (3) | 47 (1) |
| C(28) | 2363 (3) | −2121 (4) | 3749 (3) | 45 (1) |
| C(29) | 649 (3) | −1797 (5) | 2776 (3) | 57 (1) |

Table III. Selected Bond Lengths (Å) and Angles for $[CpCoSCMe_3]_2$

| | | | |
|---|---|---|---|
| Co(1)–Co(2) | 2.467 (1) | Co(2)–C(21) | 2.087 (5) |
| Co(1)–S(1) | 2.194 (1) | Co(2)–C(22) | 2.063 (5) |
| Co(1)–S(2) | 2.198 (1) | Co(2)–C(23) | 2.056 (4) |
| Co(2)–S(1) | 2.187 (1) | Co(2)–C(24) | 2.083 (5) |
| Co(2)–S(2) | 2.194 (1) | Co(2)–C(25) | 2.070 (4) |
| Co(1)–C(11) | 2.075 (5) | S(1)–C(16) | 1.874 (4) |
| Co(1)–C(12) | 2.073 (5) | S(2)–C(26) | 1.892 (4) |
| Co(1)–C(13) | 2.065 (4) | | |
| Co(1)–C(14) | 2.092 (4) | | |
| Co(1)–C(15) | 2.064 (4) | | |
| S(1)–Co(1)–S(2) | 86.0 | C(16)–S(1)–Co(1) | 118.2 (1) |
| S(1)–Co(2)–S(2) | 86.3 | C(16)–S(1)–Co(2) | 166.5 (1) |
| Co(1)–S(1)–Co(2) | 68.5 | C(26)–S(2)–Co(1) | 118.9 (1) |
| Co(1)–S(2)–Co(2) | 68.3 | C(26)–S(2)–Co(2) | 116.2 (1) |

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