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Contribution from the Institut Le Bel, Université Louis Pasteur,
4 Rue Blaise Pascal, 67070 Strasbourg, France

# Chromyl Complexes with Aryloxy and Siloxy Ligands

Pericles Stavropoulos, Nathan Bryson, Marie-Thérèse Youinou, and John A. Osborn*

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Interaction of $CrO_3$ and 1 equiv of $Ph_3CCl$ in dichloromethane yields a mixture of $CrO_2Cl_2$, $CrO_2Cl(OCPh_3)$ (**1**), and $CrO_2(OCPh_3)_2$ (**2**). Fractional crystallization gives pure samples of red **1** and orange **2**, which have been characterized by X-ray diffraction. Crystal data for **1**: space group $P\bar{1}$; $a = 9.913$ (3), $b = 10.173$ (3), $c = 9.019$ (3) Å; $\alpha = 92.93$ (2), $\beta = 92.74$ (2), $\gamma = 110.84$ (3)°; $Z = 2$; $R_1 = 0.044$, $R_2 = 0.059$. Crystal data for **2**: space group $C2/c$; $a = 23.857$ (6), $b = 8.759$ (3), $c = 15.105$ (5) Å; $\beta = 110.48$ (3)°; $Z = 4$; $R_1 = 0.036$, $R_2 = 0.057$. A similar result was obtained on reaction of $CrO_3$ and 1 equiv of $Ph_3SiCl$, giving $CrO_2Cl_2$, $CrO_2Cl(OSiPh_3)$ (**3**), and $CrO_2(OSiPh_3)_2$ (**4**). These results are compared with the in situ systems $CrO_3/Me_3SiCl$ and $CrO_3/Me_3SiOSiMe_3$, which have been studied by $^1H$ NMR spectroscopy and EI mass spectrometry.

## Introduction

Oxidation of organic molecules by oxochromium(VI) species has been a respectable tool in the organic chemist's workshop,[1] although often the nature of the active species in solution and the mechanism of action is unclear. For olefins, the stereospecific epoxidation and cis addition of the HOCl moiety using $CrO_2Cl_2$ has been carefully studied, and suggestions that direct Cr–C bond formation occurs in an intermediate have been put forward.[2] Further, gas-phase measurements[3] and theoretical considerations[4] have strengthened evidence that metal–carbon bonds in formally high-oxidation-state complexes are stable if the appropriate stabilizing ligands are present. All these considerations, of course, appear increasingly reasonable in view of the developing organometallic chemistry in high oxidation states.

We were intrigued by the observations concerning the reactions of $CrO_2X_2$ and saturated hydrocarbons. $CrO_2F_2$ has been known to ignite methane,[5] while $CrO_2(OCOCF_3)_2$ oxidizes pentane and hexane at −50 °C.[6] The Etard reaction of $CrO_2Cl_2$ on arylalkanes has been known for over 100 years, but the organometallic adducts are still uncharacterized. In contrast, chromyl alcoholates $CrO_2(OR)_2$ can oxidize olefins only under vigorous conditions.[7] We have thus investigated the synthesis of $CrO_2X_2$ systems where the reactivity may possibly be controlled and fined tuned by varying the X ligand,[8] with the further objective of understanding the nature of C–H activation in such systems. During these synthetic studies we also noted that in some of the commonly used oxidation procedures, the species supposedly present were more complicated than realized.

## Results and Discussion

**Synthesis and Characterization of Triphenylmethoxy Derivatives of Cr(VI).** The interaction of chromium trioxide ($CrO_3$) with 1 equiv of $Ph_3CCl$ in dichloromethane (eq 1) resulted in a deep red solution, which was evaporated to dryness. Extraction of the

$$\mathrm{CrO_3 + Ph_3CCl} \rightarrow \underset{\mathbf{1}}{\mathrm{CrO_2Cl(OCPh_3)}} + \underset{\mathbf{2}}{\mathrm{CrO_2(OCPh_3)_2}} + \mathrm{CrO_2Cl_2} \qquad (1)$$

bright red residue with hexane and cooling to −40 °C yielded red crystals of $CrO_2Cl(OCPh_3)$ (**1**) contaminated with minor amounts of the organic reactant. Compound **1** was purified by repeated crystallization from hexane, taking care to filter off any organic material that precipitates first upon cooling. The residue remaining after the initial extraction with hexane was extracted a second time with a 1:4 dichloromethane/hexane solution, and the solution was cooled to −40 °C to yield $CrO_2(OCPh_3)_2$ (**2**). This compound, previously synthesized from $CrO_3$ and $Ph_3COH$, has been used as a polymerization catalyst.[9]

**Table I.** Crystallographic Data for $CrO_2Cl(OCPh_3)$ (**1**) and $CrO_2(OCPh_3)_2$ (**2**)

| | **1** | **2** |
|---|---|---|
| chem formula | $C_{19}H_{15}ClCrO_3$ | $C_{38}H_{30}CrO_4$ |
| fw | 846.8 | 602.6 |
| space group | $P\bar{1}$ | $C2/c$ |
| $a$, Å | 9.913 (3) | 23.857 (6) |
| $b$, Å | 10.173 (3) | 8.759 (3) |
| $c$, Å | 9.019 (3) | 15.105 (5) |
| $\alpha$, deg | 92.93 (2) | |
| $\beta$, deg | 92.74 (2) | 110.48 (3) |
| $\gamma$, deg | 110.84 (3) | |
| $V$, Å$^3$ | 846.8 | 2956.9 |
| $\rho_{calc}$, g cm$^{-1}$ | 1.486 | 1.354 |
| $Z$ | 2 | 4 |
| $\lambda$, Å | 1.5418 (Cu K$\alpha$) | 1.5418 (Cu K$\alpha$) |
| $\mu$, cm$^{-1}$ | 7.2 | 3.5 |
| temp, °C | −100 | −100 |
| transm factors | 1.32/0.71 | 1.19/0.81 |
| $R/R_w$ | 4.4/5.9 | 3.6/5.7 |

**2** appears to be formed directly in this reaction. Ligand redistribution of $CrO_2Cl(OCPh_3)$ to give the symmetrically substituted products $CrO_2Cl_2$ and $CrO_2(OCPh_3)_2$ was too slow at room temperature to account for the observed products, minimal exchange occurring only after several days in solution. However, chromium trioxide is made of linear chains of oxo-bridged $CrO_2$ units of the form $[\text{–O–CrO}_2\text{–}]_n$.[10] Cleavage of oxo bridges of $CrO_3$ by $Ph_3CCl$ will produce smaller oligomeric intermediates bearing Cl and $OCPh_3$ terminuses, i.e. $[(CrO_3)_n\text{–}CrO_2Cl]$ and $[(CrO_3)_n\text{–}CrO_2(OCPh_3)]$. Reaction of the latter at the oxo bridge of the $\text{–}CrO_2(OCPh_3)$ terminus produces a mixture of **1** and **2**, the amounts of each depending on the orientation of the addition. Likewise, addition of $Ph_3CCl$ to $[(CrO_3)_n\text{–}CrO_2Cl]$ will give mixtures of **1** and $CrO_2Cl_2$.

The $^1H$ NMR spectrum of **1** comprises two broad signals centered at 7.40 (2 H) and 7.30 ppm (3 H) as opposed to bands of fine multiplicity observed for the chloro–siloxy derivative **3** (below). The same behavior was observed in the $^1H$ NMR spectrum of **2**, where the two broad signals are positioned at 7.25 (2 H) and 7.30 (3 H) ppm. This broadening may be related to the inherent stability of the entities $Ph_3C^\bullet$ and $Ph_3C^+$, thus allowing a rapid transfer of the $Ph_3C$ moiety from a $Ph_3C\text{–}O$ ligand onto a terminal Cr=O unit although low-temperature studies have not been carried out. Such interconversions are not without precedent.[11] In the infrared spectra, we note the sharp $\nu_{asym}$(Cr=O)

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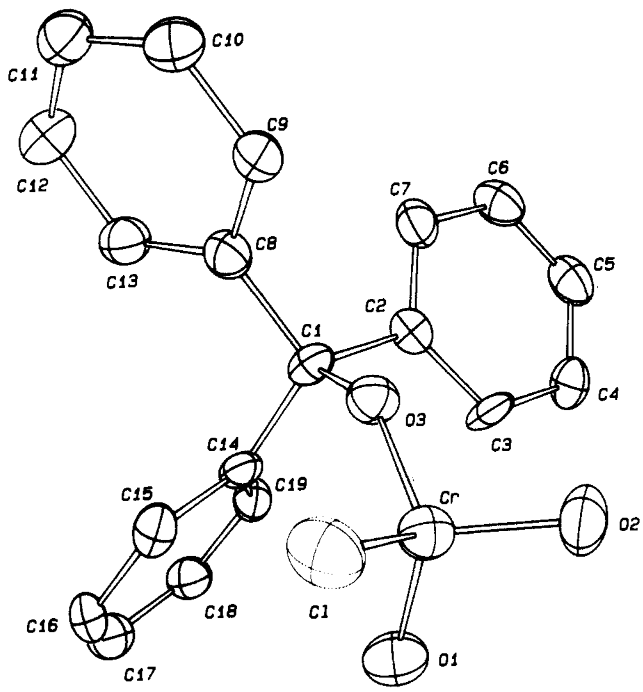

**Figure 1.** ORTEP drawing of $CrO_2(OCPh_3)$ (**1**), showing 50% probability ellipsoids.

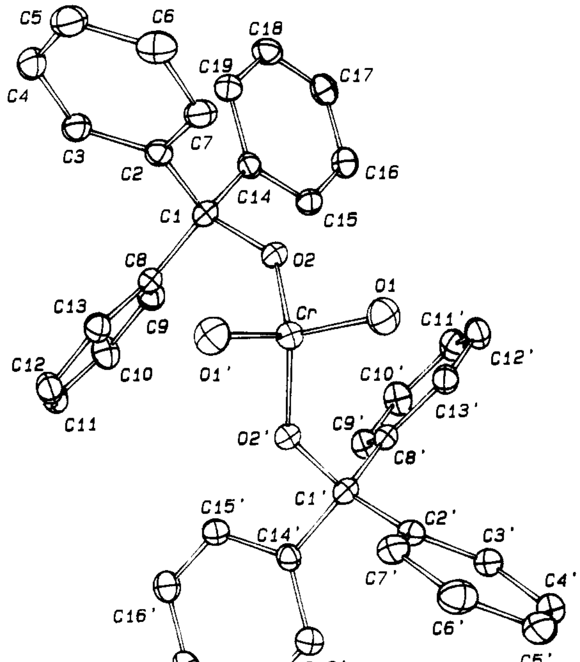

**Figure 2.** ORTEP drawing of $CrO_2(OCPh_3)_2$ (**2**), showing 50% probability ellipsoids. Primed atoms refer to $C_2$ equivalents.

and $\nu_{sym}$(Cr=O) bands at 981 and 968 cm$^{-1}$ with a shoulder at 974 cm$^{-1}$ and the $\nu$(Cr—Cl) appearing at 460 cm$^{-1}$. For $CrO_2(OCPh_3)_2$ (**2**) we observe the $\nu_{asym}$(Cr=O) at 980 cm$^{-1}$ and the $\nu_{sym}$(Cr=O) at 963 cm$^{-1}$.

Since polymeric insoluble species of the type $[CrO_2(OR)_2]_n$ and $[CrO_2Cl(OR)]_n$ have been recently prepared from secondary alcohols,[12] an X-ray diffraction analysis of the soluble compounds

**Table II.** Positional Parameters and Their Estimated Standard Deviations for **1**

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Cr | 0.1685 (1) | 0.3604 (1) | 0.1770 (2) | 4.05 (3) |
| Cl | 0.0838 (2) | 0.3580 (2) | 0.3901 (2) | 5.46 (6) |
| O1 | 0.3140 (6) | 0.4914 (5) | 0.1802 (6) | 5.0 (2) |
| O2 | 0.0542 (6) | 0.3778 (5) | 0.0565 (6) | 5.2 (1) |
| O3 | 0.1940 (5) | 0.2071 (5) | 0.1359 (5) | 3.7 (1) |
| C1 | 0.3038 (7) | 0.1450 (7) | 0.1037 (8) | 3.1 (2) |
| C2 | 0.2870 (7) | 0.1187 (7) | -0.0679 (8) | 3.3 (2) |
| C3 | 0.3101 (8) | 0.2304 (7) | -0.1567 (9) | 3.8 (2) |
| C4 | 0.2905 (8) | 0.2094 (8) | -0.3090 (8) | 4.0 (2) |
| C5 | 0.2549 (8) | 0.0741 (8) | -0.3744 (9) | 4.5 (2) |
| C6 | 0.2352 (8) | -0.0372 (8) | -0.2896 (9) | 4.4 (2) |
| C7 | 0.2503 (8) | -0.0164 (8) | -0.1344 (9) | 4.0 (2) |
| C8 | 0.2610 (8) | 0.0105 (7) | 0.1850 (8) | 3.5 (2) |
| C9 | 0.1179 (8) | -0.0700 (8) | 0.1983 (9) | 4.0 (2) |
| C10 | 0.0828 (9) | -0.1941 (8) | 0.2695 (9) | 4.8 (2) |
| C11 | 0.1881 (9) | -0.2406 (8) | 0.3268 (9) | 4.3 (2) |
| C12 | 0.3276 (8) | -0.1631 (8) | 0.311 (1) | 4.5 (2) |
| C13 | 0.3662 (8) | -0.0376 (8) | 0.2410 (9) | 4.0 (2) |
| C14 | 0.4552 (8) | 0.2487 (7) | 0.1620 (8) | 3.0 (2) |
| C15 | 0.4732 (8) | 0.3023 (8) | 0.3112 (9) | 3.9 (2) |
| C16 | 0.6090 (8) | 0.3884 (8) | 0.3700 (9) | 4.1 (2) |
| C17 | 0.7257 (8) | 0.4207 (8) | 0.283 (1) | 4.6 (2) |
| C18 | 0.7077 (8) | 0.3680 (8) | 0.1378 (9) | 4.1 (2) |
| C19 | 0.5728 (7) | 0.2830 (7) | 0.0771 (8) | 3.3 (2) |

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

**Table III.** Positional Parameters and Their Estimated Standard Deviations for **2**

| atom | *x* | *y* | *z* | *B*,[a] Å$^2$ |
|---|---|---|---|---|
| Cr | 1.000 | 0.16120 (7) | 0.750 | 2.01 (1) |
| O1 | 1.02676 (8) | 0.2648 (2) | 0.6891 (1) | 3.02 (5) |
| O2 | 0.94537 (7) | 0.0476 (2) | 0.6715 (1) | 2.09 (4) |
| C1 | 0.8900 (1) | -0.0283 (3) | 0.6675 (2) | 2.08 (6) |
| C2 | 0.8429 (1) | 0.0944 (3) | 0.6606 (2) | 2.08 (6) |
| C3 | 0.7938 (1) | 0.0620 (3) | 0.6870 (2) | 2.45 (6) |
| C4 | 0.7490 (1) | 0.1682 (4) | 0.6741 (2) | 2.96 (7) |
| C5 | 0.7525 (1) | 0.3091 (4) | 0.6364 (2) | 3.22 (7) |
| C6 | 0.8013 (1) | 0.3437 (4) | 0.6107 (2) | 3.20 (8) |
| C7 | 0.8458 (1) | 0.2360 (4) | 0.6218 (2) | 2.61 (7) |
| C8 | 0.9031 (1) | -0.1286 (3) | 0.7559 (2) | 2.07 (6) |
| C9 | 0.9063 (1) | -0.2861 (4) | 0.7525 (2) | 2.68 (7) |
| C10 | 0.9192 (1) | -0.3728 (4) | 0.8337 (2) | 2.95 (7) |
| C11 | 0.9288 (1) | -0.3041 (4) | 0.9199 (2) | 2.86 (7) |
| C12 | 0.9259 (1) | -0.1470 (4) | 0.9247 (2) | 2.74 (7) |
| C13 | 0.9129 (1) | -0.0601 (3) | 0.8434 (2) | 2.39 (6) |
| C14 | 0.8739 (1) | -0.1221 (3) | 0.5763 (2) | 2.05 (6) |
| C15 | 0.9186 (1) | -0.2005 (3) | 0.5563 (2) | 2.29 (6) |
| C16 | 0.9057 (1) | -0.2856 (4) | 0.4747 (2) | 2.69 (7) |
| C17 | 0.8478 (1) | -0.2945 (4) | 0.4114 (2) | 2.88 (7) |
| C18 | 0.8030 (1) | -0.2162 (4) | 0.4305 (2) | 2.93 (7) |
| C19 | 0.8158 (1) | -0.1316 (3) | 0.5123 (2) | 2.44 (6) |

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

**Table IV.** Selected Distances (Å) and Bond Angles (deg) for $CrO_2Cl(OCPh_3)$ (**1**)[a]

| | | | |
|---|---|---|---|
| | Distances | | |
| Cr-Cl | 2.132 (3) | Cr-O3 | 1.692 (5) |
| Cr-O1 | 1.576 (5) | O3-C1 | 1.473 (8) |
| Cr-O2 | 1.594 (5) | | |
| | Bond Angles | | |
| Cl-Cr-O1 | 108.0 (2) | O1-Cr-O3 | 111.8 (3) |
| Cl-Cr-O2 | 108.1 (2) | O2-Cr-O3 | 109.4 (3) |
| Cl-Cr-O3 | 110.0 (2) | Cr-O3-C1 | 144.0 (3) |
| O1-Cr-O2 | 109.4 (3) | | |

[a] Estimated standard deviations are given in parentheses.

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**Table V.** Selected Distances (Å) and Bond Angles (deg) for $CrO_2(OCPh_3)_2$ (**2**)[a]

| | | | |
|---|---|---|---|
| **Distances** | | | |
| Cr-O1 | 1.578 (2) | O2-C1 | 1.461 (3) |
| Cr-O2 | 1.736 (2) | | |
| **Bond Angles** | | | |
| O1-Cr-O1′ | 109.80 (10) | O2-Cr-O2′ | 110.04 (9) |
| O1-Cr-O2 | 106.94 (9) | Cr-O2-C1 | 137.80 (20) |
| O1-Cr-O2′ | 111.58 (9) | | |

[a] Estimated standard deviations are given in parentheses.

presented here was undertaken. ORTEP diagrams of $CrO_2Cl(OCPh_3)$ (**1**) and $CrO_2(OCPh_3)_2$ (**2**) are shown in Figures 1 and 2. Crystallographic data and final atomic positional parameters for the non-hydrogen atoms of compounds **1** and **2** are given in Tables I–III. Selected bond distances and angles are given in Tables IV and V.

Two equivalent molecules were observed in the unit cell of crystals of **1**. Each chromium in the cell possesses a slightly distorted tetrahedral geometry and is bound to one chloride (Cr–Cl = 2.132 (3) Å), one alkoxy oxygen (Cr–O(3) = 1.692 (5) Å), and two oxo ligands (Cr–O(1) = 1.576 (5) Å and Cr–O(2) = 1.594 (5) Å). In each of the four equivalent molecules of **2** present in the asymmetric unit, the chromium lies on a 2-fold symmetry axis. The two equivalent oxo groups, as well as the two equivalent alkoxy oxygens, contribute to the tetrahedral arrangement around the chromium.

In complexes **1** and **2** the terminal Cr=O bond distances are similar, being 1.576 (5) and 1.594 (5) Å in **1** and 1.578 Å in **2**. These values are close to those derived for $CrO_2Cl_2$ (1.577 (2) Å from electron diffraction methods[13] and 1.57 (3) Å calculated from IR spectroscopy[14]), as well as those observed in $CrO_2(OSiPh_3)_2$ (1.568 (12) Å and 1.514 (13) Å).[15] The Cr–Cl distance in $CrO_2Cl(OCPh_3)$ also agrees with calculated values for chromyl chloride, 2.122 (2)[14] and 2.12 (2) Å.[15]

Furthermore, the O–Cr–O angle is remarkably constant for a series of $CrO_2X_2$ molecules at close to 109° [10] and also, surprisingly, the X–Cr–X angle is only slightly invariant for groups X of different electronegativity and size. It would appear that the strong $\pi$-donating interaction involving binding the oxo ligands to the chromium imposes a rigid tetrahedral stereochemistry on this class of molecules. However, there is a considerable lengthening of the chromium–alkoxy bond from 1.692 (5) to 1.736 (2) Å on substitution of the chloride in **1** for a second alkoxy in **2**. It appears that replacing the chloro ligand by a stronger $\pi$-donor alkoxo group weakens the other chromium–alkoxo bond. This is understandable in terms of increasing $\pi$-donor competition between the alkoxo ligands for Cr(VI) orbitals; this interpretation would imply that the $M-O-CPh_3$ angle would also decrease on going from **1** to **2**, which is indeed observed (144.0 (3)° to 137.8 (2)°). Note that steric interactions between bulky triphenylmethyl groups may increase the $Cr-O-CPh_3$ bond length but would tend to increase the bond angle. Overall, the $CrO_2$ unit appears relatively insensitive to the changes in the X groups and may imply that changes in reactivity in $CrO_2X_2$ systems largely involve the changes in Cr–X bond properties.

**Synthesis and Characterization of Triphenylsiloxy Compounds of Cr(VI).** The interaction of $CrO_2Cl_2$ with 1 equiv of triphenylsilanol in dichloromethane (eq 2) leads to the isolation of two crystalline products from the reaction mixture. Evaporation

$$CrO_2Cl_2 + Ph_3SiOH \rightarrow \underset{\mathbf{3}}{CrO_2Cl(OSiPh_3)} + \underset{\mathbf{4}}{CrO_2(OSiPh_3)_2} + HCl \quad (2)$$

of the reaction mixture and fractional crystallization from hexane gave the red $CrO_2Cl(OSiPh_3)$ (**3**) and the yellow-orange $CrO_2(OSiPh_3)_2$ (**4**). The latter was previously obtained from the interaction of $CrO_3$ with $Ph_3SiOH$.[16]

The $^1H$ NMR spectra of the complexes are rather uninformative, showing the triphenylsiloxy ligand in the usual pattern of multiplets centered at 7.62 (2 H, Ph ortho) and 7.08 ppm (3 H, Ph meta and para). On the contrary, IR data appeared to be more revealing; for **3**, two strong bands at 989 and 981 $cm^{-1}$ are readily assigned to the $\nu_{asym}(Cr{=}O)$ and $\nu_{sym}(Cr{=}O)$ of the *cis*-$CrO_2$ unit,[17] and bands at 620 and 470 $cm^{-1}$ are attributed to Cr–OSi and Cr–Cl stretches, respectively. In the IR spectrum of **4** two sharp bands at 627 and 610 $cm^{-1}$ are observed resulting from symmetric and asymmetric Cr–OSi stretches. In addition, the metal–oxo bands of **4**, detected at 986 ($\nu_{asym}(Cr{=}O)$) and 974 $cm^{-1}$ ($\nu_{sym}(Cr{=}O)$), have shoulders at 992 and 970 $cm^{-1}$, a phenomenon commonly encountered in IR spectra of symmetrically substituted dioxo complexes due to lattice effects.[18]

Treatment of a suspension of $CrO_3$ in $CH_2Cl_2$ with 0.8 equiv of $Ph_3SiCl$ (eq 3) results in the isolation of the same products as above with the yields of **3** improved at the expense of **4**. The working-up procedure is facilitated by the use of excess $CrO_3$, which can be conveniently removed by filtration.

$$CrO_3 + Ph_3SiCl \rightarrow \underset{\mathbf{3}}{CrO_2Cl(OSiPh_3)} + \underset{\mathbf{4}}{CrO_2(OSiPh_3)_2} + CrO_2Cl_2 + Ph_3SiOSiPh_3 \quad (3)$$

Reaction of **3** with $Ph_3SiCl$ gave $CrO_2Cl_2$ by electrophilic attack of the chlorosilane on the Cr–OSi bond (eq 4). Compound **4**, on the other hand, does not react with $Ph_3SiCl$.

$$\underset{\mathbf{3}}{CrO_2Cl(OSiPh_3)} + Ph_3SiCl \rightarrow CrO_2Cl_2 + Ph_3SiOSiPh_3 \quad (4)$$

For preparative purposes, pure samples of $CrO_2(OSiPh_3)_2$ (**4**) could be obtained either by the literature procedure[8] or more conveniently by precipitation of chloride ligands in the course of the following reactions:

$$Ag_2CrO_4 + 2Ph_3SiCl \rightarrow CrO_2(OSiPh_3)_2 + 2AgCl \quad (5)$$

$$CrO_2Cl_2 + 2NaOSiPh_3 \rightarrow CrO_2(OSiPh_3)_2 + 2NaCl \quad (6)$$

The latter reactions represent useful alternatives to the more commonly utilized reaction pathways where a desiccating agent is added in order to eliminate detrimental amounts of water.

Since **4** has been reported to bring about oxidative cleavage of olefins only at high temperatures[8] and **3**, although a superior oxidant, has proven to induce chlorination along with oxidation, we focused our attention on creating a more electrophilic chromium center. The fully fluorinated ligand $(C_6F_5)_3SiO-$[10] seemed to us a judicious choice, since it combines the desirable electroattracting properties along with stability toward oxidation, especially in comparison with the other halogenated congeners.

Our first attempts to synthesize analogous chloro–alkoxy and bis(alkoxy) compounds by the interaction of $CrO_3$ with 1 equiv of $(C_6F_5)_3SiCl$ in $CH_2Cl_2$ were hampered by the production of substantial amounts of $CrO_2Cl_2$ with only traces of the expected products. In fact, the organic reactant $(C_6F_5)_3SiCl$ is a potent chlorinating agent; the enhanced electropositive character of silicon renders reaction such as (4) highly favorable.

The reaction of $Ag_2CrO_4$ with $(C_6F_5)_3SiCl$ gives respectable yields of the yellow-orange crystalline complex $CrO_2[OSi(C_6F_5)_3]_2$, the amount of $CrO_2Cl_2$ produced being kept to a minimum by the precipitation of chloride as AgCl. The $\nu(Cr{=}O)$ stretching frequencies are masked by characteristic features of the $C_6F_5-$ group, but the deformation band, $\delta(CrO_2)$, can be detected at 385 $cm^{-1}$ and the Cr–OSi stretchings appear at 632 and 623 $cm^{-1}$, as expected for the bis(siloxy) derivative.

**Reactions of $CrO_3$ with $Me_3SiCl$ and $Me_3SiOSiMe_3$.** Our experience with the chemistry of the triphenylsiloxy and tri-

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phenylmethoxy complexes led us to investigate the reactions of $CrO_3$ with chlorotrimethylsilane and hexamethyldisiloxane. Dichloromethane solutions of $CrO_3$ and $Me_3SiCl$ have been proven to be a useful reagent for the oxidation of various organic substrates,[19] and reaction mixtures of $CrO_3$ and $Me_3SiOSiMe_3$ have been previously reported[20] to yield the red, oily species $CrO_2(OSiMe_3)_2$. In both cases, rigorous characterization of the metal complex was hampered by mixtures that detonated during purification. We undertook a $^1H$ NMR investigation of the reactions between $CrO_3$ with $Me_3SiCl$, as well as with $Me_3SiOSiMe_3$, which revealed that complex situations are involved, but these can easily be related to and complement the triphenylsiloxy and triphenylmethoxy studies described above.

**Reaction of $CrO_3$ and $Me_3SiCl$.** In four parallel experiments $Me_3SiCl$ (0.33, 0.66, 1, 2 mmol) was added to a stirred suspension of $CrO_3$ (1 mmol) in $CD_2Cl_2$. After being stirred for 24 h, the samples were filtered into NMR tubes and $^1H$ spectra were acquired immediately afterward. At a $CrO_3$:$Me_3SiCl$ ratio of 1:2, the only species observed in the NMR spectrum is $Me_3SiOSiMe_3$ (0.07 ppm) with the concomitant formation of $CrO_2Cl_2$. As the amount of $CrO_3$ is increased with respect to $Me_3SiCl$, some interesting new features are observed. For instance, at a 1:1 ratio of reactants a sharp peak appears at 0.45 ppm, probably due to $CrO_2Cl(OSiMe_3)$, along with very small peaks corresponding to the reaction of $Me_3SiOSiMe_3$ and $CrO_3$ at 0.29 ($CrO_2(OSiMe_3)_2$) and 0.37 ppm. Attempts to characterize this species by electron impact mass spectrometry proved unsuccessful, giving spectra of silicon-containing species only. Nonetheless, the major characteristics of these reactions can be interpreted by the following reactions:

$$CrO_3 + Me_3SiCl \rightarrow CrO_2Cl(OSiMe_3) \tag{7}$$

$$CrO_2Cl(OSiMe_3) + Me_3SiCl \rightarrow CrO_2Cl_2 + Me_3SiOSiMe_3 \tag{8}$$

A similar example, concerning the reaction of $Cp^*_2W{=}O$ with $Me_3SiCl$, has been recently reported.[21] However in (8) further electrophilic attack by silicon appears to occur on the $Cr{-}OSiMe_3$ group rather than on $Cr{=}O$, although we cannot exclude the latter possibility.

It should be noted that residual amounts of $CrO_2Cl_2$ are always present and care should be taken in attributing the oxidizing power of 1:1 solutions of $CrO_3$ and $Me_3SiCl$ solely to $CrO_2Cl(OSiMe_3)$; $CrO_2Cl_2$ might be responsible for some of the most potent oxidations executed by these mixtures.

**Reaction of $CrO_3$ with $Me_3SiOSiMe_3$.** As above, in five parallel experiments, $Me_3SiOSiMe_3$ (0.33, 0.66, 1, 2, 5 mmol) was added to a stirred suspension of $CrO_3$ (0.1 g, 1 mmol) in $CD_2Cl_2$. These solutions were allowed to stir for 24 h and subsequently were filtered into NMR tubes. In samples where the $CrO_3$:$Me_3SiOSiMe_3$ ratio was less than 1:2, a single resonance was observed at 0.29 ppm. An electron impact mass spectrum of the reaction mixture (1:2 $CrO_3/Me_3SiOSiMe_3$) gave a series of envelopes at 171 (10), 187 (15), 202 (39), 217 (100), 232 (37), and 247 amu (21) (intensity in parentheses), which correspond to sequential losses of the six methyl groups from $CrO_2(OSiMe_3)_2$, each envelope with the expected isotopic distribution. In addition, strong peaks are observed at 147 (100, $Me_3SiOSiMe_2^+$) and 75 amu (100, $Me_2SiOH^+$).

At a $CrO_3$:$Me_3SiOSiMe_3$ ratio of 1:1, a second peak appears in the $^1H$ NMR at 0.38 ppm and a new pattern is observed in the gas chromatography electron impact mass spectrum with peaks at 347 (15), 332 (10), and 317 amu (5), consistent with the formulation $[Cr_2O_5(OSiMe_3)(OSiMe_2)]^+$, and the sequential loss of two methyl groups. Also present is the pattern characteristic of $CrO_2(OSiMe_3)_2$, which results either from cochromatography of the two species or, more likely, by loss of $CrO_3$ from $Cr_2O_5(OSiMe_3)_2$.

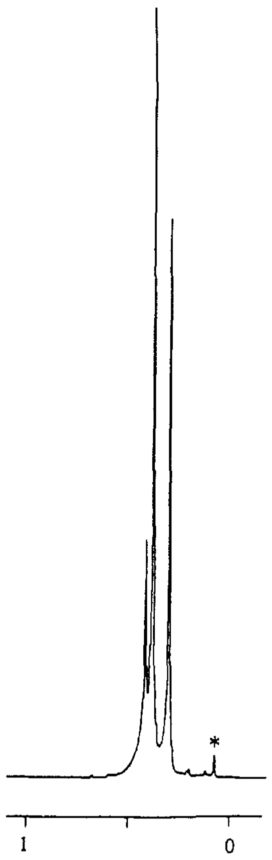
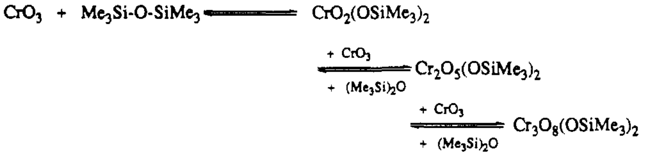


**Figure 3.** 200-MHz $^1H$ NMR spectrum of 3:1 of $CrO_3/Me_3SiOSiMe_3$ in $CD_2Cl_2$. The asterisk indicates $Me_3SiOSiMe_3$.

**Scheme I**



At $CrO_3$:$Me_3SiOSiMe_3$ ratios equal to and greater than 2, a third $^1H$ resonance grows up at 0.41 ppm. Figure 3 shows the spectrum of 2:1 $CrO_3/Me_3SiOSiMe_3$ in $CD_2Cl_2$. Mass spectra showed, apart from the fragmentation pattern of $CrO_2(OSiMe_3)_2$, peaks at 459 (10) and 359 amu (80) (intensity in parentheses), which can be formulated as $(MeSiO)Cr_4O_{12}^+$ and $(MeSiO)Cr_3O_9^+$. The spectrum also shows peaks corresponding to polychromate complexes at 500 (5, $Cr_5O_{15}^+$), 468 (10, $Cr_5O_{13}^+$), 400 (39, $Cr_4O_{12}^+$), 368 (100, $Cr_4O_{10}^+$), 300 (15, $Cr_3O_9^+$), 268 (40, $Cr_3O_7^+$) and 168 amu (30, $Cr_2O_4^+$), each with the expected isotopic distribution.

Such polynuclear oxo-bridged siloxy derivatives are analogous to the equilibria set forward for chromate–polychromate anions in aqueous solutions, where the anions $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$ have been isolated and structurally characterized.[22] Indeed, the behavior of the trimethylsilyl group is frequently cited as analogous to that of the proton in organic chemistry.[23] Furthermore, unstable *tert*-butoxy species $Cr_2O_5(OCMe_3)_2$ and $Cr_3O_8(OCMe_3)_2$ have been proposed to be contained in mixtures of $CrO_2(OCMe_3)_2$ and $CrO_3$,[24] on the basis of IR and microanalytical data.

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By analogy, we propose the equilibria shown in Scheme I, in which increasing the $CrO_3$ present causes the formation of polynuclear species formed by formally repeating insertion of a $CrO_3$ unit into a Cr–$OSiMe_3$ bond.

## Experimental Section

*Caution*! All Cr(VI) starting materials are powerful oxidants; they can react explosively with reducible organic matter. *Under no circumstances* should $CrO_3$ be ground up. Microanalyses were performed by Service de Microanalyse de l'Institut de Chimie-Strasbourg or by Service Central de Microanalyse-Lyon (CNRS). Melting points were determined in sealed tubes under argon and are uncorrected. Spectrometers: IR, Perkin-Elmer 597 (spectra in Nujol mulls in reciprocal centimeters between KBr or CsI plates); NMR, Bruker SY 200 ($^1H$ NMR, data given in parts per million relative to TMS); MS, Thomson TH 208 B.

All manipulations were carried out under vacuum or under argon. Solvents were distilled under nitrogen from sodium–benzophenone (hexane, pentane) and calcium hydride or phosphorous pentoxide (dichloromethane) and degassed prior to use. Literature routes[25] were used for the preparation of tris(pentafluorophenyl)chlorosilane. All other reagents were purchased from commercial sources and used without further purification.

**Preparation of Dioxochloro(triphenylmethoxy)chromate(VI) (1).** To a stirred suspension of $CrO_3$ (1.0 g, 10 mmol) in $CH_2Cl_2$ (50 mL) was added $Ph_3CCl$ (2.79 g, 10 mmol), and the mixture was allowed to stir for 24 h at room temperature. The resulting deep red solution was filtered and evaporated. The residue was extracted with hexane (4 × 50 mL) to yield a bright red solution and unextracted orange powder. The hexane filtrate was slightly reduced and cooled at 0 °C to yield after several hours a crop of colorless crystalline material, which was filtered off, while the red solution was cooled once again at 0 °C to afford fine red crystals of **1**. The sample might be contaminated with some organic matter, but it can be purified by repeating the crystallization procedure from hexane. Yield: 0.68 g, 18%. Anal. Calcd for $C_{19}H_{15}ClCrO_3$: C, 60.3; H, 4.0; Cl, 9.4. Found: C, 61.3; H, 4.0; Cl, 9.2. $^1H$ NMR (ppm, $CD_2Cl_2$): 7.40 (br, 2 H), 7.30 (br, 3 H). IR ($cm^{-1}$): 1593 w, 1575 w, 981 s, 974 s, 968 s, 845 s br, 755 m, 738 s, 697 vs, 637 w, 630 w, 520 w, 496 w, 460 s.

The unextracted orange powder dissolved in 25% $CH_2Cl_2$/hexane and crystallized at −20 °C as orange needles of $CrO_2(OCPh_3)_2$ (**2**). Yield: 1.63 g, 27%. Anal. Calcd for $C_{38}H_{30}CrO_4$: C, 75.7; H, 5.0. Found: C, 75.6; H, 4.9. $^1H$ NMR (ppm, $CD_2Cl_2$): 7.30 (br, 3 H), 7.25 (m, 2 H). IR ($cm^{-1}$): 1590 w, 1575 w, 980 m, 963 m, 950 m, 940 m, 908 s, 899 s, 750 m, 691 s, 526 w, 500 w, 420 w, 380 w.

**Preparation of Dioxochloro(triphenylsiloxy)chromate(VI) (3). Method 1.** To a suspension of $CrO_3$ (1.0 g, 10 mmol) in $CH_2Cl_2$ (50 mL) was added $Ph_3SiCl$ (2.36 g, 8 mmol). The mixture was allowed to stir for 24 h at room temperature. The orange-red solution was filtered and evaporated, whereupon $CrO_2Cl_2$ was transferred over as a red volatile component of the distillate. The residue was extracted with hot hexane (4 × 50 mL), the filtered extracts were combined and slightly reduced to 180 mL, and the solution was refiltered before being cooled to 0 °C in order to afford the yellow-orange needles of $CrO_2(OSiPh_3)_2$ (**4**). Yield: 1.77 g, 28%. Anal. Calcd for $C_{36}H_{30}CrO_4Si_2$: C, 68.1; H, 4.8. Found: C, 68.5; H, 4.8. $^1H$ NMR (ppm, $CD_2Cl_2$): 7.62 (d, 2 H), 7.10 (m, 3 H). IR ($cm^{-1}$): 3080 w, 1600 w, 1439 m, 1125 s, 1005 s, 992 s, 986 s, 974 s, 970 s, 855 vs, 870 vs, 721 vs, 703 vs, 627 m, 610 m, 520 vs, 360 m.

The yellow-orange needles were filtered out, and the solution was cooled at −20 °C to yield after several days red plates of $CrO_2Cl(OSiPh_3)$ (**3**). Yield: 0.75 g, 19%. Anal. Calcd for $C_{18}H_{15}ClCrO_3Si$: C, 54.8; H, 3.8; Cl, 9.0. Found C, 54.0; H, 3.7; Cl, 9.2. $^1H$ NMR (ppm, $CD_2Cl_2$): 7.6 (m, 2 H), 7.1 (m, 3 H). IR ($cm^{-1}$): 1585 w, 1425 m, 1112 s, 989 s, 981 s, 892 s, br, 710 s, 690 s, 620 m, 505 s, 470 m.

**Method 2.** To a solution of $CrO_2Cl_2$ (1.55 g, 10 mmol) in $CH_2Cl_2$ (50 mL) was added $Ph_3SiOH$ (2.76 g, 10 mmol). The mixture was stirred for 24 h and was then worked up in a manner similar to that of method 1.

**Preparation of Dioxobis[tris(pentafluorophenyl)siloxy]chromate(VI).** To a stirred suspension of $Ag_2CrO_4$ (0.332 g, 1 mmol) in $CH_2Cl_2$ (50 mL) was added $(C_6F_5)_3SiCl$ (1.13 g, 2 mmol), and the mixture was stirred for 24 h at room temperature. Filtration and evaporation of the resulting orange-red solution followed by extraction of the residues with hexane (3 × 30 mL), reduction of the extracts to ca. 70 mL, and subsequent filtration of the solution led to orange crystals on cooling at −20 °C. Yield: 0.29 g, 25%. Anal. Calcd for $C_{36}CrF_{30}O_4Si_2$: C, 36.8. Found: C, 36.6. IR ($cm^{-1}$): 1635 s, 1510 s, 1285 s, 1080 vs, 1035 vs, 970 vs, 940 vs, 750 m, 722 m, 632 m, 623 m, 521 s, 445 m, 430 s, 385 w, 333 m.

**Reaction of $CrO_3$ with $Me_3SiCl$.** In four parallel experiments $Me_3SiCl$ (0.036 g, 0.33 mmol; 0.054 g, 0.66 mmol; 0.109 g, 1 mmol; 0.218 g, 2 mmol) was added to a stirred suspension of $CrO_3$ (0.1 g, 1 mmol) in $CD_2Cl_2$ (1.0 mL). After being stirred for 24 h, the samples were filtered into NMR tubes.

**Reaction of $CrO_3$ with $Me_3SiOSiMe_3$.** In five parallel experiments $Me_3SiOSiMe_3$ (0.054 g, 0.33 mmol; 0.081 g, 0.66 mmol; 0.162 g, 1 mmol; 0.324 g, 2 mmol; 0.810 g, 5 mmol) was added to a stirred suspension of $CrO_3$ (0.1 g, 1 mmol) in $CD_2Cl_2$ (1 mL). The solutions were allowed to stir for 24 h and subsequently filtered into NMR tubes. MS (1:2 $CrO_3/Me_3SiOSiMe_3$): 247 (22), 232 (35), 217 (100), 202 (38), 187 (15), 171 amu (10); (1:1 $CrO_3/Me_3SiOSiMe_3$): 347 (12), 321 (8), 147 amu (100, $Me_3SiOSiMe_3$).

**Crystallography.** Red crystals of **1** and orange crystals of **2** were obtained from hexane at −20 and 0 °C, respectively. All data were collected on a Philips PW1100/16 diffractometer equipped with a low-temperature device using nickel-filtered Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å). The crystal data and data parameters are summarized in Table I. No significant changes were observed for three standard reflections, which were monitored hourly during the data collection period. The Enraf-Nonius SDP package[26] was used for all calculations, except that a local data reduction program was employed. The initial step-scan data was converted to intensities by the method of Lehmann–Larson[27] and then corrected for Lorentz, polarization, and absorption factors, the latter computed by the method of Wacker and Stuart.[28]

Both structures were solved by using the heavy-atom method. After refinement of the heavy atoms, a difference Fourier map revealed maxima of residual electron density close to positions expected for hydrogen atoms that were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic structure factors such that $B(H) = 1 + B_{eqv}(C)$ Å$^2$ but not refined. Full-least squares refinements converged to the conventional $R$ factors shown in Table I. Final difference maps revealed no significant maxima.

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**Supplementary Material Available:** Tables of crystallographic data, anisotropic temperature factors, hydrogen atom coordinates, and complete interatomic distances and angles (7 pages); listings of observed and calculated structure factor amplitudes for all observed reflections (11 pages). Ordering information is given on any current masthead page.

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