

# Notes

## A 12-Membered Inorganic Heterocycle: Synthesis and Structural Characterization of a Bimetallic Chromium(VI) Siloxane Complex

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### Introduction

Chromium supported on silica is being used as a catalyst for the coordinative polymerization of ethene.<sup>1</sup> Well-known examples of industrially used systems are the Phillips catalyst, essentially CrO<sub>3</sub> on SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>, and the Union Carbide system, which is prepared from ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Cr<sup>II</sup> and SiO<sub>2</sub>.<sup>2</sup> In addition, well-characterized homogeneous model systems for heterogeneous ethene polymerization catalysts containing chromium have been reported. These include oxo alkyls of Cr(IV) and Cr(V)<sup>3</sup> and a constrained geometry chromium(III) alkyl complex.<sup>4</sup> Very recently, Theopold *et al.* reported the first chromium-based catalysts that are capable of polymerizing  $\alpha$ -olefins.<sup>5</sup> A very nice approach to model the interactions of organometallic fragments with silicious supports, which is lacking in many homogeneous models, is provided by the work of Feher on silsesquioxane metal complexes.<sup>6</sup> As a part of this work, Cr(III) and Cr(VI) silsesquioxanes<sup>7</sup> were reported, including a silsesquioxane chromate ester that is a suitable precatalyst for the coordination polymerization of ethene. Interestingly, the polyethene produced in this case is similar to that obtained from Phillips-like catalysts.

We have recently embarked on a project where we would like to develop new transition metal complexes using siloxanes as ligands. Here we report on the synthesis and molecular structure of a siloxane chromate ester that is surprisingly stable and easy to synthesize. Due to these characteristics, this compound may be of interest for future work in the area of chromium-mediated alkene polymerization.

### Experimental Section

**Synthesis. Caution!** Chromium(VI) oxide is a cancer suspected strong oxidant; combinations with organic materials may cause explosions.

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- (1) See for instance: Krauss, H. L. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: New York, 1988.
- (2) Karol, F. J.; *et al.* *J. Polym. Sci., Part A-1* **1972**, *10*, 2621.
- (3) Noh, S.-K.; Heintz, R. A.; Haggerty, B. S.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1992**, *114*, 1892.
- (4) Liang, Y.; Yap, G. P. A.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1996**, *15*, 5284.
- (5) White, P. A.; Calabrese, J.; Theopold, K. H. *Organometallics* **1996**, *15*, 5473.
- (6) For a general review, see: Feher, F. J.; Budzichowski, T. A. *Polyhedron* **1995**, *14*, 3239.
- (7) (a) Feher, F. J.; Blanski, R. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1614. (b) Feher, F. J.; Walzer, J. F. *Inorg. Chem.* **1990**, *29*, 1604.

[Cr(=O)<sub>2</sub>{(OSiPh<sub>2</sub>)<sub>2</sub>O}]<sub>2</sub> (**1**). A suspension of 1,1,3,3-tetraphenyldisiloxane-1,3-diol<sup>8</sup> (7.50 g, 18.1 mmol) and chromium trioxide (2.5 g, 25 mmol) in 100 mL of carbon tetrachloride containing activated 4 Å molecular sieves was magnetically stirred overnight. The resulting voluminous bright yellow suspension was decanted from a residue containing the molecular sieves together with some dark precipitate. Subsequent removal of the solvent in *vacuo* and trituration of the residue with hexane (100 mL) afforded 7.33 g (85%) of yellow powder that was already analytically pure [Anal. Calcd for C<sub>48</sub>H<sub>40</sub>Cr<sub>2</sub>O<sub>10</sub>Si<sub>4</sub>: C, 58.05; H, 4.06. Found: C, 58.44; H, 3.79]. The compound can be crystallized in large block-shaped yellow crystals from hot carbon tetrachloride solutions. Anal. Calcd for C<sub>48</sub>H<sub>40</sub>Cr<sub>2</sub>O<sub>10</sub>Si<sub>4</sub>: C, 58.05; H, 4.06; Cr, 10.47. Found: C, 58.18; H, 3.83; Cr, 10.45. Mp: ~180 °C (dec). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 23 °C, TMS):  $\delta$  7.52 (d, 2H, Ar *o*-H), 7.42 (t, 1H, Ar *p*-H), 7.27 (t, 2H, Ar *m*-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 23 °C, TMS):  $\delta$  134.57 (Ar, *o*-C), 131.99 (Ar, C<sub>ipso</sub>), 130.89 (Ar, *m*-C), 128.00 (Ar, *p*-C). <sup>29</sup>Si NMR (79.5 MHz, CH<sub>2</sub>Cl<sub>2</sub>, 23 °C, TMS, 0.02 M Cr(acac)<sub>3</sub>):  $\delta$  -31.91.

**Structure Determination and Refinement of 1.** A transparent, yellow plate-shaped crystal was mounted on the top of a glass-fiber (using the inert-oil technique) and transferred to the cold nitrogen stream of an Enraf-Nonius CAD4T diffractometer for data collection at 150 K [rotating anode, 50 kV, 70 mA, graphite-monochromated Mo K $\alpha$  radiation,  $\omega$ -scan mode;  $\Delta\omega = (0.64 + 0.35 \tan \theta)^\circ$ ]. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with  $9.94 < \theta < 14.04^\circ$ . The unit cell parameters were checked for the presence of higher lattice symmetry.<sup>9</sup> A total of 11 160 reflections were collected and merged into a unique dataset of 5259 reflections ( $R_{av} = 0.0491$ ). Three intensity control reflections, (231, 222, 332) monitored every 1 h showed a small decay of 0.8% during the 26.8 h of X-ray exposure time. The structure was solved with direct methods (SHELXS-86)<sup>10</sup> and subsequent difference Fourier analyses. Refinement on  $F^2$  with all 5259 unique reflections was carried out by full-matrix least-squares techniques. H atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters; H atoms with isotropic thermal parameters related to the  $U_{eq}$  of the carrier atoms.

Weights were introduced in the final refinement cycles; convergence was reached at  $R1 = 0.0381$  [calculated for 4166 reflections with  $F_o > 4\sigma(F_o)$ ],  $wR2 = 0.0836$  (for all unique reflections), and  $w = 1.0/[\sigma^2(F_o^2) + (0.0390P)^2 + 0.58P]$  with  $P = (F_o^2 + 2F_c^2)/3$ . A final difference Fourier map shows no features outside the range  $-0.52$  to  $+0.50$  e/Å<sup>3</sup>.

Crystal data and numerical details of the structure determination are given in Table 1. Neutral atom scattering factors and anomalous dispersion factors were taken from ref 11. All calculations were performed with SHELXL93<sup>12</sup> and the PLATON<sup>13</sup> package (geometrical calculations and illustrations) on a DEC-5000 cluster.

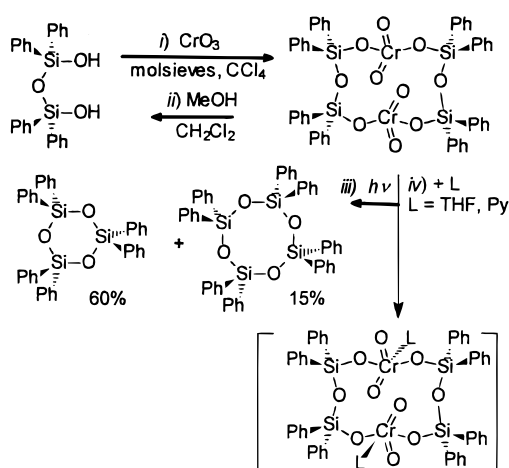
### Results and Discussion

**Synthesis and Stability of [Cr(=O)<sub>2</sub>{(OSiPh<sub>2</sub>)<sub>2</sub>O}]<sub>2</sub> (**1**).** The reaction of 1,1,3,3-tetraphenyldisiloxane-1,3-diol, Ph<sub>2</sub>Si(OH)OSi(OH)Ph<sub>2</sub>, with chromium trioxide in carbon tetrachloride at room temperature proceeds surprisingly smooth with near quantitative formation of the yellow, bimetallic chromium(VI) complex **1** (Scheme 1, step *i*).

- (8) Harris, G. I. *J. Chem. Soc.* **1963**, 5978.
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- (10) Sheldrick, G. M. *SHELXS-86, Program for crystal structure determination*; University of Gottingen: Federal Republic of Germany, 1986.
- (11) Wilson, A. J. C., Ed. *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.
- (12) Sheldrick, G. M. *SHELXS-86, Program for crystal structure refinement*; University of Gottingen: Federal Republic of Germany, 1993.
- (13) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

**Table 1.** Crystal Data for **1**

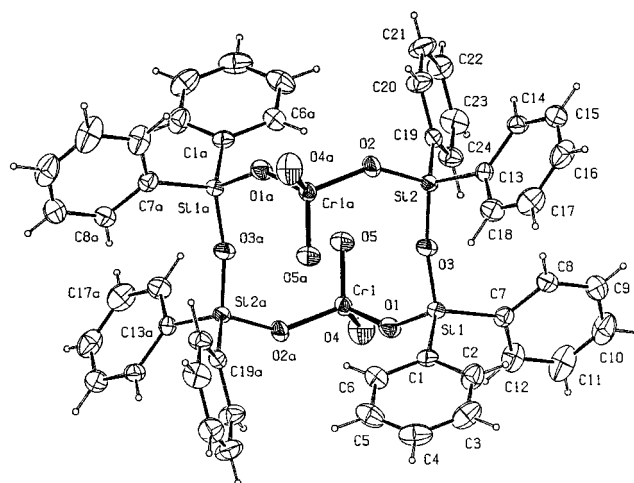
compd	C <sub>48</sub> H <sub>40</sub> Cr <sub>2</sub> Si <sub>4</sub> O <sub>10</sub>
mol wt	993.17
cryst system	triclinic
space group	P1 (No. 2)
a, b, c (Å)	9.4843(5), 10.5514(7), 13.3024(9)
α, β, γ (deg)	111.568(5), 107.088(5), 95.951(5)
V (Å <sup>3</sup> )	1149.30(14)
Z	1
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.435
F(000)	512
μ (cm <sup>-1</sup> )	6.4
cryst size (mm)	0.15 × 0.40 × 0.40
θ <sub>min</sub> , θ <sub>max</sub>	1.77, 27.50
radiation	Mo Kα (graphite-monochr), 0.710 73 Å
tot. data	11160
tot. unique data	5259
final R1 {Σ( F <sub>o</sub>   -  F <sub>c</sub>   )/Σ F <sub>o</sub>  }	0.0381
wR2 {Σ[w(F <sub>o</sub> <sup>2</sup> - F <sub>c</sub> <sup>2</sup> ) <sup>2</sup> ]/Σ[w(F <sub>o</sub> <sup>2</sup> ) <sup>0.5</sup> ]}	0.1016
S {Σ[w(F <sub>o</sub> <sup>2</sup> - F <sub>c</sub> <sup>2</sup> ) <sup>2</sup> ]/(n - p)}	1.041

**Scheme 1.** Synthesis and Reactivity of the Bimetallic Chromium(VI) Complex **1**

Complex **1** can be easily crystallized from hot carbon tetrachloride, affording **1** as air- and water-stable yellow crystals that only start to thermally decompose at ca. 180 °C. Related siloxy complexes of the type  $[(t\text{-Bu})_3\text{SiO}]_2\text{M}(=\text{O})_2$  (M = Cr, Mo) were also reported to have good thermal stabilities and resistance to hydrolysis.<sup>14</sup> The entire synthesis and storage of **1**, however, should be performed in the dark since the complex is, both as a solid and in solution, somewhat light sensitive.

An alternative attempt to synthesize the chromium complex **1** starting from diphenylsilanediol, instead of its condensation product 1,1,3,3-tetraphenyldisiloxane-1,3-diol, failed. In this case, the diol did not react at room temperature over a period of several days while, at prolonged reflux in  $\text{CCl}_4$ , hexaphenylcyclotrisiloxane was formed in ca. 30% yield. Under these conditions, formation of the cyclotrisiloxane also occurs in the absence of  $\text{CrO}_3$ .

With coordinating solvents as pyridine or tetrahydrofuran, the chromium complex **1** forms unstable adducts (Scheme 1, step iv). This adduct formation can be easily observed by <sup>29</sup>Si NMR. When pyridine or tetrahydrofuran is added to a dichloromethane solution of **1**, the <sup>29</sup>Si resonance of **1** at  $\delta$  -31.91 directly shifts to higher field, -40.36 or -39.61 ppm, respectively. Due to the instability of these adducts, attempts to isolate them failed; as a result of their decomposition, substantial amounts of hexaphenylcyclotrisiloxane are formed. The reaction of **1** with methanol also seems to give, initially, an adduct, but in this case rapid decomposition takes place in which the 1,1,3,3-

**Figure 1.** Structure of  $[\text{Cr}(=\text{O})_2\{\text{OSiPh}_2\}_2]_2$  (**1**) in the crystal: ORTEP drawing with 50% probability ellipsoids. "a" indicates symmetry operation  $2 - x, 1 - y, 1 - z$ .

tetraphenyldisiloxane-1,3-diol used for the synthesis of **1** is formed back (Scheme 1, step ii).

The photochemical decomposition of **1** has been investigated in some detail by <sup>29</sup>Si NMR [79.5 MHz, 298K,  $\text{CH}_2\text{Cl}_2$ , 0.02 M  $\text{Cr}(\text{acac})_3$ ] (Scheme 1, step iii). Dichloromethane solutions of **1** turn black when exposed to daylight in the course of about 1 h. The chromium-free siloxanes that result from this decomposition are hexaphenylcyclotrisiloxane together with octaphenylcyclotetrasiloxane in a 4:1 ratio, respectively; the yield of these siloxanes is ca. 75%.

The activity of **1** for polymerization of ethene was briefly examined. Addition of ca. 10 equiv of  $\text{Me}_3\text{Al}$  to a solution of **1** (25 mg in 10 mL of toluene) in an ethene atmosphere results in a green solution that slowly produces small quantities of polyethene (ca. 75 mg in 18 h). This low activity is comparable to that of  $(\text{Ph}_3\text{SiO})_2\text{CrO}_2$  and may be limited by the relative electron-donating properties of the siloxy ligands present in both complexes. In contrast, the polymerization activity for the related silsesquioxane complex  $[(c\text{-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{-CrO}_2]$ ,<sup>7a</sup> which has a strongly electron-withdrawing silicious ligand instead,<sup>15</sup> was reported to be much higher.

**Solid-State Structure of  $[\text{Cr}(=\text{O})_2\{\text{OSiPh}_2\}_2]_2$  (**1**).** Since an unambiguous assignment of the structure of the chromium complex **1** could not be made on the basis of the spectroscopic data alone, an X-ray structure of this compound was determined. Suitable crystals were obtained from a hot tetrachloromethane solution of **1** that was allowed to cool slowly to 20 °C. The crystal structure of **1** consists of one discrete centrosymmetric dinuclear molecule in a triclinic unit cell. An ORTEP drawing of **1**, along with the adopted numbering scheme is shown in Figure 1; selected bond distances and angles are given in Table 2.

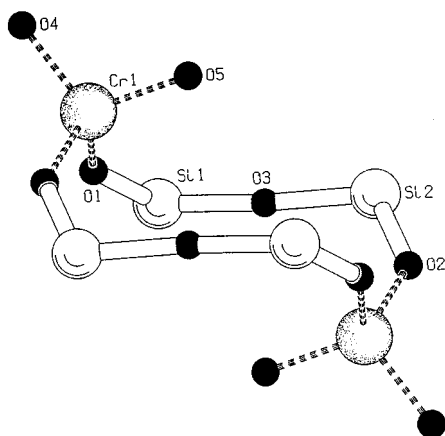
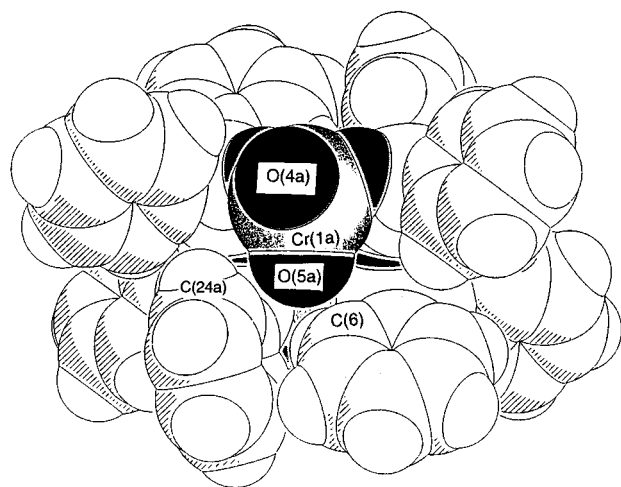
The structure determination shows **1** to be a dinuclear tetracoordinate chromium species,  $[\text{Cr}(=\text{O})_2\{\text{OSiPh}_2\}_2]_2$ . In this structure, each of two dianionic disiloxanediolate ligands binds to two chromium dioxo units, generating a unique 12-membered metallacyclic fragment (Figure 2) with *pseudo* chair type conformation.

The chromium dioxo functionalities in **1** are incorporated in a remarkably close-packed ligand array involving the phenyl groups of the siloxanes and the *pseudo*equatorial chromium oxo functions (Figure 3). In the solid-state structure intramolecular contacts are present between  $\text{O}(5a)\cdots\text{C}(6)$  [3.412(3) Å] and  $\text{O}(5a)\cdots\text{C}(24a)$  [3.395(3) Å].

(14) Weidenbruch, M.; Pierrard, C.; Resel, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1465.(15) Feher, F. J.; Budzichowski, T. A. *J. Organomet. Chem.* **1989**, *379*, 33.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for **1**

Bond Lengths					
Cr(1)–O(1)	1.7245(19)	O(1)–Si(1)	1.644(2)	O(2)–Si(2)	1.6573(17)
Cr(1)–O(4)	1.579(2)	Si(1)–O(3)	1.611(2)	Si(2)–O(3)	1.614(2)
Cr(1)–O(5)	1.568(2)	Si(1)–C(1)	1.852(3)	Si(2)–C(13)	1.843(2)
Cr(1)–O(2a)	1.7242(19)	Si(1)–C(7)	1.855(3)	Si(2)–C(19)	1.843(3)
Bond Angles					
O(1)–Cr(1)–O(4)	108.76(10)	Cr(1)–O(1)–Si(1)	146.89(14)		
O(1)–Cr(1)–O(5)	109.90(11)	O(1)–Si(1)–O(3)	108.49(10)		
O(1)–Cr(1)–O(2a)	110.27(9)	O(1)–Si(1)–C(1)	105.48(11)		
O(4)–Cr(1)–O(5)	109.00(11)	O(1)–Si(1)–C(7)	107.15(11)		
Si(1)–O(3)–Si(2)	169.25(13)	C(1)–Si(1)–C(7)	113.45(12)		
Cr(1a)–O(2)–Si(2)	142.20(14)	O(2)–Si(2)–O(3)	108.33(10)		
O(2)–Si(2)–C(19)	106.14(10)	O(2)–Si(2)–C(13)	106.39(11)		
C(19)–Si(2)–C(13)	114.14(10)				

**Figure 2.** View at the *pseudo* chair type conformation of the 12-membered metallacyclic fragment present in the structure of **1**.**Figure 3.** Space-filling drawing of the chromium dioxo complex **1** showing the crowded coordination sphere around the *pseudo* equatorial oxo function.

The tetrahedral coordination of the metal centers in **1** is near perfect. As expected, the Cr=O bond lengths of both chromium oxo functions [1.568(2) and 1.579(2) Å] are substantial shorter than those present in the chromium siloxy units [Cr–O–Si: both 1.724(2) Å]. In **1**, the two similar terminal Cr=O bond distances are close to those derived for CrO<sub>2</sub>Cl<sub>2</sub> [1.577(2) Å]<sup>16</sup> as well as to the Cr=O distances found in the silsesquioxane complex,<sup>7a</sup> [(*c*-C<sub>6</sub>H<sub>11</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>11</sub>(OSiMe<sub>3</sub>)Cr(=O)<sub>2</sub>] [1.557(5) and 1.574(4) Å]. In addition, there is a good agreement with the Cr=O distances present in the simple siloxy complexes<sup>17</sup> Cr(=O)<sub>2</sub>Cl(OCPh<sub>3</sub>) [1.576(5) and 1.594(5) Å] and Cr(=O)<sub>2</sub>(OCPh<sub>3</sub>)<sub>2</sub> [1.578(2) Å].

(16) Palmer, K. J. *J. Am. Chem. Soc.* **1983**, *60*, 2360.(17) Stavropoulos, P.; Bryson, N.; Youinou, M.-T.; Osborn, J. A. *Inorg. Chem.* **1990**, *29*, 1807–1811.

The Si–O distances in the chromium siloxy functions [O(1)–Si(1) = 1.644(2) Å; O(2)–Si(2) = 1.657(2) Å] are significantly larger than those present in the siloxane unit [Si(1)–O(3) = 1.611(2) Å; Si(2)–O(3) = 1.614(2) Å]. This may be ascribed to a stronger  $p\pi$ – $d\pi$  electron donation of the oxygen lone pairs to the electron deficient chromium center than to the silicon atom. Consistent with this explanation is the finding that in a related low-valent chromium complex, [Cr{OSiPh<sub>2</sub>OSiPh<sub>2</sub>O}- $\mu$ -Na(THF)<sub>2</sub>]<sub>2</sub>,<sup>18</sup> that has a chromium center with formal oxidation state 2+ (*cf.* 6+ for both chromium centers in **1**), the Si–O distance in the chromium siloxy unit is shortened to 1.589(6) Å.

The Si–O distances in the siloxane unit of **1** are typical for configurational unstrained siloxanes,<sup>19</sup> the Si–O–Si angle [Si(1)–O(3)–Si(2) = 169.25(13)°] being rather large. The conformation of siloxane functions, however, is known to be very flexible, thus providing siloxanes with a means to alleviate steric strain arising, for instance, from packing effects in the solid. A nice example of this comes from the X-ray structure of the starting siloxane in the synthesis of **1**, Ph<sub>2</sub>Si(OH)OSi(OH)Ph<sub>2</sub>, where the solid-state structure comprises three independent molecules with Si–O–Si angles of 147.8, 157.0, and 162.5°.<sup>20</sup> Lower-end values for related Si–O–Si angles, ranging from 123 to 133°, are found in a series of spirocyclic complexes of the type [M{OSiPh<sub>2</sub>OSiPh<sub>2</sub>O}- $\mu$ -M'(L)<sub>2</sub>]<sub>2</sub>, reported by Sullivan *et al.*<sup>21</sup> In **1**, as in siloxanes in general, the bond angles around silicon [105.5(1)–114.1(1)°] show only minor deviations from the ideal tetrahedral value.

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**Supporting Information Available:** An X-ray crystallographic file, in CIF format, for complex **1** is available on the Internet only. Access information is given on any current masthead page.

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