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Chromium(II) and Chromium(III) Tri-*tert*-butoxysiloxy Complexes

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We have been exploring the structure, bonding, and chemistry of transition-metal and main-group complexes that possess oxygen-rich alkoxysiloxy ligands such as $-OSi(O^tBu)_3$.[1-4] A primary focus of these studies is the development of molecular, single-source precursors to homogeneous, ultrapure metal silicates. We have found that titanium, zirconium, hafnium, and aluminum derivatives of $-OSi(O^tBu)_3$ thermally decompose at low temperatures (100–200 °C) with elimination of isobutylene and water to give metal-containing silicates.[3,4] For example, $\{Zr[OSi(O^tBu)_3]_4\}_2$ decomposes at ca. 100–140 °C with elimination of 12 equiv of isobutylene and 6 equiv of water per zirconium. This reaction has been used to produce high surface area, amorphous zirconium silicates, which segregate upon further heating to nanosize zirconia particles dispersed in a silica matrix.[3] These observations suggested the possible use of this methodology in new syntheses of supported catalysts, particularly since chemical reactivities and selectivities are known to be very sensitive to the size and shape of the supported metal catalyst particles.[5]

Silica- and aluminosilica-supported chromium catalysts are used widely for the catalytic polymerization of ethylene.[6] To examine alkoxysiloxy derivatives of chromium as precursors to chromium-supported catalysts, we have begun to explore synthetic routes to $Cr-OSi(O^tBu)_3$ complexes. On the basis of previously reported routes to siloxide and alkoxide complexes of chromium, approaches based on either the silanol $HOSi(O^tBu)_3$ or alkali-metal derivatives $MOSi(O^tBu)_3$ (M = Li, Na, K) as starting materials seem possible.[7-10] Here we report two siloxide complexes which result from the reaction of $Cr(NEt_2)_4$ with $HOSi(O^tBu)_3$. While this reaction does not provide a high yield of a single product that can be used in a convenient route to chromium silicate materials, it does offer the opportunity to closely compare analogous chromium(II) and chromium(III) siloxide complexes $Cr[OSi(O^tBu)_3]_2(NHEt_2)_2$ (1) and $Cr[OSi(O^tBu)_3]_3(NHEt_2)_2$ (2).

Experimental Section

All manipulations were performed under an atmosphere of argon or nitrogen using standard Schlenk techniques and/or a Vacuum Atmospheres glovebox. Infrared spectra were recorded on a Perkin Elmer 1330 spectrometer. Magnetic susceptibilities were determined by Evans' method[11] with a GE QE-300 FT or a Varian EM-390 NMR spectrometer. Elemental analyses were performed by Mikroanalytiches Labor Pascher. Dry and oxygen-free solvents were used throughout. The silanol $(^tBuO)_3SiOH$[12] and $Cr(NEt_2)_4$[13] were prepared by literature methods.

Table I. Crystallographic Data for $Cr[OSi(O^tBu)_3]_2(NHEt_2)_2$ (1)

chem formula $C_{32}H_{76}CrN_2O_8Si_2$	space group $P2_1/n$ (No. 14)
fw 725.2	$T = 22$ °C
$a = 9.882(2)$ Å	$\lambda = 0.710\,73$ Å (Mo Kα)
$b = 15.065(4)$ Å	$\rho_{calcd} = 1.075$ g cm^{-3}
$c = 15.056(5)$ Å	$\mu = 0.340$ mm^{-1}
$\beta = 92.16(2)°$	data/param = 10.2
$V = 2239.8(10)$ Å^3	weighting scheme: $w^{-1} = \sigma^2(F) + 0.0012F^2$
$Z = 2$	scan type: Wycoff
$R_F = 7.85\%$[a]	scan speed = 6.01–26.04° min^{-1}
$R_{wF} = 10.86\%$[b]	GOF = 2.36

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Crystallographic Data for $Cr[OSi(O^tBu)_3]_3(NHEt_2)_2$ (2)

chem formula $C_{44}H_{103}CrN_2O_{12}Si_3$	space group $P2_1/n$ (No. 14)
fw 988.6	$T = -125$ °C
$a = 14.352(5)$ Å	$\lambda = 0.710\,73$ Å (Mo Kα)
$b = 16.860(6)$ Å	$\rho_{calcd} = 1.120$ g cm^{-3}
$c = 24.222(8)$ Å	$\mu = 0.299$ mm^{-1}
$\beta = 90.95(3)°$	data/param = 9.8
$V = 5860(3)$ Å^3	weighting scheme: $w^{-1} = \sigma^2(F) + 0.0005F^2$
$Z = 4$	scan type: Wycoff
$R_F = 5.86\%$[a]	scan speed = 10.19° min^{-1} (constant)
$R_{wF} = 5.69\%$[b]	GOF = 1.29

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

$Cr[OSi(O^tBu)_3]_2(NHEt_2)_2$ (1) and $Cr[OSi(O^tBu)_3]_3(NHEt_2)_2$ (2). A toluene solution (30 mL) of $(^tBuO)_3SiOH$ (1.442 g, 0.005 45 mol) was added to a toluene solution (30 mL) of $Cr(NEt_2)_4$(0.464 g, 0.001 36 mol) at room temperature. The resulting mixture was refluxed for 2 days. After removal of volatiles under dynamic vacuum, the resulting dark purple solid was extracted into pentane (30 mL). Concentration and cooling (−30 °C) of this solution gave a 1:4 mixture of compounds **1** and **2**. From this mixture was separated by hand 0.054 g of crystalline **1**, and the remaining mixture was fractionally crystallized to give pure samples of **1** and **2** (these compounds may be readily separated by fractional crystallization, since **1** is much less soluble in pentane). A second crop from the original pentane extract gave 0.313 g of **2**. The combined isolated yields for **1** and **2** from this reaction were 7% and 50%, respectively.

Anal. Calcd for compound **1**, $C_{32}H_{76}CrN_2O_8Si_2$: C, 53.5; H, 10.5. Found: C, 53.2; H, 10.6. IR (Nujol, CsI, cm^{-1}): 3180 m, 1360 m, 1238 w, 1210 w sh, 1192 m, 1150 vw, 1050 vs, 1020 vs sh, 1004 vs sh, 818 m, 720 vw sh, 695 m, 686 m sh, 640 vw, 465 w, br. $\mu_{eff} = 4.7\ \mu_B$ (benzene, 60 °C; heating the solution was required to dissolve all of **1**).

Anal. Calcd for compound **2**, $C_{44}H_{103}CrN_2O_{12}Si_3$: C, 53.0; H, 10.6. Found: C, 53.0; H, 10.5. IR (Nujol, CsI, cm^{-1}): 3235 m, 1360 s, 1238 s, 1219 m, 1193 s, 1125 w sh, 1050 vs, br, 1024 s sh, 1000 s, br sh, 980 s, br sh, 910 vw sh, 840 vw sh, 820 s, 800 vw sh, 772 w, 695 s sh, 688 s, 644 vw, 600 vw sh, 590 vw, 525 vw sh, 504 w sh, 480 m sh, 460 m, 430 w sh, 364 w, 342 w, $\mu_{eff} = 3.7\ \mu_B$ (benzene).

Structure Determination for 1. A summary of crystallographic data is provided in Table I. A green parallelpiped of approximate dimensions 0.6 × 0.4 × 0.5 mm was mounted in a glass capillary in an inert-atmosphere glovebox, after which the capillary was flame-sealed. Centering on 25 randomly selected reflections with 15° ≤ 2θ ≤ 30° provided the unit cell dimensions. Axial photographs confirmed the lattice assignment as monoclinic. Data were collected over the 2θ range 3° ≤ 2θ ≤ 48°. Of 3016 reflections collected, 2697 were independent and 1637 were observed with $F \geq 6.0\sigma(F)$. The chromium atom was located by direct methods, and subsequent Fourier synthesis revealed the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically except for the *tert*-butoxy methyl carbons, which were refined isotropically. Hydrogen atoms were added in idealized positions.

Structure Determination for 2. A summary of crystallographic data is provided in Table II. A purple fragment of approximate dimensions

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Table III. Selected Bond Distances (Å) and Angles (deg) for 1

(a) Bond Distances

Cr–O(2)	1.959(6)	Cr–N	2.147(7)
Si(1)–O(2)	1.566(6)	Si(1)–O(3)	1.623(6)
Si(1)–O(4)	1.631(6)	Si(1)–O(1)	1.632(8)
O(1)–C(14)	1.41(1)	O(3)–C(15)	1.42(1)
O(4)–C(16)	1.45(1)	N–C(3)	1.49(1)
N–C(4)	1.48(1)		

(b) Bond Angles

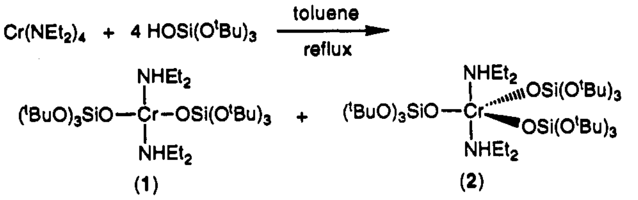
O(2)–Cr–O(2a)	180.0(1)	N–Cr–N(a)	180.0(1)
O(2)–Cr–N	90.3(2)	O(2)–Cr–N(a)	89.7(2)
Cr–O(2)–Si(1)	146.9(4)	O(2)–Si(1)–O(4)	107.9(3)
O(2)–Si(1)–O(3)	114.9(3)	O(2)–Si(1)–O(1)	114.3(3)
O(4)–Si(1)–O(3)	111.1(3)	O(4)–Si(1)–O(1)	102.4(4)
O(3)–Si(1)–O(1)	105.6(4)	Si(1)–O(3)–C(15)	133.9(6)
Si(1)–O(1)–C(14)	134.5(7)	Si(1)–O(4)–C(16)	133.7(6)
Cr–N–C(4)	114.4(5)	Cr–N–C(3)	113.2(6)

0.6 × 0.4 × 0.5 mm was mounted in a glass capillary in an inert-atmosphere glovebox, after which the capillary was flame-sealed. Centering on 20 reflections selected from a rotation photograph in the 2θ range $9.88° \leq 2\theta \leq 30.63°$ provided the unit cell dimensions. Data were collected for the 2θ range $3° \leq 2\theta \leq 45°$. Of 11 161 reflections collected, 10 313 were independent and 5708 were observed with $F \geq 4.0\sigma(F)$. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. C(44) was disordered and modeled as half-atoms, C(44a) and C(44b). Residual electron density peaks of ca. 1.0–1.5 e Å^{-3} near O(10), O(11), and O(12) reveal an additional 20% disorder for these three atoms. Extending this disorder model to the ^{t}Bu groups bonded to these oxygen atoms gave little improvement in residual electron density and the *R* factors. Amine hydrogens H(1) and H(2) were located with a difference map. The remaining hydrogen atoms were added in idealized positions.

Important geometrical parameters for **1** and **2** are listed in Tables III–VI.

Results and Discussion

The chromium(IV) tetrasiloxide $Cr(OSiEt_3)_4$ has been prepared by silanolysis of both $Cr(O^tBu)_4$ and $Cr(NEt_2)_4$.[10] Initial attempts to obtain chromium siloxide complexes from the reaction of $Cr(O^tBu)_4$ with 4 equiv of $HOSi(O^tBu)_3$ in refluxing benzene did not give crystalline, chromium-containing products by fractional crystallization. However, reaction of $Cr(NEt_2)_4$ with 4 equiv of $HOSi(O^tBu)_3$ in refluxing toluene afforded a crystalline product which contains the very air-sensitive complexes **1** (green) and **2** (purple) in a ratio of ca. 1:8 (eq 1). These compounds cocrystallize from the reaction mixture, but pure samples are readily obtained by fractional crystallization.



(1)

As expected,[14] **1** is a high-spin d^4 complex with a square planar geometry (vide infra). The magnetic moment, determined by Evans' method in benzene, is 4.7 μ_B, comparable to the value reported for the distorted square planar complex $Cr(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_2)_2(THF)_2$ (4.68 μ_B).[15] The d^3 complex **2** has a magnetic moment of 3.7 μ_B (Evans' method; benzene solution), which compares well with the magnetic moment of 3.6 μ_B reported for $Cr\{OSi[C(SiMe_3)_3]Me_2\}_3$.[16]

Table IV. Selected Bond Distances (Å) and Angles (deg) for 2

(a) Bond Distances

Cr–O(1)	1.879(3)	Cr–O(2)	1.899(3)
Cr–O(3)	1.891(3)	Cr–N(1)	2.113(4)
Cr–N(2)	2.113(4)	Si(1)–O(1)	1.577(3)
Si(2)–O(2)	1.584(3)	Si(3)–O(3)	1.592(3)
Si(1)–O(4)	1.626(3)	Si(1)–O(5)	1.632(3)
Si(1)–O(6)	1.633(3)	Si(2)–O(7)	1.630(3)
Si(2)–O(8)	1.626(3)	Si(2)–O(9)	1.640(3)
Si(3)–O(10)	1.614(4)	Si(3)–O(11)	1.637(5)
Si(3)–O(12)	1.629(4)		

(b) Bond Angles

O(1)–Cr–O(2)	101.2(1)	O(1)–Cr–O(3)	126.1(1)
O(2)–Cr–O(3)	132.7(1)	N(1)–Cr–N(2)	177.6(2)
N(1)–Cr–O(1)	89.7(1)	N(1)–Cr–O(2)	90.4(1)
N(1)–Cr–O(3)	91.6(1)	N(2)–Cr–O(1)	89.8(1)
N(2)–Cr–O(2)	87.4(1)	N(2)–Cr–O(3)	90.7(1)
Cr–O(1)–Si(1)	152.2(2)	Cr–O(2)–Si(2)	147.0(2)
Cr–O(3)–Si(3)	161.7(2)	Cr–N(1)–C(37)	112.8(3)
Cr–N(1)–C(39)	110.6(3)	Cr–N(2)–C(41)	111.9(3)
Cr–N(2)–C(43)	114.5(3)		

Table V. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 1

	x	*y*	*z*	*U*(eq)[a]
Cr	0	5000	5000	31(1)
Si(1)	−715(3)	3479(2)	3399(2)	38(1)
O(1)	−577(7)	2468(5)	3782(4)	59(3)
O(2)	52(5)	4194(4)	3981(3)	43(2)
O(3)	−267(6)	3428(5)	2375(4)	59(3)
O(4)	−2335(6)	3668(4)	3454(4)	44(2)
N	−2116(7)	4727(5)	5127(4)	39(3)
C(1)	−1597(13)	3403(9)	6040(7)	86(6)
C(2)	−2724(12)	6032(8)	4212(8)	82(5)
C(3)	−2981(10)	5532(7)	5036(7)	60(5)
C(4)	−2438(11)	4222(8)	5932(6)	67(5)
C(5)	285(22)	1311(14)	4540(13)	214(10)
C(6)	−4598(15)	3848(10)	2920(10)	116(5)
C(7)	285(17)	1279(11)	2980(10)	134(6)
C(8)	−540(18)	4917(11)	1865(11)	154(7)
C(9)	−243(15)	3658(9)	851(9)	114(5)
C(10)	−3269(14)	2560(10)	2453(9)	108(5)
C(11)	−4015(16)	2688(10)	3960(9)	118(5)
C(12)	1839(17)	2179(11)	3819(11)	138(6)
C(13)	1552(16)	4221(11)	1827(11)	134(6)
C(14)	450(12)	1821(8)	3790(7)	64(5)
C(15)	74(11)	4075(8)	1735(6)	59(4)
C(16)	−3540(9)	3189(7)	3149(6)	52(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The molecular structure of **1** is shown in Figure 1, and important bond distances and angles are collected in Table III. The complex is centrosymmetric about the chromium atom, which results in a crystallographically imposed square plane. This coordination geometry is further reflected in the O–Cr–N angles, which are very close to 90°. Two related aryloxide complexes, $Cr(O\text{-}2,6\text{-}{}^tBu_2\text{-}4\text{-}MeC_6H_2)_2(THF)_2$[15] and $Cr(O\text{-}2,4,6\text{-}{}^tBu_3C_6H_2O)_2(py)_2$,[17] also have square planar geometries. The Cr–O distance in **1**, 1.959(6) Å, is very similar to the corresponding values of ca. 1.95 Å observed in the aryloxide complexes. The Cr–N bond length for **1**, 2.147(7) Å, is slightly longer than the Cr–N(py) distance of 2.251(2) Å in $(2,4,6\text{-}{}^tBu_3C_6H_2O)_2Cr(py)_2$.

An ORTEP plot of **2** is shown in Figure 2, and important geometrical parameters are listed in Table IV. This trigonal bipyramidal complex has equatorial $OSi(O^tBu)_3$ ligands but inequivalent O–Cr–O angles of 101.2(1), 126.1(1), and 132.7(1)°. However, the N(1)–Cr–N(2) angle is close to 180° (177.6(2)°), and the N–Cr–O angles are all approximately 90°. Consistent with expected trends in ionic radii, the chromium–ligand bond distances in **2** are slightly shorter than the corre-

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Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for 2

	x	*y*	*z*	*U*(eq)[a]
Cr	3529(1)	2645(1)	877(1)	19(1)
N(1)	3569(3)	1421(2)	692(2)	22(1)
N(2)	3435(3)	3873(2)	1044(2)	31(1)
Si(1)	1953(1)	2724(1)	1883(1)	25(1)
Si(2)	2293(1)	2473(1)	−298(1)	23(1)
Si(3)	5856(1)	2484(1)	1222(1)	23(1)
O(1)	2636(2)	2446(2)	1419(1)	26(1)
O(2)	2756(2)	2829(2)	247(1)	25(1)
O(3)	4835(2)	2676(2)	991(1)	32(1)
O(4)	1240(2)	2026(2)	2065(1)	31(1)
C(1)	632(3)	1508(3)	1756(2)	35(2)
C(2)	1175(4)	773(3)	1600(3)	56(2)
C(3)	222(5)	1915(4)	1258(2)	61(3)
C(4)	−139(4)	1284(3)	2150(2)	50(2)
O(5)	2463(2)	3008(2)	2457(1)	32(1)
C(5)	2961(4)	2596(3)	2892(2)	40(2)
C(6)	2253(5)	2256(5)	3283(3)	93(3)
C(7)	3549(5)	1961(4)	2658(2)	86(3)
C(8)	3524(5)	3215(4)	3187(3)	85(3)
O(6)	1419(2)	3520(2)	1659(1)	32(1)
C(9)	816(4)	4062(3)	1949(2)	41(2)
C(10)	289(4)	3657(3)	2411(2)	47(2)
C(11)	133(4)	4381(3)	1521(2)	61(3)
C(12)	1406(5)	4722(3)	2182(3)	68(3)
O(7)	3054(2)	2249(2)	−765(1)	32(1)
C(13)	3558(3)	2711(3)	−1159(2)	36(2)
C(14)	3914(4)	3471(3)	−897(2)	47(2)
C(15)	4362(4)	2205(3)	−1332(2)	59(2)
C(16)	2905(4)	2910(4)	−1644(2)	75(3)
O(8)	1535(2)	3049(2)	−602(1)	32(1)
C(17)	897(4)	3660(3)	−423(2)	39(2)
C(18)	74(4)	3634(3)	−830(2)	52(2)
C(19)	1394(4)	4447(3)	−462(3)	70(3)
C(2)	579(4)	3499(4)	156(2)	57(2)
O(9)	1829(2)	1618(2)	−134(1)	29(1)
C(21)	1211(4)	1090(3)	−441(2)	32(2)
C(22)	218(4)	1360(3)	−366(2)	50(2)
C(23)	1448(4)	1075(4)	−1044(2)	62(3)
C(24)	1361(4)	279(3)	−182(3)	56(2)
O(10a)	5801(12)	1781(9)	1701(7)	18(4)
O(10)	5866(3)	1561(3)	1399(2)	33(2)
C(25)	6389(4)	1087(3)	1800(2)	35(2)
C(26)	6185(4)	260(3)	1598(3)	58(2)
C(27)	7420(4)	1261(4)	1773(3)	74(3)
C(28)	6057(5)	1178(4)	2375(3)	78(3)
O(11a)	6489(13)	3172(10)	1416(8)	36(5)
O(11)	6106(3)	3028(3)	1764(2)	39(2)
C(29)	6665(4)	3707(3)	1878(2)	37(2)
C(30)	6530(4)	4385(4)	1480(3)	71(3)
C(31)	6302(5)	3932(5)	2428(3)	100(4)
C(32)	7693(4)	3502(4)	1933(3)	69(3)
O(12a)	6434(11)	2020(9)	727(6)	23(4)
O(12)	6702(3)	2676(3)	802(2)	42(2)
C(33)	6954(4)	2514(4)	252(2)	55(2)
C(34)	7894(5)	2861(6)	215(4)	153(5)
C(35)	6940(7)	1698(5)	51(4)	138(5)
C(36)	6293(6)	2980(6)	−87(3)	134(5)
C(37)	3670(3)	917(3)	1193(2)	27(2)
C(38)	3527(4)	32(3)	1108(2)	37(2)
C(39)	4284(3)	1254(3)	264(2)	29(2)
C(40)	4018(3)	641(3)	−170(2)	37(2)
C(41)	3893(4)	4084(3)	1580(2)	55(2)
C(42)	3854(5)	4946(4)	1749(3)	90(3)
C(43)	3693(5)	4387(3)	581(3)	70(3)
C(44a)	4584(8)	4513(7)	385(5)	53(5)
C(44b)	3325(10)	5126(7)	557(6)	77(6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

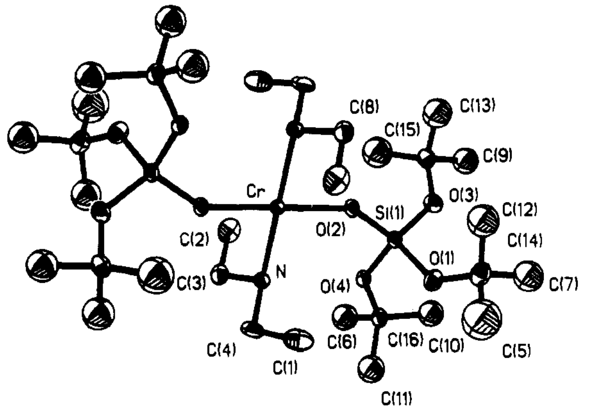

Figure 1. ORTEP view of $Cr[OSi(O^tBu)_3]_2(NHEt_2)_2$ (**1**). The atoms are drawn with 30% probability thermal ellipsoids.

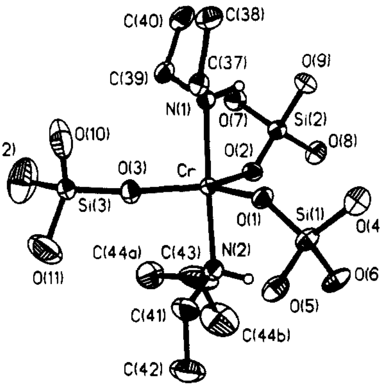

Figure 2. ORTEP view of $Cr[OSi(O^tBu)_3]_3(NHEt_2)_2$ (**2**) showing the disordered, half-atom occupancies for C(44). The *tert*-butyl groups were omitted for clarity. The atoms are drawn with 50% probability thermal ellipsoids.

sponding distances in **1** (by only ca. 0.04 Å for Cr–N; by ca. 0.07 Å for Cr–O), despite the higher coordination number for **2**. Note that the Cr–O distances for **2** (1.879(3), 1.899(3), and 1.891(3) Å) are longer than those reported for $LiCr(OCH^tBu_2)_4(THF)$ (1.823(4) Å) and $Cr(OCH^tBu_2)_4$ (1.771(3) Å).[18] Finally, considerable flexibility in the steric properties of the tri-*tert*-butoxysiloxy ligands is indicated by the Cr–O–Si angles in **2**, which vary from 147.0(2) to 161.7(2)°.

Attempts to obtain $Cr–OSi(O^tBu)_3$ derivatives from Cr(IV) precursors have resulted in only reduced Cr products. From the results described here, it appears that $Cr[OSi(O^tBu)_3]_4$, unlike the analogous titanium(IV) complex $Ti[OSi(O^tBu)_3]_4$,[3] may be unstable. Whereas the reaction of $Cr(NEt_2)_4$ with $HOSiEt_3$ produces the tetravalent siloxide $Cr(OSiEt_3)_4$, the analogous reaction involving $HOSi(O^tBu_3)_3$ has so far afforded only Cr(II) and Cr(III) siloxide complexes. Our exploration of synthetic routes to tri-*tert*-butoxysiloxide complexes of chromium are continuing.

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Supplementary Material Available: Tables giving crystal data and details of the structure determinations, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (14 pages). Ordering information is given on any current masthead page.

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[18] Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Chem. Commun.* **1980**, 1863.