

## Synthesis, Structure, and Homogeneous Catalytic Activity of the Novel (Cyclosiloxy)oxovanadium(IV) complex $\text{VO}\{\text{O}(\text{SiPh}_2\text{O})_2\}_2 \cdot \mu\text{-(Li(THF)}_2)_2$

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# Synthesis, Structure, and Homogeneous Catalytic Activity of the Novel (Cyclosiloxy)oxovanadium(IV) Complex VO{O(SiPh<sub>2</sub>O)<sub>2</sub>}<sub>2</sub>-μ-(Li(THF)<sub>2</sub>)<sub>2</sub>

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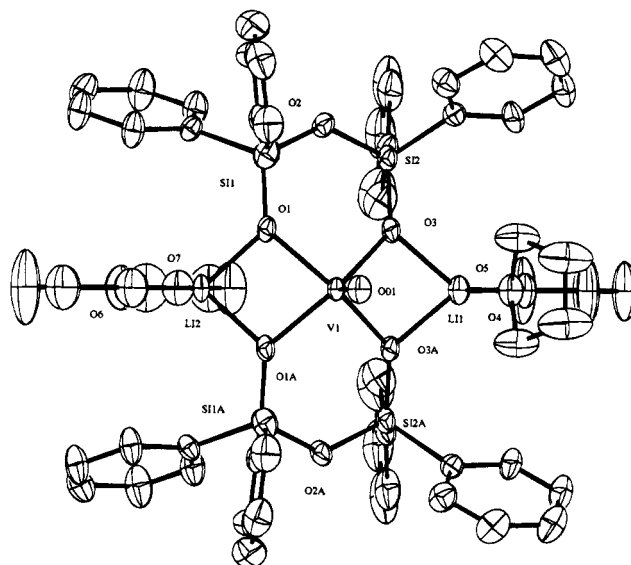
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**Summary:** Treatment of VCl<sub>4</sub> with 3 molar equiv of the lithium compound [O(SiPh<sub>2</sub>OLi)<sub>2</sub>·2THF] gave the oxovanadium(IV) cyclosiloxane [VO{O(SiPh<sub>2</sub>O)<sub>2</sub>}<sub>2</sub>-μ-(Li(THF)<sub>2</sub>)<sub>2</sub>·toluene, **1**·toluene. Analogous reactions with the sodium compound [O(SiPh<sub>2</sub>ONa)<sub>2</sub>·2THF] however led only to intractable mixtures. Compound **1** is to our knowledge the first V(IV) metallasiloxane and was characterized spectroscopically by IR, UV/vis, ESR, and **1**·toluene was characterized by a single-crystal X-ray study. It is an active precatalyst, in conjunction with AlMe<sub>3</sub>, for the polymerization of ethylene and a moderate catalyst for the polymerization of propylene.

Vanadium chloride and oxochloride compounds in various oxidation states have long been recognized as precatalysts, in conjunction with *σ*-organometal compounds for the polymerization of olefins.<sup>1</sup> Active vanadium catalysts having oxidation states II, III, and IV have been suggested in various different studies where oxovanadium(V) halides were the starting material. Low-valent supported vanadium complexes have also been investigated.<sup>2</sup> However vanadium(V)-containing silsesquioxanes have recently been proposed as models for silica-supported vanadium catalyst systems.<sup>3</sup> These complexes are moderate catalysts for olefin polymerization in conjunction with 1 molar equivalent of AlMe<sub>3</sub>. Compelling evidence for an active site involving vanadium(V) was presented for these systems.

A number of vanadium(V) siloxides are known, eg. [VO(c-C<sub>6</sub>H<sub>11</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>12</sub>]<sub>2</sub>,<sup>3</sup> VO(OSiPh<sub>3</sub>)<sub>3</sub>,<sup>4</sup> and [V(O)ClO<sub>2</sub>Si-Bu<sub>2</sub>]<sub>3</sub>,<sup>5</sup> and all of these have tetrahedral geometry around the central metal atom. Reports of V(IV) siloxides are restricted to V(OSiPh<sub>3</sub>)<sub>4</sub>,<sup>6</sup> where the characterization is based on elemental analysis, and a recent mention that the compound VO(OSiPh<sub>3</sub>)<sub>2</sub> has been synthesized.<sup>7</sup> Compound **1** therefore would appear to be the first well-characterized example of a V(IV) siloxide.

**Synthesis.** Compound **1** was the unexpected product isolated as blue-green crystals from the toluene soluble reaction products of VCl<sub>4</sub> and the lithium compound



**Figure 1.** Molecular structure of compound **1** with thermal ellipsoids drawn to include 20% electron density. Selected bond lengths (Å) and angles (deg) are as follows: V(1)–O(01) = 1.579(7), V(1)–O(1) = 1.981(5), V(1)–O(3) = 1.997(5), Si(1)–O(1) = 1.591(5), Si(1)–O(2) = 1.632(5), Si(2)–O(2) = 1.630(5), Si(2)–O(3) = 1.601(5), Si–Cav = 1.880(4), Li(1)–O(3) = 1.95(2), Li(1)–O(4) = 2.00(2), Li(1)–O(5) = 1.96(2), Li(2)–O(1) = 1.921(12), Li(2)–O(7) = 1.96(2), O(01)–V(1)–O(1) = 106.2(3), O(1)–V(1)–O(1A) = 81.2(3), O(01)–V(1)–O(3) = 107.0(3), O(1A)–V(1)–O(3) = 146.8(2), O(1)–V(1)–O(3) = 90.1(2), O(3)–V(1)–O(3A) = 79.8(3), O(1)–Si(1)–O(2) = 111.4(3), O(3)–Si(2)–O(2) = 112.4(3), O–Si–Cav = 109.0(3), C–Si–Cav = 108.0(2), Si(1)–O(2)–Si(2) = 130.1(3), Si(1)–O(1)–V(1) = 134.0(3), Si(2)–O(3)–V(1) = 135.6(3), Li(1)–O(3)–V(1) = 92.1(5), O(3)–Li(1)–O(3A) = 82.3(8), O(3)–Li(1)–O(5) = 113.1(7), O(3)–Li(1)–O(4) = 124.3(7), O(5)–Li(1)–O(4) = 100.2(9), O(1)–Li(2)–O(1A) = 84.4(7), O(1)–Li(2)–O(6) = 118.7(8), O(1)–Li(2)–O(7) = 111.3(8), O(6)–Li(2)–O(7) = 110.4(8).

[O(SiPh<sub>2</sub>OLi)<sub>2</sub>·2THF] (1:3 molar ratio). The expected lithium-bridged tris-chelated product, of the type, [V{O(SiPh<sub>2</sub>O)<sub>2</sub>}<sub>3</sub>-μ-(Li(THF)<sub>2</sub>)<sub>2</sub>], analogue of the related zirconium and hafnium tris-chelate,<sup>8</sup> was not observed. However, in addition to **1** colorless crystals of the cyclic trisiloxane [Ph<sub>2</sub>SiO]<sub>3</sub> were isolated. The formation of **1** probably involves oxygen abstraction by vanadium from a coordinated siloxy fragment.

**X-ray Crystal Structure of 1·toluene.** The structure of **1** is shown in Figure 1, and the crystal structure data for **1**·toluene are collated in Table 1. Atomic coordinates and selected bond lengths and angles are given in

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Table 1. Crystal Data and Structure Refinement

identification code	SS87
empirical formula	C <sub>71</sub> H <sub>80</sub> Li <sub>2</sub> O <sub>11</sub> Si <sub>4</sub> V
fw	1286.53
<i>T</i>	293(2) K
wavelength	0.710 69 Å
cryst system	monoclinic
space group	<i>Cm</i>
unit cell dimens	<i>a</i> = 21.770(5) Å; $\alpha$ = 90° <i>b</i> = 16.566(5) Å; $\beta$ = 105.50(5)° <i>c</i> = 10.501(3) Å; $\gamma$ = 90°
<i>V</i>	3649(2) Å <sup>3</sup>
<i>Z</i>	2
density (calculated)	1.171 g/cm <sup>3</sup>
abs coeff	0.256 mm <sup>-1</sup>
<i>F</i> (000)	1358
cryst size	0.25 × 0.35 × 0.30 mm
$\theta$ range for data collen	1.57–24.98°
index ranges	–24 ≤ <i>h</i> ≤ 25, 0 ≤ <i>k</i> ≤ 19, –12 ≤ <i>l</i> ≤ 1
reflens collod	3631
indpt reflens	3534 [ <i>R</i> (int) = 0.0097]
refinement method	full-matrix least squares on <i>F</i> <sup>2</sup>
data/restraints/params	3534/2/375
goodness-of-fit on <i>F</i> <sup>2</sup>	0.853
final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0667, <i>R</i> <sub>w</sub> 2 = 0.1756
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0976, <i>R</i> <sub>w</sub> 2 = 0.1884
absolute structure param	0.06(5)
extinction coeff	0.0032(8)
largest diff peak and hole	0.643 and –0.303 e·Å <sup>-3</sup>
radiation monochromator	graphite
radiation source	fine-focus sealed tube
measurement device	Enraf-Nonius CAD4 4-circle diffractometer
measurement method	2 $\theta$ / $\omega$
abs corr type	empirical
abs corr transm factor	90.87–99.98%

Tables 2 and 3, respectively. Compound 1 closely resembles that of the famous VO(acac)<sub>2</sub> compound<sup>9</sup> with the oxyanions of the chelating disiloxanediolate ligands forming the base of a square pyramid. The vanadium atom sits slightly above the basal plane defined by the four oxyanions. The 6-membered vanadasiloxane rings are roughly planar but not coplanar, with the angle between the planes of the rings being 153° (the angle between the planes defined by the atoms of the disiloxanediolate excluding the vanadium is 163°). The *trans*-(Si)OVO(Si) angles are 146.6°. These features of the molecular structure mirror those of related vanadium acetylacetonate rings in VO(acac)<sub>2</sub> where the angle between the acetylacetonate skeletons is 162° and the *trans*-(C)OVO(C) angles are 145.5(3) and 149.6(3)°. The two halves of molecule 1 are related by a mirror plane containing the two bridging lithium atoms and the VO unit. However while Li(1) and the vanadium atom are collinear within this plane, Li(2) is deflected some 1.34 Å from linearity in the direction of the vacant sixth coordination site. Furthermore, while the coordinated THF molecules on Li(1) lie on either side of the central basal plane with that distal from the vanadyl oxygen in the mirror plane and that proximal to the vanadyl oxygen bisected by the mirror plane, both THF molecules on Li(2) lie on one side of the central basal plane

Table 2. Atomic Coordinates (×10<sup>4</sup>) and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup> × 10<sup>3</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
V(1)	1(1)	0	1(1)	49(1)
Si(1)	–751(1)	1737(1)	–666(2)	56(1)
Si(2)	568(1)	1707(1)	–930(2)	59(1)
O(1)	–708(2)	779(3)	–595(5)	60(1)
O(2)	–107(2)	2130(3)	–923(6)	68(1)
O(3)	594(2)	773(3)	–524(5)	60(1)
O(01)	175(4)	0	1560(7)	68(2)
Li(1)	1292(9)	0	–100(18)	67(5)
Li(2)	–1348(7)	0	–1404(18)	65(4)
C(1)	–862(2)	2205(3)	880(4)	66(2)
C(2)	–824(3)	1753(3)	2014(5)	80(2)
C(3)	–866(3)	2134(5)	3168(4)	109(3)
C(4)	–947(4)	2966(5)	3187(6)	117(4)
C(5)	–986(4)	3417(3)	2052(8)	115(4)
C(6)	–943(3)	3037(3)	899(6)	90(3)
C(7)	–1439(2)	2072(4)	–2076(4)	61(2)
C(8)	–2051(2)	2057(5)	–1908(5)	94(3)
C(9)	–2566(2)	2302(5)	–2931(6)	108(4)
C(10)	–2470(2)	2562(5)	–4121(5)	107(3)
C(11)	–1858(3)	2576(5)	–4289(5)	121(4)
C(12)	–1343(2)	2332(5)	–3267(5)	95(3)
C(13)	1214(2)	2285(3)	263(5)	64(2)
C(14)	1838(2)	2251(4)	168(6)	88(3)
C(15)	2324(2)	2622(5)	1123(7)	108(4)
C(16)	2185(3)	3026(5)	2173(6)	125(5)
C(17)	1561(4)	3059(4)	2267(6)	117(4)
C(18)	1075(2)	2689(4)	1312(6)	90(3)
C(19)	643(3)	1823(4)	–2665(5)	77(2)
C(20)	613(4)	1154(4)	–3479(7)	119(4)
C(21)	635(5)	1255(7)	–4780(7)	173(8)
C(22)	687(4)	2024(8)	–5268(6)	163(8)
C(23)	718(4)	2693(6)	–4454(9)	171(9)
C(24)	696(3)	2592(4)	–3153(8)	126(5)
O(4)	2023(4)	0	–921(10)	98(3)
C(25)	2056(9)	0	–2184(17)	224(18)
C(26)	2726(11)	0	–2155(27)	252(21)
C(27)	3075(9)	0	–931(24)	200(14)
C(28)	2639(9)	0	–58(28)	241(19)
O(5)	1757(4)	0	1776(8)	87(2)
C(29)	1780(9)	688(8)	2630(12)	142(6)
C(30)	2230(13)	434(9)	3937(16)	211(10)
O(6)	–2154(4)	0	–917(9)	94(3)
C(31)	–2158(10)	0	430(19)	132(7)
C(32)	–2875(11)	0	384(27)	163(9)
C(33)	–3206(12)	0	–943(37)	303(29)
C(34)	–2799(8)	0	–1844(26)	148(8)
O(7)	–1506(5)	0	–3331(9)	106(3)
C(35)	–2046(10)	0	–4369(19)	159(8)
C(36)	–1738(17)	0	–5555(19)	185(12)
C(37)	–1095(16)	0	–5172(28)	191(12)
C(38)	–942(11)	0	–3734(19)	173(10)
C(1A)	83(19)	5000	–524(39)	228(12)
C(2A)	–109(11)	4249(13)	–1307(24)	192(7)
C(3A)	–433(13)	4353(16)	–2412(29)	217(9)
C(4A)	–733(24)	5000	–3246(53)	368(19)
C(5A)	436(26)	4732(30)	738(59)	319(24)

<sup>a</sup> *U* (eq) is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

distal from the vanadyl oxygen and in the mirror plane of the molecule. There is no obvious reason for this break in the symmetry of the molecule; for example, there are no short contacts between the vanadium atom and the hydrogens of the THF extending into the space generated by the vacant sixth coordination site. Nor are there any short contacts between the vanadyl oxygen and the hydrogens of the proximal THF attached to Li(1). This departure from the otherwise totally centrosymmetric relationships within the molecule is presumably brought about by packing forces. However it is clear that the presence of the THF-solvated bridging lithiums in compound 1 imparts major structural and reactivity (see below) differences compared to VO(acac)<sub>2</sub>.

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Table 3. Selected Bond Lengths (Å) and Angles (deg)<sup>a</sup>

V(1)—O(01)	1.579(7)	Li(2)—O(7)	1.96(2)
V(1)—O(1) <sup>i</sup>	1.981(5)	O(4)—C(25)	1.35(2)
V(1)—O(1)	1.981(5)	O(4)—C(28)	1.40(2)
V(1)—O(3)	1.997(5)	C(25)—C(26)	1.45(3)
V(1)—O(3) <sup>i</sup>	1.997(5)	C(26)—C(27)	1.31(3)
Si(1)—O(1)	1.591(5)	C(27)—C(28)	1.48(3)
Si(1)—O(2)	1.632(5)	O(5)—C(29)	1.443(13)
Si(1)—C(1)	1.873(4)	O(5)—C(29) <sup>i</sup>	1.443(13)
Si(1)—C(7)	1.887(4)	C(29)—C(30)	1.52(2)
Si(2)—O(3)	1.601(5)	C(30)—C(30) <sup>i</sup>	1.44(3)
Si(2)—O(2)	1.630(5)	O(6)—C(31)	1.42(2)
Si(2)—C(13)	1.877(5)	O(6)—C(34)	1.48(2)
Si(2)—C(19)	1.883(5)	C(31)—C(32)	1.55(3)
O(1)—Li(2)	1.921(12)	C(32)—C(33)	1.39(4)
O(3)—Li(1)	1.95(2)	C(33)—C(34)	1.46(3)
Li(1)—O(3) <sup>i</sup>	1.95(2)	O(7)—C(35)	1.37(2)
Li(1)—O(5)	1.96(2)	O(7)—C(38)	1.40(2)
Li(1)—O(4)	2.00(2)	C(35)—C(36)	1.56(3)
Li(2)—O(1) <sup>i</sup>	1.921(12)	C(36)—C(37)	1.35(4)
Li(2)—O(6)	1.96(2)	C(37)—C(38)	1.46(3)
O(01)—V(1)—O(1) <sup>i</sup>	106.2(3)	O(5)—Li(1)—O(4)	100.2(9)
O(01)—V(1)—O(1)	106.2(3)	O(1)—Li(2)—O(1) <sup>i</sup>	84.4(7)
O(1) <sup>i</sup> —V(1)—O(1)	81.2(3)	O(1)—Li(2)—O(6)	118.7(8)
O(01)—V(1)—O(3)	107.0(3)	O(1) <sup>i</sup> —Li(2)—O(6)	118.7(8)
O(1) <sup>i</sup> —V(1)—O(3)	146.8(2)	O(1)—Li(2)—O(7)	111.3(8)
O(1)—V(1)—O(3)	90.1(2)	O(1) <sup>i</sup> —Li(2)—O(7)	111.3(8)
O(01)—V(1)—O(3) <sup>i</sup>	107.0(3)	O(6)—Li(2)—O(7)	110.4(8)
O(1) <sup>i</sup> —V(1)—O(3) <sup>i</sup>	90.1(2)	C(25)—O(4)—C(28)	110.0(14)
O(1)—V(1)—O(3) <sup>i</sup>	146.8(2)	C(25)—O(4)—Li(1)	132.9(12)
O(3)—V(1)—O(3) <sup>i</sup>	79.8(3)	C(28)—O(4)—Li(1)	117.0(14)
O(1)—Si(1)—O(2)	111.4(3)	O(4)—C(25)—C(26)	107(2)
O(1)—Si(1)—C(1)	113.1(3)	C(27)—C(26)—C(25)	110(2)
O(2)—Si(1)—C(1)	107.1(3)	C(28)—C(27)—C(26)	108(2)
O(1)—Si(1)—C(7)	110.8(3)	C(27)—C(28)—O(4)	105(2)
O(2)—Si(1)—C(7)	106.9(3)	C(29)—O(5)—C(29) <sup>i</sup>	104.4(12)
C(1)—Si(1)—C(7)	107.4(2)	C(29)—O(5)—Li(1)	123.2(6)
O(3)—Si(2)—O(2)	112.4(3)	C(29) <sup>i</sup> —O(5)—Li(1)	123.2(6)
O(3)—Si(2)—C(13)	110.4(3)	O(5)—C(29)—C(30)	104.5(11)
O(2)—Si(2)—C(13)	107.1(3)	C(30) <sup>i</sup> —C(30)—C(29)	106.1(7)
O(3)—Si(2)—C(19)	110.5(3)	C(31)—O(6)—C(34)	114(2)
O(2)—Si(2)—C(19)	105.8(3)	C(31)—O(6)—Li(2)	120.4(12)
C(13)—Si(2)—C(19)	110.5(3)	C(34)—O(6)—Li(2)	126.0(13)
Si(1)—O(1)—Li(2)	128.5(4)	O(6)—C(31)—C(32)	104(2)
Si(1)—O(1)—V(1)	134.0(3)	C(33)—C(32)—C(31)	106(2)
Li(2)—O(1)—V(1)	96.6(4)	C(34)—C(33)—C(32)	114(2)
Si(1)—O(2)—Si(2)	130.1(3)	C(33)—C(34)—O(6)	102(2)
Si(2)—O(3)—Li(1)	131.7(5)	C(35)—O(7)—C(38)	113(2)
Si(2)—O(3)—V(1)	135.6(3)	C(35)—O(7)—Li(2)	134.1(13)
Li(1)—O(3)—V(1)	92.1(5)	C(38)—O(7)—Li(2)	112.7(11)
O(3)—Li(1)—O(3) <sup>i</sup>	82.3(8)	O(7)—C(35)—C(36)	100(2)
O(3)—Li(1)—O(5)	113.1(7)	C(37)—C(36)—C(35)	113(2)
O(3) <sup>i</sup> —Li(1)—O(5)	113.1(7)	C(36)—C(37)—C(38)	104(3)
O(3)—Li(1)—O(4)	124.3(7)	O(7)—C(38)—C(37)	110(2)
O(3) <sup>i</sup> —Li(1)—O(4)	124.3(7)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: (i)  $x, -y, z$ ; (ii)  $x, -y + 1, z$ .

The vanadyl oxygen distance in **1** of 1.579(7) Å is similar to that in VO(acac)<sub>2</sub> (1.571(10) Å) (and also to that in a number oxovanadium(V) compounds, e.g. 1.564(8) Å in [VO(c-C<sub>6</sub>H<sub>11</sub>)<sub>7</sub>Si<sub>7</sub>O<sub>12</sub>]<sub>2</sub>,<sup>4</sup> 1.572(2) Å in VO(OSiPh<sub>3</sub>)<sub>3</sub>,<sup>3</sup> and 1.589(11) Å in [V(O)Cl(O<sub>2</sub>SiBu<sub>t</sub>)<sub>3</sub>]<sub>3</sub>.<sup>5</sup> The other V—O distances in **1**, VO(Si)(av) (1.989(5) Å), and in VO(acac)<sub>2</sub>, VO(C)(av) (1.973 Å) are very similar. The bond distances VO(Si)(av) (1.989(5) Å) and SiO(V)(av) (1.596(5) Å) in **1** are significantly longer and shorter respectively than those in V(V) siloxide compounds.<sup>3–5</sup> These differences in bond distances between **1** and the vanadium(V) siloxy compounds are most likely attributable to **1** having different stereochemistry from the V(V) group of compounds, but may also reflect greater covalency in the VO(Si) bonds of the higher oxidation state compounds. The SiO(V) distances in **1** are shorter than the SiO(Si) distances, a feature noted in a range of

similar spirocyclic compounds.<sup>10</sup> The small SiOSi angles are also typical of other compounds with 6-membered metallasiloxane rings that we have characterized.<sup>10</sup>

**Spectroscopic Features of 1. ESR.** The spectrum was recorded on toluene solutions of **1** at room temperature. An eight-line spectrum typical of d<sup>1</sup>, V(IV) complexes was observed (<sup>51</sup>V has nuclear spin  $I = 7/2$ ). Values for  $g_{av}$  (2.015) and  $A$  (99.15 G) are close to those found in a range of oxovanadium(IV) complexes.<sup>11</sup>

**UV/Visible.** The spectra recorded in toluene solutions showed the predicted three bands for the d<sup>1</sup> ion in a ligand field of essentially C<sub>4v</sub> symmetry, e.g. (I) 12 654 cm<sup>-1</sup> (112) (b<sub>2</sub>-e), (II) 16 155 cm<sup>-1</sup> (70) (b<sub>2</sub>-b<sub>1</sub>), and (III) 24 576 cm<sup>-1</sup> (43) (b<sub>2</sub>-a<sub>1</sub>).<sup>11,12,13</sup> The observed energies of these transitions and values of extinction coefficients are within expected ranges. When spectra were recorded on solutions containing pyridine in large relative molar excess of **1**, the original three bands were observed but with smaller extinction coefficients, i.e. (I) 12 484 cm<sup>-1</sup> (24), (II) 16 025 cm<sup>-1</sup> (13), and (III) 25 252 cm<sup>-1</sup> (26.5). Weak coordination of a sixth ligand is known to cause a 100 nm shift of transition II to lower energy in VO(acac)<sub>2</sub> and related complexes.<sup>13</sup> It would appear that there is no coordination of pyridine at the vacant site in compound **1**. It seems likely that access to the sixth coordination site is restricted by the protrusion of one of the lithium-coordinated THF groups into this space. The reduction in band intensities may reflect a small change in the coordination environment of the vanadium resulting from replacement of some coordinated THF at the lithium sites with pyridine.

**IR.** The main diagnostic feature of the IR spectrum is associated with  $\nu_{v=0}$  stretching frequency which occurs at 992 cm<sup>-1</sup>, close to that observed for the related VO(acac)<sub>2</sub> complex.

**Homogeneous Catalysis.** The homogeneous and heterogeneous catalytic activity of vanadium complexes in olefin polymerization processes have been extensively investigated. These investigations often implicate low oxidation state vanadium among possible active sites, but recent work by Feher and Blanski has shown that vanadium(V) may also be important. For the catalytic studies reported here the vanadium precatalyst mixture consisted of a toluene solution of compound **1**, i.e. V(IV) and Me<sub>3</sub>Al in 1:10 molar ratio. This catalyst system gelled after 30 s under ethylene at 35 bar. The polymer samples obtained were examined by DSC but were too insoluble (even in hot 1,2-dichlorobenzene), probably because of exceptionally high molecular weight, to carry out GPC analysis. Compound **1** was also found to be a moderate cocatalyst for propylene oligomerization.

In an attempt to investigate the nature of the vanadium species in the precatalyst mixture a sample of the brown tar obtained after the toluene and any unreacted Me<sub>3</sub>Al had been removed under vacuum was redissolved in toluene. This solution was found to be catalytically active for the polymerization of ethene and was also examined by UV/vis and ESR spectroscopy. The UV/vis spectrum displayed sharp bands at 373, 382, and 456 nm with a long tail stretching toward the 800 nm region. This spectrum suggested a range of oxidation

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states. The room-temperature ESR spectrum however displayed only the eight-line pattern of V(IV) with  $g_{av} = 1.997$  and  $A = 62.26$  G. The much smaller  $A$  value observed following addition of  $\text{Me}_3\text{Al}$  to toluene solutions of **1** suggests a change to a more covalent ligand environment compared to that in **1**. Further studies on this and related group 5 catalyst systems are in progress, but it is clear that the catalyst mixture contains a vanadium(IV) species which is very different from the starting compound **1**. Further work is in progress.

### Experimental Section

All manipulations were carried out in an atmosphere of purified nitrogen using standard Schlenk techniques. The chemicals  $\text{VCl}_4$  and  $\text{Me}_3\text{Al}$  (Aldrich) and ethylene were used as supplied. Propylene was dried by passage through neat  $\text{Et}_3\text{Al}$  prior to use. Spectrometer used were as follows: IR, PE 1720X; UV/vis Hitachi U-2000; ESR, Bruker 200 D X band.

**Preparation of  $\text{VO}\{\text{O}(\text{SiPh}_2\text{O})_2\}_2\text{-}\mu\text{-(Li(THF)}_2\text{)-toluene, 1-toluene}$ .** To a stirred solution of  $\text{O}[\text{SiPh}_2\text{OLi(THF)}]_2$  (7.24 mmol) in THF at 0 °C was added, dropwise, neat  $\text{VCl}_4$  (0.26  $\text{cm}^3$ , 0.472 g, 2.44 mmol). The original colorless solution went from yellow to dark orange and finally to dark green. After the solution was stirred overnight the volatiles were removed under vacuum and toluene was added to the blue-green solid residue. The toluene soluble products were filtered off, and the resultant blue-green solution was concentrated to 15  $\text{cm}^3$ . Blue-green crystals (1.74 g, 55.4%), mp 163–165 °C, were deposited from the toluene solution at room temperature. Anal. Found: C, 63.06; H, 6.10. Calcd. for  $\text{C}_{71}\text{H}_{80}\text{Li}_2\text{O}_{11}\text{Si}_4\text{V}$ , **1-toluene**: C, 66.3; H, 6.2. Calcd. for  $\text{C}_{64}\text{H}_{72}\text{Li}_2\text{O}_{11}\text{Si}_4\text{V}$ , **1**: C, 64.35; H, 6.08. ESR:  $g_{av}$ , 2.015,  $A$ , 99.15 G. UV/vis: (I) 12 654  $\text{cm}^{-1}$  (112) ( $b_2\text{-e}$ ); (II) 16 155 (70) ( $b_2\text{-b}_1$ ); (III) 24 576  $\text{cm}^{-1}$  (43) ( $b_2\text{-a}_1$ ). IR:  $\nu_{\text{v=O}}$  992  $\text{cm}^{-1}$ .  $\mu_{\text{eff}}$ (Evans method) = 1.63  $\mu_B$ .

**Polymerization Reactions. Ethylene Polymerization.** A precatalyst mixture consisting of **1-toluene** (0.021 g, 0.0163 mmol) in toluene (20  $\text{cm}^3$ ) and  $\text{Me}_3\text{Al}$  (0.09  $\text{cm}^3$  of a 2 mol  $\text{dm}^{-3}$  solution in toluene) was pressurized to 35 bar with ethylene gas (used as supplied without further purification) at room temperature. The reaction was allowed to proceed for 30 s (after which the reaction mixture gelled and magnetic stirring ceased). The DSC melting curve of the polyethylene obtained

(5.37 g) showed onset of melting  $T_m$  at 131.76 °C (typical of high density PE). The sample was too insoluble (even in hot 1,2-dichlorobenzene), probably because of exceptionally high molecular weight, to carry out GPC analysis. Potential catalytic activity is estimated at  $2.16 \times 10^6$  g of PE (g of V) $^{-1}$  h $^{-1}$ .

**Propylene Polymerization.** A catalyst mixture of **1** (0.024 g, 0.019 mmol) in toluene (250  $\text{cm}^3$ ),  $\text{Me}_3\text{Al}$  (5.0  $\text{cm}^3$ , of a 2 M solution in toluene; 10 mmol), and propylene at 5.8 bar was held at 40 °C for 0.5 h. The resultant oligomeric polypropylene (0.8 g) had  $M_w = 408$  and  $M_n = 333$ . Catalytic activity is estimated at  $1.56 \times 10^3$  g of PP (g of V) $^{-1}$  h $^{-1}$ .

**X-ray Crystallography.** Crystal data for compound **1-toluene**:  $\text{C}_{71}\text{H}_{80}\text{Li}_2\text{O}_{11}\text{Si}_4\text{V}$ ,  $M = 1286.53$ , monoclinic,  $a = 21.770(5)$  Å,  $b = 16.566(5)$  Å,  $c = 10.501(3)$  Å,  $\beta = 105.50(5)^\circ$ ,  $V = 3649(2)$  Å $^3$ ,  $Z = 2$ , space group  $Cm$ ,  $D_c = 1.171$  g  $\text{cm}^{-3}$ ;  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 0.256$   $\text{mm}^{-1}$ ,  $F(000) = 1358$ . Data were recorded on a crystal (0.25  $\times$  0.35  $\times$  3.0 mm) sealed in a glass capillary under nitrogen with a CAD4 diffractometer operating in the  $\omega/2\theta$  scan mode. The structure was solved by standard heavy-atom techniques and refined by least squares using SHELX-93,<sup>14</sup> with phenyl groups treated as rigid hexagons ( $\text{C-C} = 1.395$  Å,  $\text{C-C-C} = 120^\circ$ ) and with inclusion of hydrogen atoms at fixed positions ( $\text{C-H} = 0.96$  Å). A total of 3631 reflections were measured of which 3534 were unique. The final  $R$  indices were  $R1 = 0.0667$ ,  $Rw2 = 0.01756$  for  $[I > 2\sigma(I)]$  and  $R1 = 0.0976$ ,  $Rw2 = 0.1884$  (all data) for 375 parameters.  $R1 = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $Rw2 = (\sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4])^{1/2}$ .

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**Supplementary Material Available:** Tables of anisotropic thermal parameters, final fractional atomic coordinates and  $U(\text{eq})$  values for hydrogen atoms, and bond lengths and angles and text describing SHELXL-93 (9 pages). Ordering information is given on any current masthead page.

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