Lewis Acid Adducts of Oxovanadium(V) Alkyl and Triphenylsiloxy Complexes: Synthesis, Characterization, and Reactivity toward Ethylene

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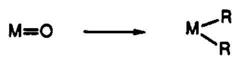
Summary: The reaction of triphenylsilanol with $V(O)(CH_2SiMe_3)_3$ (**2**) *gives* $V(O)(CH_2SiMe_3)_2(OSiPh_3)$ (**3**), $V(O)(CH_2SiMe_3)(OSiPh_3)_2$ (**4**), *and* $V(O)(OSiPh_3)_3$ (**5**), *each of which can be isolated in good yield under the appropriate reaction conditions. The reactions of* **2–5** *with* $Al(CH_2SiMe_3)_3$ *produce dark maroon solutions. Multinuclear NMR data—especially* ^{17}O *and* ^{51}V *NMR data—indicate that the product formed in each case is a Lewis adduct derived from coordination of Al to the terminus of the VO group, suggesting that the oxo ligand is the most Lewis basic site in* **2–5**. *Preliminary reactivity studies indicate that coordination of* $Al(CH_2SiMe_3)_3$ *to the oxo ligand facilitates insertion of ethylene into the V–C bonds of* **2–4**.

Introduction

Complexes containing terminal oxo ligands are used extensively for the preparation of transition-metal catalysts.[1] In some cases, such as olefin metathesis catalysis, the oxo ligand appears to play the role of a spectator and it is not directly involved in catalytically relevant reactions.[2] In other cases, such as metal–oxo-catalyzed rearrangements of propargylic and allylic alcohols,[3] oxo ligands are active participants in the catalytic process; they are consumed and re-formed during the catalytic cycle. In most cases, however, oxo complexes originally present as the precatalyst react via poorly defined pathways to produce small amounts of unidentified, highly active catalytic species. The Phillips catalyst[4] for ethylene polymerization is a particularly good example of this situation, where monodisperse silica-supported chromates can be reduced by a variety of methods to produce non-oxo-containing Cr(II) surface complexes, which initiate olefin polymerization by a currently unknown process.

The "activation" of metal–oxo precatalysts frequently requires the addition of main-group-metal alkyls to produce metal–carbon bonds. Reductive monoalkylation (reaction 1a), deoxygenative dialkylation (reaction 1b), and deoxygenative carbene formation (reaction 1c) are three of the many reactions which could conceivably produce metal–carbon bonds, but little is known with certainty about the mechanisms for any of these transformations. Even the conceptually simplest reaction between a metal–oxo complex and a Lewis acidic main-group-metal alkyl complex—formation of a Lewis acid/base adduct (reaction 1d)—has received surprisingly little attention.[5]

$$M{=}O \longrightarrow M{-}R \qquad (1a)$$

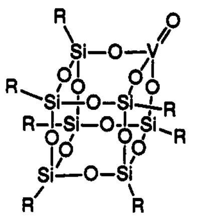


(1b)

(1c)

$$M{=}O \longrightarrow M{=}O{-}M'R_n \qquad (1d)$$

Our recent discovery that vanadate **1**[6] reacts with trialkylaluminum reagents to produce catalysts for the polymerization of olefins prompted us to examine the reactions of stoichiometrically simpler oxovanadium(V) complexes with alkylaluminum reagents.



1 (R = c-C_6H_{11})

In this paper we report that the initial product in all cases from the reaction of $V(O)(CH_2SiMe_3)_n(OSiPh_3)_{3-n}$ (n = 0–3) with $Al(CH_2SiMe_3)_3$ is a Lewis adduct formed by coordination of aluminum to the oxo ligand. The synthesis, spectroscopic characterization, and reactivity of these Lewis adducts—including their chemistry with ethylene—are discussed.

Results and Discussion

Synthesis and Characterization of $V(O)(CH_2SiMe_3)_n(OSiPh_3)_{3-n}$ (n = 0–3). Prior to the start of our work there were many examples of stable trialkyl-

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[1] For a review of oxo complexes and their use in catalysis see: Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

[2] Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* 1982, *104*, 448–56.

[3] (a) Belgacem, J.; Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* 1992, *114*, 1501–2. (b) Matsubara, S.; Okazoe, T.; Oshima, K.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* 1985, *58*, 844–9. (c) Hosogai, T.; Fujita, Y.; Ninagawa, Y.; Nishida, T. *Chem. Lett.* 1982, 357–60. (d) Chabardes, P.; Kuntz, E.; Varagnat, J. *Tetrahedron* 1977, *33*, 1775–83.

[4] (a) McDaniel, M. P.; Leigh, C. H.; Wharry, S. M. *J. Catal.* 1989, *120*, 170–81. (b) Krauss, H. L. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: New York, 1988; pp 163–8. (c) McDaniel, M. P. *Adv. Catal.* 1985, *33*, 47–98. (d) McDaniel, M. P. In *Transition Metal Catalyzed Polymerization; Part B*, Quirk, R. P., Ed.; Harwood Academic Press: New York, 1983; Part B, pp 713–35. (e) Hogan, J. P. *J. Polym. Sci., Polym. Chem. Ed.* 1970, *8*, 2637–52; (f) Woo, T. W.; Woo, S. I. *J. Catal.* 1990, *123*, 215–27.

[5] For examples and discussion of Lewis adducts between neutral oxo complexes and neutral main-group complexes: (a) Fischer, J.; Kress, J.; Osborn, J. A.; Ricard, L.; Wesolek, M. *Polyhedron* 1987, *6*, 1839–42. (b) Kress, J.; Wesolek, M.; Le Ny, J.-P.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* 1981, 1039–40. (c) Nakamura, S.; Dedieu, A. *Nouv. J. Chim.* 1982, *6*, 23–30.

[6] (a) Feher, F. J.; Blanski, R. L. *J. Am. Chem. Soc.* 1992, *114*, 5886. (b) Feher, F. J.; Walzer, J. F.; Blanski, R. L. *J. Am. Chem. Soc.* 1991, *113*, 3618–9.

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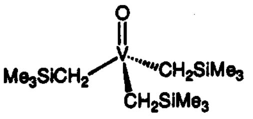
and trisilylvanadate complexes (e.g., $V(O)(OBu\text{-}t)_3$[7a] and $V(O)(OSiPh_3)_3$[7b,c]), but there were only isolated reports of stable oxovanadium(V) alkyl complexes. Wilkinson[8a] reported the synthesis of $V(O)(CH_2SiMe_3)_3$ (2) in 1972, and Thiele[8b] and Preuss[8c] later described the preparation of several oxovanadium complexes containing alkyl and alkoxy groups as basal ligands, but a well-characterized series of complexes with the general formula $[V(O)R_n(OR')_{3-n}]$ had not been prepared. We therefore focused our initial efforts on synthesizing a complete set of such complexes. Triphenylsiloxy (i.e., Ph_3SiO) and (trimethylsilyl)methyl (i.e., Me_3SiCH_2) ligands were selected for this study because of their relevance to our ongoing efforts to identify the polymerization catalyst obtained from the reaction of 1 with $Al(CH_2SiMe_3)_3$.[6a]

Wilkinson's oxovanadium trialkyl complex 2 reacts rapidly with most small alcohols and silanols above 60 °C to afford good yields of the corresponding vanadate esters $V(O)(OR)_3$. In the case of triphenylsilanol (Ph_3SiOH), however, protonolysis becomes increasingly difficult as Me_3SiCH_2 groups are replaced by Ph_3SiO groups. This provides some degree of control over the extent of protonolysis and has allowed us to prepare oxovanadium complexes containing both Me_3SiCH_2 and Ph_3SiO ligands.



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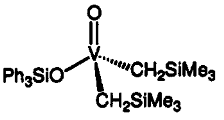

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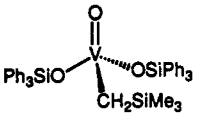

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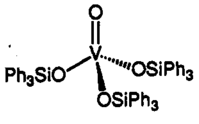

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The reaction of 2 and Ph_3SiOH (1 equiv) in toluene affords a 4:92:4 mixture of unreacted 2, dialkyl complex 3, and monoalkyl complex 4 after 1 h at 40 °C. Both 2 and 3 are soluble in hexane and can be easily separated from 4 by extraction, but unreacted 2 gradually decomposes to a black tar, which cannot be completely removed from 3. The preparation of pure 3 is best accomplished by reacting 2 with more than 1 equiv of Ph_3SiOH and allowing protonolysis to proceed until all 2 is consumed. For example, the reaction of 2 with 2 equiv of Ph_3SiOH under the conditions described above (toluene, 40 °C, 1 h) completely consumes the trialkyl complex to produce 3 and 4 in a 89:11 ratio. Evaporation of the volatiles and extraction of the crude product mixture with hexanes easily separates dialkyl complex 3 from unreacted Ph_3SiOH and the poorly soluble monoalkyl product (4). Evaporation of the hexane extracts (25 °C, 0.1 mTorr) afforded 3 as a lemon yellow oil in 74% yield. This complex has resisted crystallization, and it rapidly darkens upon standing at room temperature, but the product obtained in this fashion is spectroscopically pure (^1H and ^{13}C NMR); it appears to be indefinitely stable at −40 °C.

From a practical standpoint (vide infra), 4 is most conveniently obtained from reactions like the one described above, where 3 is the major product. Although 4 is much less soluble in hexanes than 3, both 3 and 4 are highly soluble in pentane at 25 °C. Extraction of the crude product mixture described above with pentane therefore separates 3 and 4 from the unreacted Ph_3SiOH. Evaporation of the pentane affords a yellow semisolid containing a 60:40 mixture of 3 and 4. Analytically pure 4 can then be obtained as yellow microcrystals (27%) by recrystallizing the remaining residue from toluene/hexane at −40 °C.

Higher yields of 4 can be obtained by allowing the reaction of 2 with 2 equiv of Ph_3SiOH to consume all of the silanol, but the product is invariably contaminated by small amounts of 5. For the reaction of 2 with Ph_3SiOH (2 equiv) in toluene at 40 °C, 3, 4, and 5 are obtained in a ratio of 1:8:1 after all of the silanol is consumed (12 h). The small amount of 3 could be easily removed from the product mixture by washing with hexanes, but the solubility properties of 4 and 5 are similar enough to make the selective crystallization of pure 4 extremely difficult. In most cases, samples of 4 containing less than 5% of 5 can be obtained by recrystallization from toluene/hexane.

Samples containing ^{17}O-enriched oxo groups were synthesized from $V(O)(CH_2SiMe_3)_3$ (23% ^{17}O), which was obtained from the reaction of $V(CH_2SiMe_3)_4$[8a] with isotopically enriched water (23% ^{17}O). The yield for this reaction is typically less than 30%, but it provides an efficient and inexpensive method for introducing the ^{17}O label. The mechanism for this reaction is not known, but we suspect that the same reaction occurs when $V(O)(CH_2SiMe_3)_3$ is prepared according to Wilkinson's published procedure,[8a] which calls for eluting $V(CH_2SiMe_3)_4$ across a cellulose column. (Dioxygen by itself is not the oxidant because the reaction of $V(CH_2SiMe_3)_4$ with 1 equiv of oxygen produces an extremely complex product mixture containing no $V(O)(CH_2SiMe_3)_3$ by ^{51}V NMR spectroscopy.)

^1H and ^{13}C NMR spectral data from 2–5 are summarized in Table I. For all complexes containing CH_2SiMe_3 ligands, ^1H and ^{13}C resonances for the methylene groups attached to vanadium are broadened due to unresolved coupling to ^{51}V ($I = 7/2$; 100%). The ^{13}C resonances for the methylene groups all appear between 91 and 94 ppm with no obvious trends. In contrast, ^1H NMR resonances for the methylene groups show a clear trend toward lower field chemical shifts as the number of Ph_3SiO groups increases. For complexes 2 and 4, protons on the methylene groups are magnetically equivalent and appear as a singlet in the ^1H NMR spectrum. In the case of 3, the methylene protons are diastereotopic and are coupled to each other; each proton appears as a ^{51}V-broadened doublet.

^{51}V and ^{17}O NMR spectral data for 2–5 are collected in Table I. ^{17}O resonances for the terminal oxo group appear over a surprisingly narrow range centered near +1150 ppm, and there is no obvious correlation with the nature or number of alkyl or siloxy substituents. In contrast, the ^{51}V chemical shifts are profoundly influenced by the substituents on vanadium, and each replacement of a (trimethylsilyl)methyl group by a triphenylsiloxy group shifts the ^{51}V resonance upfield by nearly 700 ppm. Similar

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(7) (a) Prandtl, W.; Hess, L. Z. *Anorg. Allg. Chem.* **1913**, *82*, 103. (b) Chamberlin, M. M.; Jabs, G. A.; Wayland, B. B. *J. Org. Chem.* **1962**, *27*, 3321–3. (c) Sekiguchi, S.; Kurihara, A. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1453–4.

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Table I. Selected NMR Data for 2–5 and Their Lewis Adducts with $Al(CH_2SiMe_3)_3$

compd	conditions	$\delta(^{51}V)$ ($w_{1/2}$, Hz)	$\delta(^{17}O)$ ($w_{1/2}$, Hz)	$\delta(^{29}Si)$ ($w_{1/2}$, Hz)	$\delta(^{13}C)$ ($w_{1/2}$ and J, Hz)	$\delta(^{1}H)$ ($w_{1/2}$, Hz)
2	*a*	+1205 (50)	1138 (366)	0.1	92.78 ($w_{1/2}$ = 610, $^1J_{V-C}$ = 87), 1.09	1.80 (80), 0.15
3	*a*	+627 (500)	1130 (325)	2.1, −11.2 (90)	135.65, 130.50, 128.25, 93.75 ($w_{1/2}$ = 640), 1.00	7.81, 7.18, 2.67 (40), 1.82 (40), 0.095
4	*a*	−47 (400)	1144 (430)	3.9, −8.7 (90)	135.64, 135.26, 130.48, 128.29, 91.30 ($w_{1/2}$ = 500), 0.65	7.79, 7.18, 7.14, 3.05 (27), 0.08
5	*a*	−723 (100)	1189 (430) 320 (1990)		135.79, 134.92, 130.37, 128.24	7.62, 7.10, 6.99
2·$Al(CH_2SiMe_3)_3$	*c*	+1575 (111)	857 (650)	*d*	118.52 ($w_{1/2}$ = 566), 3.71, 2.28, 1.23	3.11 (95), 0.34, 0.07, −0.35
3·$Al(CH_2SiMe_3)_3$	*b*	+883 (1350)	830 (360)	6.6, 0.5, −1.5 (26)	135.85, 133.15, 131.54, 119.84 ($w_{1/2}$ = 230), 3.89, 1.73, 1.08	7.73, 7.23, 3.63 (29), 3.39 (29), 0.42, −0.06, −0.46
4·$Al(CH_2SiMe_3)_3$	*b*	+43 (2100)	843 (375)	7.6, 0.3, 0.1 (sh)	135.94, 135.63, 132.94, 131.39, 113.53 ($w_{1/2}$ = 260), 3.80, 1.62, 0.67	7.54, 7.18, 7.13, 3.94 (22), 0.35, −0.10, −0.58
5·$Al(CH_2SiMe_3)_3$	*b*	−779 (525)	903 (415) 375 (1990)	1.9 (55), 0.2	135.76, 132.96, 131.17, 128.58, 3.44, 1.48	7.45, 7.17, 7.02, 0.23, −0.66
6	*c*	+470 (58)				
7	*c*	−210 (44)				
8	*c*	−676 (19)				
6·$Al(CH_2SiMe_3)_3$	*c*	+727 (158)				
7·$Al(CH_2SiMe_3)_3$	*c*	−143 (226)				
8·$Al(CH_2SiMe_3)_3$	*c*	−742 (119)				

[a] C_6D_6, 20 °C. [b] C_7D_8, −50 °C. [c] C_7D_8, 20 °C. [d] Poorly soluble at low T and decomposes upon warming.

trends have been observed by Maatta[9] and Preuss[8c] in related systems, but the magnitude and regularity of the substituent effects are much higher in this case (vide infra).

Reactions of $V(O)(CH_2SiMe_3)_n(OSiPh_3)_{3-n}$ (n = 0–3) with $Al(CH_2SiMe_3)_3$. The addition of 1 equiv of $Al(CH_2SiMe_3)_3$[10] to toluene-d_8 solutions of **2**–**5** at 25 °C produces dark maroon solutions, which gradually decompose over several hours at room temperature. These solutions appear to be quite stable below −50 °C, but we have not been able to isolate stable products. Infrared spectra of these solutions were complex and generally uninformative,[11] but ^1H and ^{13}C NMR spectra recorded below −50 °C indicate that (i) the same ligands remain coordinated to each vanadium center, (ii) the molecular symmetry of each vanadium complex is unchanged by its interaction with the aluminum reagent, and (iii) the alkyl groups on Al are always equivalent on the NMR time scale. Several different modes of interaction between $Al(CH_2SiMe_3)_3$ and the vanadium complexes would be consistent with these observations—especially if $Al(CH_2SiMe_3)_3$ groups exchange coordination sites faster than the ^1H and ^{13}C NMR time scales—but coordination of $Al(CH_2SiMe_3)_3$ to the oxo ligands in **2**–**5** is strongly implicated by ^{17}O and ^{13}C NMR spectroscopy. In each case, the addition of $Al(CH_2SiMe_3)_3$ shifts the ^{17}O resonance for the oxo group upfield by approximately 300 ppm and the ^{13}C resonance for the methylene group attached to vanadium downfield by 25 ppm. These uniform shifts are consistent with coordination of the oxo ligand to a second metal,[12] and they strongly suggest that the nature of the interaction is the same regardless of the identity of the other ligands on vanadium.

The change in ^{51}V chemical shifts observed upon addition of $Al(CH_2SiMe_3)_3$ is less straightforward because the addition of $Al(CH_2SiMe_3)_3$ causes a moderate to large downfield shift (90–370 ppm) in the case of **2**–**4** and a modest upfield shift (56 ppm) in the case of **5**. These results appear to suggest that $Al(CH_2SiMe_3)_3$ interacts differently with **5** than with the other vanadium complexes, but a closer analysis of our ^{51}V NMR data strongly suggests that the nature of the interaction is in fact the same for all of these complexes and that it involves coordination of $Al(CH_2SiMe_3)_3$ to the oxo ligand.

Like most NMR-active nuclei, chemical shifts for ^{51}V are dominated by paramagnetic contributions to the overall shielding (σ_{para}).[13] Chemical shifts are influenced by many factors and are notoriously difficult to predict, but for closely related compounds there is normally a trend toward higher field chemical shifts as purely σ-bonding ligands are replaced by ligands with increasing electronegativity and better π-donating ability.[9,13,14] This trend is also observed for the complexes reported here.

^{51}V NMR data for **2**–**5** and their $Al(CH_2SiMe_3)_3$ adducts are collected in Table I and plotted in Figure 1 versus the number of triphenylsiloxy substituents attached to vanadium in each complex. As indicated by the two lines in Figure 1, replacement of a σ-donating (trimethylsilyl)methyl group by a π-donating triphenylsiloxy group results in a large upfield shift. The chemical shift dependence is remarkably linear in both cases, but the effects of substitution are greater for the $Al(CH_2SiMe_3)_3$ adducts. The line corresponding to the $Al(CH_2SiMe_3)_3$ adducts therefore crosses the line for **2**–**5** between n = 2 and n = 3 and leads to an unusual situation which could be easily misinterpreted. Rather than suggesting that **5** interacts differently with $Al(CH_2SiMe_3)_3$ than with **2**–**4**, the upfield shift observed in the ^{51}V NMR spectrum of **5** upon addition of $Al(CH_2SiMe_3)_3$ strongly supports our assertion that **2**–**5**

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[9] Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408–16.

[10] Tessier-Youngs, C. T.; Beachley, O. T. *Inorg. Synth.* **1986**, *24*, 92–7.

[11] (a) In principle,[11b] it should be possible to detect coordination of Al to the oxo ligands in **2**–**5** by IR spectroscopy. In practice, however, there are too many overlapping absorbances in the M=O region of the spectrum to permit objective structural assignments. (b) See ref 1, p 230.

[12] (a) Kintzinger, J.-P.; Marsmann, H. *Oxygen-17 and Silicon-29*; Springer-Verlag: New York, 1981. (b) St. Amour, T.; Fiat, D. *Bull. Magn. Reson.* **1979**, *1*, 118–29. (c) Klemperer, W. G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 246–54.

[13] Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33–83.

[14] (a) Priebsch, W.; Rehder, D. *Inorg. Chem.* **1985**, *24*, 3058–62. (b) Preuss, F.; Becker, H. *Z. Naturforsch.* **1986**, *41B*, 185–90.

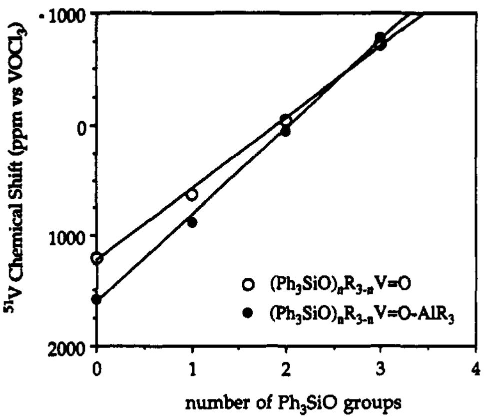


Figure 1. ^{51}V chemical shifts for **2**–**5** and their Lewis adducts with $Al(CH_2SiMe_3)_3$.

all react with $Al(CH_2SiMe_3)_3$ to produce Lewis adducts containing VO–AlR_3 groups.

In spite of the argument presented above, it is nonetheless interesting to speculate why coordination of $Al(CH_2SiMe_3)_3$ would cause a moderate upfield ^{51}V shift for **5** and much larger downfield shifts for **2**–**4**. The solution to this puzzle is not immediately obvious, but Maatta's recent analysis of stoichiometrically similar $[(p\text{-Z-}C_6H_4)N]VX_3$ compounds[9] provides an important clue: the ^{51}V resonance of $[(p\text{-}F_3C\text{-}C_6H_4)N]VCl_3$ appears more than 100 ppm upfield from the resonance for $[(p\text{-}H_3C\text{-}C_6H_4)N]VCl_3$. This clearly suggests that attachment of purely σ-withdrawing groups to the terminus of a VO group should produce an upfield shift when the three basal ligands are electronegative π-donor ligands. Consistent with this argument, an upfield shift is indeed observed when **5** is reacted with $Al(CH_2SiMe_3)_3$; it is also observed when $V(O)(OBu\text{-}t)_3$[7a] and vanadate **1**[6a] are reacted with $Al(CH_2SiMe_3)_3$ (vide infra). An upfield shift therefore appears to be quite "normal", and the more appropriate question would appear to be "Why are the ^{51}V resonances for **2**–**4** shifted downfield upon reaction with $Al(CH_2SiMe_3)_3$?".

To answer this question, it is instructive to compare our ^{51}V data with data reported for other stoichiometrically related compounds. Of particular relevance are Maatta's complexes with the formula $(Me_3SiCH_2)_nCl_{3-n}V[N(4\text{-tolyl})]$ (n = 0–3), which span a chemical shift range of δ 1046 (n = 3) to δ 305 (n = 0).[9] ^{51}V chemical shifts for these complexes follow the same trend observed for **2**–**5**, but the overall range of chemical shifts is much smaller than the ranges defined by **2** (δ +1205) and either $VOCl_3$ (δ 0) or **5** (δ −723). If by analogy to purely organic systems the π-donating ability of heteroatoms in these complexes increases from Cl to O to N, the chemical shift data indicate that basal ligand substituent effects are greatest when (i) poor π-donating ligands (e.g., alkyls) are progressively substituted for more electronegative, better π-donating basal ligands (e.g., alkoxides or siloxides) and (ii) good π-donating apical ligands (e.g., imido) are replaced by weaker π-donor ligands (e.g., oxo). This suggests that the increased basal ligand substituent effect observed upon coordination of $Al(CH_2SiMe_3)_3$ to **2**–**5** (Figure 1) is a consequence of *poorer π-donation* from O to V when Al is coordinated to the VO group.

Reactions of $V(O)(CH_2SiMe_3)_n(OBu\text{-}t)_{3-n}$ (n = 0–3) with $Al(CH_2SiMe_3)_3$. The trends observed in Figure 1 are very interesting, but the extent to which they could be applied to other oxovanadium systems was unclear.

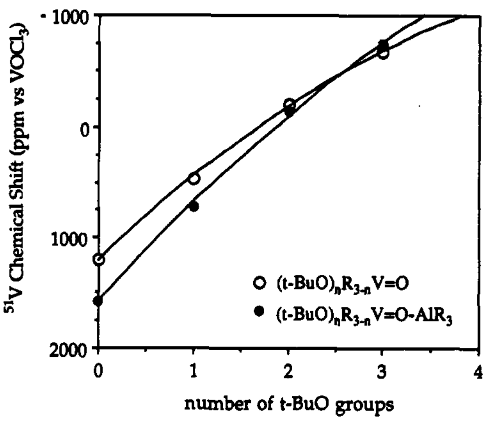
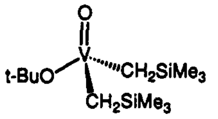


Figure 2. ^{51}V chemical shifts for **2**, **6**, **7**, and **8** and their Lewis adducts with $Al(CH_2SiMe_3)_3$.

We therefore decided to examine the behavior of oxovanadium(V) complexes containing *tert*-butoxy and CH_2SiMe_3 ligands. These complexes are stoichiometrically similar to both our Ph_3SiO and silsesquioxane-containing complexes, and three of the four molecules in the series have already been described.[7,8] ($V(O)(CH_2SiMe_3)_2(OBu\text{-}t)$ was the exception.)[15] The conproportionation of **2** and $V(O)(OBu\text{-}t)_3$ (**8**) occurs slowly with extensive decomposition upon prolonged heating, but a reasonably clean 46:4:4:46 mixture of **2**, **6**, **7**, and **8** can be prepared by briefly heating (80 °C, 2 min) a 1:1 mixture of **2** and **8** in toluene-d_8. Neither **6** nor **7** can be isolated from these mixtures, but their presence is strongly supported on the basis of the NMR spectral data collected in Table I.



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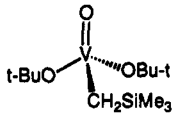

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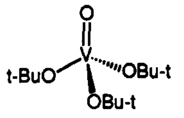

8

A ^{51}V NMR spectrum of the mixture containing **2**, **6**, **7**, and **8** exhibits four resonances at δ +1205 (46%), +470 (4%), −210 (4%), and −676 (46%). As in the case of **2**–**5**, there are large upfield shifts as CH_2SiMe_3 groups are formally replaced by *t*-BuO groups, but the chemical shift dependence is not as regular (Figure 2). The addition of $Al(CH_2SiMe_3)_3$ (1 equiv, 25 °C) to this mixture again produces a deep maroon color and causes the ^{51}V resonances for **2**, **6**, **7**, and **8** to shift. In the case of **2**, **6**, and **7**, the ^{51}V resonances are shifted downfield by 370, 257, and 67 ppm. In the case of **8**, however, the ^{51}V resonance is shifted upfield by 66 ppm. These results are analogous to those observed for **2**–**5**, and they are again most consistent with the formation of Lewis adducts derived from coordinaton of Al to the terminus of the VO group.

Reactivity of Oxovanadium(V) Alkyl Complexes toward Ethylene. Samples of pure **2**–**5** exhibit no detectable reaction with ethylene (300 psig) after 3 h in C_6H_6 (25 °C). Some polymerization activity is, however, observed from **2** and **3** at longer reaction times, as their solutions noticeably darken due to thermal decomposition. In light of our previous work with vanadium-containing

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[15] Preuss[8c] has observed that $(t\text{-BuO})_2V(O)R$ decomposes in solution at 25 °C to give resonances for $(t\text{-BuO})_3VO$, as well as ^{1}H NMR resonances attributable to new *t*-BuO and Me_3SiCH_2 groups (1:2). These observations are clearly consistent with the formation of $(t\text{-BuO})V(O)R_2$, but no complexes were isolated from these reactions and no other supporting data were provided.

Table II. Polymerization Activity of 2–5[a]

precatalyst	amt added $\mathrm{Al(CH_2TMS)_3}$, equiv	yield of PE, mg	no. of turnovers[b]	T_m, °C
2	0	0		na
3	0	0		na
4	0	0		na
5	0	0		na
2	3	950	372	132.15
3	3	840	329	132.59
4	3	225	88	127.19
5	3	183	72	125.66

[a] Polymerization reactions were performed in benzene (100 mL) for 3 h at 25 °C using 0.0913 mmol of precatalyst. Matheson polymerization grade ethylene (300 psig) was used without further purification. [b] The number of turnovers corresponds to (mg of PE)/[28/(mmol of precatalyst)].

silsesquioxanes,[6] which implicated an unusual Al-coordinated oxovanadium(V) alkyl complex as the precatalyst, we were interested to see if olefin polymerization could be initiated by adding small amounts of trialkylaluminum reagents (e.g., $\mathrm{Al(CH_2SiMe_3)_3}$) to **2**–**4**. The results from our investigations are briefly summarized in Table II.

In all cases, ethylene polymerization is initiated when $\mathrm{Al(CH_2SiMe_3)_3}$ (3 equiv) is added to ~1 mM solutions of **2**–**5** in benzene (25 °C, 300 psig $\mathrm{C_2H_4}$). None of the catalysts are particularly effective, all are quickly deactivated, and none appear to be as active as the catalyst derived from **1**,[6a] but it appears that vanadium complexes with greater numbers of alkyl groups are most effective. In the case of **2**–**4**, initiation is very rapid, and we suspect that it coincides with coordination of $\mathrm{Al(CH_2SiMe_3)_3}$ to the terminal oxo ligand. Vanadate **5** is slower to initiate, and its catalytic activity appears to arise from small amounts of **4** which form when **5** is reacted with an excess of $\mathrm{Al(CH_2SiMe_3)_3}$. (The $\mathrm{Al(CH_2SiMe_3)_3}$ adduct of **4** (~1%) can be observed by ^{51}V NMR spectroscopy when 3 equiv of $\mathrm{Al(CH_2SiMe_3)_3}$ is added to **5** in the absence of ethylene.)

Conclusions

In this paper we have described the synthesis and characterization of a complete series of oxovanadium(V) complexes with the formula $\mathrm{V(O)(CH_2SiMe_3)_{\mathit{n}}(OSiPh_3)_{3-\mathit{n}}}$ (n = 0–3). These complexes react with $\mathrm{Al(CH_2SiMe_3)_3}$ to form Lewis adducts derived from coordination of Al to the terminus of the VO group, suggesting that the oxo ligand is the most Lewis basic site in all of these molecules. On the basis of ^{51}V NMR data, it appears that coordination of Al to the oxo ligand reduces the degree of π-donation from the oxo ligand to vanadium and facilitates insertion of ethylene into the V–C bonds of **2**–**4**. A full account of our efforts to elucidate the mechanism(s) for olefin polymerization by oxovanadium(V) alkyl complexes, including vanadium-containing silsesquioxanes, will be provided in due course.[16]

Experimental Section

Except where noted, all operations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-Lab. Aromatic and aliphatic solvents were distilled from dark purple solutions of potassium or sodium benzophenone ketyl containing tetraglyme. NMR spectra were recorded on General Electric GN-500 or Omega-500 (^{1}H, 500.1 MHz; ^{13}C, 125.03 MHz; ^{17}O, 67.78 MHz) NMR spectrometers. ^{1}H, ^{13}C, and ^{29}Si chemical shifts are reported relative to $\mathrm{SiMe_4}$. All ^{29}Si spectra were recorded with inverse-gated proton decoupling in order to increase resolution and minimize nuclear Overhauser effects. ^{51}V chemical shifts are reported relative to neat $\mathrm{VOCl_3}$ as an external reference. ^{17}O chemical shifts are reported relative to neat $\mathrm{H_2O}$ as an external reference. Electron impact mass spectral analyses were conducted on a VG 7070e high-resolution mass spectrometer. Combustion analyses (C, H) were performed by Galbraith Microanalytical Laboratories. Melting points were measured in sealed capillaries under dry nitrogen with a Mel-Temp melting point apparatus and are uncorrected. $\mathrm{V(O)(CH_2SiMe_3)_3}$ (**2**),[8a] $\mathrm{V(O)(OSiPh_3)_3}$ (**5**),[7b] $\mathrm{V(CH_2TMS)_4}$,[8a] $\mathrm{V(O)(OBu\text{-}\mathit{t})_3}$,[7a] and $\mathrm{Al(CH_2SiMe_3)_3}$[10] were synthesized according to literature methods.

Synthesis of ^{17}O-Labeled $\mathrm{V(O)(CH_2SiMe_3)_3}$ (2). ^{17}O-enriched $\mathrm{H_2O}$ (23% ^{17}O, 200 mg, 0.6087 mmol) was slowly added to an agitated solution of $\mathrm{V(CH_2TMS)_4}$ (900 mg, 2.25 mmol) in THF (8 mL). The solution rapidly turned yellow and deposited a brown precipitate. Vacuum filtration and evaporation of the volatiles (25 °C, 10^{-4} Torr) afforded spectroscopically pure **2** as a lemon yellow solid (200 mg, 27% based on V). Selected NMR data ($\mathrm{C_6D_6}$): ^{51}V NMR δ 1205.7 ($w_{1/2}$ = 50 Hz, $^{51}\mathrm{V{=}}^{17}\mathrm{O}$), δ 1205 ($w_{1/2}$ = 50 Hz, $^{51}\mathrm{V{=}}^{16}\mathrm{O}$); ^{17}O NMR δ 1138 ($w_{1/2}$ = 366 Hz).

Synthesis of $\mathrm{V(O)(CH_2SiMe_3)_2(OSiPh_3)}$ (3) and $\mathrm{V(O)(CH_2SiMe_3)(OSiPh_3)_2}$ (4). A solution of triphenylsilanol (673 mg, 2.44 mmol) and **5** (400 mg, 1.22 mmol) in toluene (3 mL) was heated for 2 h at 40 °C. Evaporation of the solvent, extraction of the residue with pentane, and evaporation of the pentane afforded a brownish yellow solid, which was suspended in hexanes and placed in a −40 °C freezer overnight. The solution was filtered, and the filter cake was washed with a small amount of cold hexanes. Evaporation of the filtrate (25 °C, 0.1 Torr) afforded spectroscopically pure **3** as a yellow oil (444 mg, 56%). Pure **4** was isolated as lemon yellow crystals (300 mg, 28%) by dissolving the filter cake in a minimum amount of toluene, diluting 3-fold with hexanes, and cooling to −40 °C overnight.

For **3**: ^{1}H NMR (500.1 MHz, $\mathrm{C_6D_6}$, 20 °C) δ 7.81 (m, 5 H, Ph), 7.18 (m, 10 H, Ph), 2.67 (br s, $w_{1/2}$ = 40 Hz, 2 H, $\mathrm{VC}H_2\mathrm{Si(CH_3)_3}$), 1.82 (br s, $w_{1/2}$ = 40 Hz, 2 H, $\mathrm{VC}H_2\mathrm{Si(CH_3)_3}$), 0.095 (s, 18 H, $\mathrm{VCH_2Si(C}H_3\mathrm{)_3}$); ^{13}C{^{1}H} NMR (125.76 MHz, $\mathrm{C_6D_6}$, 20 °C) δ 135.65, 130.50, 128.25 (Ph), 93.75 ($w_{1/2}$ = 640 Hz, $\mathrm{V}C\mathrm{H_2Si(CH_3)_3}$), 1.00 ($\mathrm{VCH_2Si(}C\mathrm{H_3)_3}$); ^{29}Si NMR (99.35 MHz, $\mathrm{C_6D_6}$, 20 °C) δ 2.1 ($\mathrm{VCH_2}Si\mathrm{(CH_3)_3}$), −11.2 ($w_{1/2}$ = 90 Hz, V–O–$Si\mathrm{Ph_3}$); ^{51}V NMR (131.54 MHz, $\mathrm{C_6D_6}$, 20 °C) δ +627 ($w_{1/2}$ = 500 Hz); ^{17}O NMR (67.79 MHz, $\mathrm{C_6D_6}$, 20 °C) δ +1130 ($w_{1/2}$ = 325 Hz). Attempts to crystallize or distill **3** were unsuccessful. The complex decomposes upon warming to room temperature, but it appears to be indefinitely stable at −40 °C.

For **4**: ^{1}H NMR (500.1 MHz, $\mathrm{C_6D_6}$, 20 °C) δ 7.79 (d, 12 H, J = 7 Hz, Ph), 7.18 (d, 6 H, J = 7 Hz, Ph), 7.14 (d, 12 H, J = 7 Hz, Ph), 3.05 (br s, $w_{1/2}$ = 27 Hz, 2 H, $\mathrm{VC}H_2\mathrm{Si(CH_3)_3}$), 0.08 (s, 9 H, $\mathrm{VCH_2Si(C}H_3\mathrm{)_3}$); ^{13}C{^{1}H} NMR (125.76 MHz, $\mathrm{C_6D_6}$, 20 °C) δ 135.64, 135.26, 130.48, 128.29 (Ph), 91.30 ($w_{1/2}$ = 500 Hz, $\mathrm{V}C\mathrm{H_2Si(CH_3)_3}$), 0.65 ($\mathrm{VCH_2Si(}C\mathrm{H_3)_3}$); ^{29}Si NMR (99.35 MHz, $\mathrm{C_6D_6}$, 20 °C) δ 3.9 ($\mathrm{VCH_2}Si\mathrm{(CH_3)_3}$), −8.7 ($w_{1/2}$ = 90 Hz, V–O–$Si\mathrm{Ph_3}$); ^{51}V NMR (131.54 MHz, $\mathrm{C_6D_6}$, 20 °C) δ −47 ($w_{1/2}$ = 500 Hz); ^{17}O NMR (67.79 MHz, $\mathrm{C_6D_6}$, 20 °C) δ +1144 ($w_{1/2}$ = 430 Hz).

Reactions of 2–5 with $\mathrm{Al(CH_2SiMe_3)_3}$. In a typical reaction, $\mathrm{Al(CH_2SiMe_3)_3}$ (100 μL, 0.2754 mmol) was syringed into a solution of **2**, **3**, **4** or **5** (0.272 mmol) in toluene-d_8 (2 mL) at 25 °C. In each case, the solution changed from colorless or yellow to deep maroon. Repeated attempts to isolate stable Lewis adducts were unsuccessful. Spectroscopic data collected from each reaction are as follows.

(a) Reaction of 2 with $\mathrm{Al(CH_2SiMe_3)_3}$. ^{1}H NMR (500.1 MHz, $\mathrm{C_7D_8}$, 20 °C): δ 3.11 (br s, $w_{1/2}$ = 95 Hz, 6 H, $\mathrm{VC}H_2\mathrm{Si(CH_3)_3}$), 0.34 (s, 27 H, $\mathrm{AlCH_2Si(C}H_3\mathrm{)_3}$), 0.07 (s, 27 H, $\mathrm{VCH_2Si(C}H_3\mathrm{)_3}$), −0.35 (s, 6 H, $\mathrm{AlC}H_2\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (125.76 MHz, $\mathrm{C_7D_8}$, 20 °C): δ 118.52 ($w_{1/2}$ = 566 Hz, $\mathrm{V}C\mathrm{H_2Si(CH_3)_3}$), 3.71 ($\mathrm{VCH_2Si(}C\mathrm{H_3)_3}$), 2.28 ($\mathrm{Al}C\mathrm{H_2Si(CH_3)_3}$), 1.23 ($\mathrm{AlCH_2Si(}C\mathrm{H_3)_3}$).

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(16) Feher, F. J.; Blanksi, R. L., manuscript in preparation for submission to *J. Am. Chem. Soc.*

^{51}V NMR (131.54 MHz, $\mathrm{C_7D_8}$, 20 °C): δ +1576 ($w_{1/2}$ = 60 Hz). ^{17}O NMR (67.79 MHz, $\mathrm{C_7D_8}$, 20 °C): δ +857 ($w_{1/2}$ = 650 Hz, $J_{^{51}\mathrm{V}-^{17}\mathrm{O}}$ = 90 Hz).

(b) Reaction of 3 with $\mathbf{Al(CH_2SiMe_3)_3}$. ^{1}H NMR (500.1 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 7.73 (br s, 5 H, Ph), 7.23 (br s, 10 H, Ph), 3.63 (br s, $w_{1/2}$ = 29 Hz, 2 H, $\mathrm{VC}\mathit{H}_2\mathrm{Si(CH_3)_3}$), 3.39 (br s, $w_{1/2}$ = 29 Hz, 2 H, $\mathrm{VC}\mathit{H}_2\mathrm{Si(CH_3)_3}$), 0.42 (s, 27 H, $\mathrm{AlCH_2Si(C}\mathit{H}_3)_3$), −0.06 (s, 18 H, $\mathrm{VCH_2Si(C}\mathit{H}_3)_3$), −0.46 (s, 6 H, $\mathrm{AlC}\mathit{H}_2\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (125.76 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 135.85, 133.15, 131.54 (Ph), 119.84 ($w_{1/2}$ = 230 Hz, $\mathrm{V}\mathit{C}\mathrm{H_2Si(CH_3)_3}$), 3.89 ($\mathrm{AlCH_2Si(}\mathit{C}\mathrm{H_3)_3}$), 1.73 ($\mathrm{Al}\mathit{C}\mathrm{H_2Si(CH_3)_3}$), 1.08 ($\mathrm{VCH_2Si(}\mathit{C}\mathrm{H_3)_3}$). ^{29}Si NMR (99.35 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 6.6 ($\mathrm{VCH_2}\mathit{Si}\mathrm{(CH_3)_3}$), 0.5 ($\mathrm{AlCH_2}\mathit{Si}\mathrm{(CH_3)_3}$), −1.5 ($w_{1/2}$ = 26 Hz, V–O–$\mathit{Si}\mathrm{Ph_3}$). ^{51}V NMR (131.54 MHz, $\mathrm{C_7D_8}$, −50 °C): δ +883 ($w_{1/2}$ = 1350 Hz). ^{17}O NMR (67.79 MHz, $\mathrm{C_7D_8}$, −50 °C): δ +830 ($w_{1/2}$ = 360 Hz).

(c) Reaction of 4 with $\mathbf{Al(CH_2SiMe_3)_3}$. ^{1}H NMR (500.1 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 7.54 (br s, 12 H, Ph), 7.18 (br s, 6 H, Ph), 7.13 (br s, 12 H, Ph), 3.94 (br s, $w_{1/2}$ = 22 Hz, 2 H, $\mathrm{VC}\mathit{H}_2\mathrm{Si(CH_3)_3}$), 0.35 (s, 27 H, $\mathrm{AlCH_2Si(C}\mathit{H}_3)_3$), −0.10 (s, 9 H, $\mathrm{VCH_2Si(C}\mathit{H}_3)_3$), −0.58 (s, 6 H, $\mathrm{AlC}\mathit{H}_2\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (125.76 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 135.94, 135.63, 132.94, 131.39 (Ph), 113.53 ($w_{1/2}$ = 260 Hz, $\mathrm{V}\mathit{C}\mathrm{H_2Si(CH_3)_3}$), 3.80 ($\mathrm{AlCH_2Si(}\mathit{C}\mathrm{H_3)_3}$), 1.62 ($\mathrm{Al}\mathit{C}\mathrm{H_2Si(CH_3)_3}$), 0.67 ($\mathrm{VCH_2Si(}\mathit{C}\mathrm{H_3)_3}$). ^{29}Si NMR (99.35 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 7.6 ($\mathrm{VCH_2}\mathit{Si}\mathrm{(CH_3)_3}$), 0.3 ($\mathrm{AlCH_2}\mathit{Si}\mathrm{(CH_3)_3}$), 0.1 (sh, V–O–$\mathit{Si}\mathrm{Ph_3}$). ^{51}V NMR (131.54 MHz, $\mathrm{C_7D_8}$, 50 °C): δ +43 ($w_{1/2}$ = 2100 Hz). ^{17}O NMR (67.79 MHz, $\mathrm{C_7D_8}$, −50 °C): δ +843 ($w_{1/2}$ = 375 Hz).

(d) Reaction of 5 with $\mathbf{Al(CH_2SiMe_3)_3}$. ^{1}H NMR (500.1 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 7.45 (m, 18 H, Ph), 7.17 (m, 9 H, Ph), 7.02 (m, 18 H, Ph), 0.23 (s, 27 H, $\mathrm{AlCH_2Si(C}\mathit{H}_3)_3$), −0.66 (s, 6 H, $\mathrm{AlC}\mathit{H}_2\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (125.76 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 135.76, 132.96, 131.17, 128.58 (Ph), 3.44 ($\mathrm{AlCH_2Si(}\mathit{C}\mathrm{H_3)_3}$), 1.48 ($\mathrm{Al}\mathit{C}\mathrm{H_2Si(CH_3)_3}$). ^{29}Si NMR (99.35 MHz, $\mathrm{C_7D_8}$, −50 °C): δ 1.9 ($w_{1/2}$ = 55 Hz, V–O–$\mathit{Si}\mathrm{Ph_3}$), 0.2 ($\mathrm{AlCH_2}\mathit{Si}\mathrm{(CH_3)_3}$). ^{51}V NMR (131.54 MHz, $\mathrm{C_7D_8}$, −50 °C): δ −779 ($w_{1/2}$ = 525 Hz). ^{17}O NMR (67.79 MHz, $\mathrm{C_7D_8}$, −50 °C): δ +903 ($w_{1/2}$ = 415 Hz, V=O), 375 ($w_{1/2}$ = 1990 Hz).

Formation and Reactions of $\mathbf{V(O)(CH_2SiMe_3)_{\mathit{n}}(OBu\text{-}\mathit{t})_{3-\mathit{n}}}$ with $\mathbf{Al(CH_2SiMe_3)_3}$. A solution of $(t\text{-}\mathrm{BuO})_3\mathrm{V(O)}$ (50 mg, 0.158 mmol) and $\mathrm{(Me_3SiCH_2)_3V(O)}$ (52 mg, 0.158 mmol) in toluene-d_8 (0.5 mL) was heated for 2 min at 80 °C. The yellow solution darkened slightly. A ^{51}V NMR spectrum (131.54 MHz, $\mathrm{C_7D_8}$, 20 °C) revealed resonances for four complexes: δ −676 ($w_{1/2}$ = 19 Hz, $(t\text{-}\mathrm{BuO})_3\mathrm{V(O)}$, 46%), −210 ($w_{1/2}$ = 44 Hz, $(t\text{-}\mathrm{BuO})_2\mathrm{V(O)CH_2SiMe_3}$, 4%), +470 ($w_{1/2}$ = 58 Hz, $(t\text{-}\mathrm{BuO})\mathrm{V(O)(CH_2SiMe_3)_2}$, 4%), +1204 ($w_{1/2}$ = 39 Hz, $\mathrm{(Me_3SiCH_2)_3V(O)}$, 46%). The addition of $\mathrm{Al(CH_2SiMe_3)_3}$ (115 μL, 0.316 mmol) to this solution produced a deep maroon color. A ^{51}V NMR spectrum (131.54 MHz, $\mathrm{C_7D_8}$, 20 °C) revealed resonances for four new complexes: δ −742 ($w_{1/2}$ = 119 Hz, $(t\text{-}\mathrm{BuO})_3\mathrm{V(O){\cdot}Al(CH_2SiMe_3)_3}$, 46%), −143 ($w_{1/2}$ = 226 Hz, $(t\text{-}\mathrm{BuO})_2\mathrm{V(O)CH_2SiMe_3{\cdot}Al(CH_2SiMe_3)_3}$, 4%), +727 ($w_{1/2}$ = 158 Hz, $(t\text{-}\mathrm{BuO})\mathrm{V(O)(CH_2SiMe_3)_2{\cdot}Al(CH_2SiMe_3)_3}$, 4%), +1575 ($w_{1/2}$ = 60 Hz, $\mathrm{(Me_3SiCH_2)_3V(O){\cdot}Al(CH_2SiMe_3)_3}$, 46%).

Polymerization Reactions. In a typical polymerization reaction a solution of 2, 3, 4, or 5 (0.091 35 mmol) in 2 mL of $\mathrm{C_7H_8}$ was syringed into 100 mL of $\mathrm{C_6H_6}$ in a Parr Mini-Reactor fitted with a 200 mL glass reaction vessel (20-mm glass thickness) under an atmosphere of ethylene. $\mathrm{Al(CH_2SiMe_3)_3}$ (100 μL, 79.5 mg, 0.2754 mmol) was syringed into the reactor to produce a maroon solution, the ethylene pressure was increased to 300 psig, and the valve from the reactor to the ethylene cylinder was left open for 15 min to allow the system to equilibrate. After a total of 3 h the excess ethylene was vented, 2-propanol (2 mL) was added, and the mixture was stirred for 1 h. The solid (PE) was collected by vacuum filtration, washed with $\mathrm{C_6H_6}$/2-propanol, and dried in vacuo (25 °C, 0.01 Torr, 12 h). Gas chromatographic analysis revealed no linear alkanes or olefins with fewer than 30 carbon atoms.

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