Further studies, especially on the temperature and acidity dependence of this exchange process in small alkanes, are in progress.

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Registry No. Isobutane, 75-28-5.

Olefin Polymerization by Vanadium-Containing Silsesquioxanes: Synthesis of a Dialkyl–Oxo–Vanadium(V) Complex That Initiates Ethylene Polymerization

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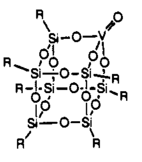
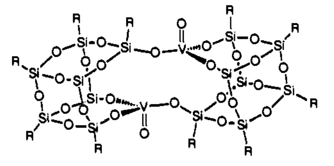
Silica-supported vanadium[1-6] catalysts have attracted attention as olefin polymerization catalysts because their excellent hydrogen response and high comonomer incorporation potentially allow greater control over the properties of the polymer.[3] Low-valent vanadium surface species have been implicated as active sites for polymerization in many of these systems,[4-6] but to the best of our knowledge, there is no direct evidence to objectively support any of the surface species which have been implicated in these systems. In this paper we report our preliminary efforts to elucidate the identity of the olefin polymerization catalyst formed by the reaction of **1**[7] with small amounts (2–5 equiv) of trialkylaluminum reagents.[8]



1 (R = c-C_6H_{11})



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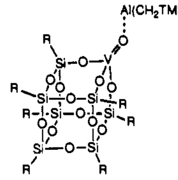

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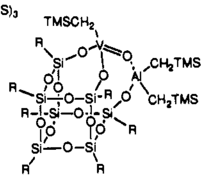

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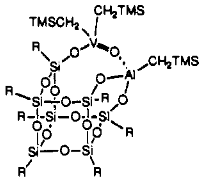

5

As reported previously,[7] vanadate **1** can be prepared by the reaction of $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$[9] with $(n\text{-PrO})_3VO$. The dimerization of **1** to **2** is enthalpically favored ($\Delta H° = -6.02 \pm 0.27$ kcal/mol), but the large negative entropy for dimerization ($\Delta S° = -17.1 \pm 0.2$ eu) can be exploited to prepare solutions containing predominantly (>95%) **1**. At 25 °C, a 0.1 M solution of **1** and **2** in toluene-d_8 contains ~75% of monomer **1** (by ^{51}V NMR spectroscopy), but the proportion of **1** can be increased to >96:4 by first heating the solution to 110 °C and then rapidly cooling it in a dry ice/acetone bath (−78 °C). Addition of $Al(CH_2SiMe_3)_3$[10] (1 equiv) to this toluene-d_8 solution at −78 °C produces a deep red solution, which at −50 °C exhibits ^1H, ^{13}C, ^{29}Si, ^{51}V, and ^{17}O NMR spectra[11] consistent with Lewis adduct **3**. Of particular relevance were a ^{51}V resonance at δ −705, a ^{17}O resonance at δ 934, and three silsesquioxane ^{29}Si resonances with relative integrated intensities of 3:1:3, one of which was broadened ($w_{1/2}$ = 40 Hz) due to unresolved two-bond coupling between ^{51}V ($I = {}^7/_2$) and the ^{29}Si nuclei closest to the vanadium center.

Lewis adduct **3** is stable below −50 °C, but upon warming to −20 °C, it reacts rapidly to produce a new vanadium complex in quantitative NMR yield. This complex, which is only stable below −10 °C (vide infra), was identified as **4** on the basis of multinuclear NMR spectra (obtained at −50 °C):[12] (i) the ^{29}Si NMR spectrum exhibits five resonances for the c-$C_6H_{11}Si$ groups (2:1:1:1:2), indicating that the metallasilsesquioxane framework of **4** is bisected by a mirror plane of symmetry; (ii) the ^{51}V resonance (δ 54.5) appears more than 700 ppm downfield from the starting vanadate,[13] and only one ^{29}Si resonance (for two Si) is broadened ($w_{1/2}$ = 35 Hz) by coupling to ^{51}V, consistent with alkyl transfer from

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(11) For **3**: ^1H NMR (500.1 MHz, C_7D_8, −50 °C) δ 2.00 (br m, 13 H), 1.55 (br m, 38 H), 1.10 (br m, 26 H), 0.44 (s, 27 H, $\mathrm{CH_2Si(C}H_3)_3$), −0.36 (s, 6 H, $\mathrm{C}H_2\mathrm{Si(CH_3)_3}$); $^{13}C\{^1H\}$ NMR (125.76 MHz, C_7D_8, −50 °C) δ 27.50, 27.35, 27.21, 26.95, 26.85, 26.77 (CH_2), 23.25, 22.88, 22.78 (CH, 1:3:3), 3.48 ($\mathrm{CH_2Si(}CH_3)_3$), 1.50 ($CH_2\mathrm{Si(CH_3)_3}$); $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_7D_8, −50 °C) δ 0.662 ($\mathrm{CH_2}Si\mathrm{(CH_3)_3}$), −61.96 ($w_{1/2}$ = 40 Hz), −68.18, −68.72 (3:1:3); ^{51}V NMR (131.54 MHz, C_7D_8, −50 °C) δ −705 ($w_{1/2}$ = 1800 Hz); ^{17}O NMR (67.79 MHz, C_7D_8, −50 °C) δ +934 ($w_{1/2}$ = 800 Hz).

(12) For **4**: ^1H NMR (500.1 MHz, C_7D_8, −50 °C) δ 3.82 (br s, 2 H, $\mathrm{V}CH_2\mathrm{Si(CH_3)_3}$), 2.11 (br m, 14 H), 1.60 (br m, 35 H), 1.21 (br m, 28 H), 0.46 (s, 18 H, $\mathrm{AlCH_2Si(C}H_3)_3$), 0.08 (s, 9 H, $\mathrm{VCH_2Si(C}H_3)_3$), −0.45 (d, J = 13 Hz, 2 H, $\mathrm{AlC}H_2\mathrm{Si(CH_3)_3}$), −0.51 (d, 2 H, J = 13 Hz, $\mathrm{AlC}H_2\mathrm{Si(CH_3)_3}$); $^{13}C\{^1H\}$ NMR (125.76 MHz, C_7D_8, −50 °C) δ 116 (br s, $w_{1/2}$ = 400 Hz, $\mathrm{V}CH_2\mathrm{Si(CH_3)_3}$), 28.40, 28.13, 27.95, 27.65, 27.54, 27.32, 27.23, 27.09 (CH_2), 25.75, 24.39, 23.69, 23.40 (CH, 1:2:2:2), 3.32 ($\mathrm{AlCH_2Si(}CH_3)_3$), 0.291 ($\mathrm{VCH_2}Si(CH_3)_3$), −1.43 ($\mathrm{Al}CH_2\mathrm{Si(CH_3)_3}$); $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_7D_8, −50 °C) δ 7.24 ($\mathrm{VCH_2}Si\mathrm{(CH_3)_3}$), 0.85 ($\mathrm{AlCH_2}Si\mathrm{(CH_3)_3}$), −63.54 ($w_{1/2}$ = 35 Hz), −67.74, −68.56, −68.65, −69.58 (2:1:1:1:2); ^{51}V NMR (131.54 MHz, C_7D_8, −50 °C) δ +54.5 ($w_{1/2}$ = 1800 Hz); ^{17}O NMR (67.79 MHz, C_7D_8, −50 °C) δ +825 ($w_{1/2}$ = 850 Hz).

(13) (a) ^{51}V resonances for **1** and $(Me_3SiCH_2)_3VO$ appear at δ −676 and +1205, respectively. Similar trends are seen for ^{51}V NMR data from other $R_n(OR)_{3-n}VZ$ (Z = NR or O) systems.[13b-d] (b) Preuss, F.; Ogger, L. *Z. Naturforsch.* **1982**, *37b*, 957–964. (c) Lachowicz, A.; Thiele, K. H. *Z. Anorg. Allg. Chem.* **1977**, *431*, 88–94. (d) Devore, D. D.; Lichtenhan, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408–16.

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Al to V; (iii) alkyl transfer is also supported by ^1H and ^{13}C NMR spectra, which both exhibit two sets of characteristic resonances for Me_3SiCH_2 groups on Al and V; and (iv) the ^{17}O resonance at δ 825 indicates the presence of a V–O double bond, which is coordinated to aluminum in the molecular plane of symmetry because the methylene protons on $Al(CH_2SiMe_3)$ groups are diastereotopic, while the methylene protons on the $V(CH_2SiMe_3)$ group are equivalent.

Upon warming above −10 °C, complex **4** undergoes a clean first-order reaction ($t_{1/2}$ = 21 min at 5 °C) to produce a new oxo–vanadium(V) alkyl complex, which affords poorly diffracting orange crystals from pentane (−40 °C, 2 weeks, 45%). Solution molecular weight data, combustion analysis, and multinuclear NMR data strongly suggest that this complex is **5**.[14] The ^{51}V resonance at δ 907 and the ^{17}O resonance at δ 777 are both consistent with an oxo–vanadium(V) dialkyl moiety; the ^{29}Si NMR spectrum indicates that the complex is still bisected by a molecular plane of symmetry and that there is only one V–O–Si linkage; the ^1H NMR data reveal that the methylene protons on $V(CH_2SiMe_3)$ groups are diastereotopic, while the methylene protons on the $Al(CH_2SiMe_3)$ group are equivalent.

Complex **5** is indefinitely stable in toluene-d_8 at 25 °C, and there is no evidence for the formation of low-valent species. Exposure of toluene-d_8 solutions of **5** to ethylene (1 atm, 25 °C) quickly initiates olefin polymerization, which continues until gelation of the solution prevents further uptake of ethylene. The polymer obtained in this fashion is similar to the polyethylene produced from the reactions of **1** with Me_3Al or $Al(CH_2SiMe_3)$,[8,15] but the polydispersity is somewhat larger (M_w/M_n = 5.72). Numerous attempts were made to spectroscopically detect Me_3SiCH_2 end groups on the polymer, but the number of these groups was too small to observe. Chain propagation and transfer are clearly much faster than initiation, and only a small amount of **5** (<5%) reacts before gelation occurs.[16]

The stoichiometric similarity of this system to several SiO_2-supported catalysts provides a compelling case for high-valent, oxo–vanadium(V) alkyl complexes as active sites in at least some of these systems.[17] It also suggests a new manifold of reactions for the alkylaluminum cocatalysts that are so often added to these catalysts. High-valent vanadium alkyl complexes are clearly reasonable candidates for active sites on SiO_2-supported polymerization catalysts. A full account of our efforts to elucidate the role of **5** in the polymerization of olefins, as well as its relationship to more conventional models for silica-supported vanadates (e.g., $R_{3-n}(Ph_3SiO)_nVO$), will be reported in due course.

Acknowledgment. These studies were supported by the National Science Foundation (CHE-9011593) and an NSF Presidential Young Investigator Award (CHE-8657262). Acknowledgement is also made to the UCI Academic Senate Committee on Research and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. F.J.F. gratefully acknowledges financial support from an Alfred P. Sloan Foundation research fellowship.

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(14) For **5**: ^1H NMR (500.1 MHz, C_7D_8, 20 °C) δ 3.43 (br d, J = 6 Hz, 2 H, $VCH_2Si(CH_3)_3$), 3.16 (br d, J = 6 Hz, 2 H, $VCH_2Si(CH_3)_3$), 2.10 (br m, 13 H), 1.70 (br m, 35 H), 1.30 (br m, 22 H), 1.00 (br m, 7 H), 0.56 (s, 9 H, $AlCH_2Si(CH_3)_3$), 0.12 (s, 18 H, $VCH_2Si(CH_3)_3$), −0.32 (s, 2 H, $AlCH_2Si(CH_3)_3$); $^{13}C\{^1H\}$ NMR (125.76 MHz, C_7D_8, 20 °C) δ 120 (br s, $w_{1/2}$ = 250 Hz), 28.45, 28.18, 28.03, 27.87, 27.65, 27.54, 27.39, 27.25 (CH_2), 25.45, 24.62, 24.03, 23.60 (CH, 2:3:1:1), 3.03 ($AlCH_2Si(CH_3)_3$), 0.959 ($VCH_2Si(CH_3)_3$), −6.75 ($AlCH_2Si(CH_3)_3$); $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_7D_8, 20 °C) δ 6.72 ($VCH_2Si(CH_3)_3$), 1.52 ($AlCH_2Si(CH_3)_3$), −67.08 (br sh), −67.22, −67.82, −68.18, −70.18 (1:1:2:1:2); ^{51}V NMR (131.54 MHz, C_7D_8, 20 °C) δ +907 ($w_{1/2}$ = 510 Hz); ^{17}O NMR (67.79 MHz, C_7D_8, 20 °C) δ +777 ($w_{1/2}$ = 480 Hz). Anal. Calcd (Found) for $C_{54}H_{110}Si_{10}O_{13}VAl$: C, 48.9 (48.4); H, 8.36 (8.02).

(15) IR and ^1H and ^{13}C NMR spectra indicate that the polymer is comprised of linear chains with methyl and vinyl termini: GPC analysis, M_n = 22 470 and M_w = 128 500 Da; DSC analysis, T_m = 133.9 °C.

(16) The amount of **5** consumed during the polymerization was monitored by comparing the integrated ^1H NMR intensities of its methylene resonances (i.e., $TMSCH_2V$) versus a ferrocene internal standard. Numerous spectra were recorded using long recycle delays to ensure accurate integrated intensities.

(17) A referee has (correctly) noted that the formation of **5** only requires 1 equiv of R_3Al per V but that the system described in ref 8 is most active when **1** is reacted with ~2 equiv of R_3Al. Although seemingly contradictory, it is important to realize that the "maximum activity" measured in ref 8 does not necessarily reflect the true stoichiometry of the catalyst-producing reaction. Possible roles for the "extra" R_3Al will be discussed in a forthcoming full paper.

2-Butyne and Hydrogen Chloride Cocrystallized: Solid-State Geometry of Cl–H···π Hydrogen Bonding to the Carbon–Carbon Triple Bond

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Hydrogen bonding of the type X–H···π, from a hydrogen-halide molecule HX to the π-electron density of the carbon–carbon double or triple bond, has been studied repeatedly and by various methods, mainly by microwave and IR spectroscopy as well as theoretical calculations.[1-5] Weakly bound complexes, considered to be the first stage of an electrophilic addition to the alkene or alkyne, are usually assigned a T-shaped configuration, i.e., with the X–H bond oriented perpendicular to the C–C multiple bond. Whereas most of the studies refer to the gaseous state or an argon matrix, the following[6] is a first report on relevant crystal structures, viz., of the two low-melting complexes 2-butyne·HCl and 2-butyne·2HCl.

The complexes were observed to form individual solid phases, melting at −100 (decomposition) and −113 °C, respectively, by applying difference thermal analysis to the whole underlying (quasi)binary system. Sample preparation and handling had to be done exclusively at low temperatures to avoid any irreversible attack on the triple bond, of which a large variety of possible products is known.[7] The melting diagram obtained differs from that of an earlier report.[5] In particular, a third intermediary solid phase, 2-butyne·4HCl, could not be confirmed.

Using simple cooling for 2-butyne·HCl and a miniature zone-melting technique[8] for 2-butyne·2HCl, single crystals of the complexes were grown in thin-walled quartz-glass capillaries on a Siemens AED2 four-circle diffractometer. The instrument was equipped with a low-temperature device and used also for the subsequent X-ray measurements with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The data were processed and all atoms directly localized and refined without constraints in the usual way; see Table I. The program system SHELXTL PLUS[9] was used on a VAXStation 3200 (Digital) computer. A somewhat lower accuracy for the 1:1 complex noticeably affects only the positions of the methyl H atoms, which appear less satisfactory than in the 1:2 complex, possibly connected with an inherent but not easily resolved disorder.

The molecular geometry of the complexes in the solid state, with interatomic distances and angles, is depicted in Figure 1. The T shape, as referred to above, is convincingly displayed by the

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