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Silsesquioxane Portfolio and catalytic activity of
organometallic Representatives in Ethylene Polymerisation**

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Progress in the Compilation of an Oxovanada-Silsesquioxane Portfolio and catalytic activity of organometallic Representatives in Ethylene Polymerisation

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Dedicated to Prof. Dr. Herbert Schumann in memoriam

Keywords: silsesquioxanes; models; vanadium; polymerisation; complex

Employing various incompletely condensed silsesquioxanes as ligand precursors in reactions with simple oxovanadates a variety of oxovanadium silsesquioxanes could be synthesized, that might be regarded as models for oxovanadium units on silica surfaces. These include a tetranuclear vanadium(IV) compound as well as two complexes where O_2V^+ units are coordinated to two siloxide functions as part of a silsesquioxane framework. Moreover, compounds containing $Cp^*V(O)^{2+}$ moieties were prepared, whose

activities as polymerization procatalysts has been examined: They turned out to be moderately active for the polymerization of ethylene. All compounds were fully characterised, in case of the tetranuclear vanadium(IV) complex this also includes the investigation of magnetic behaviour. Moreover, for two complexes also the molecular structures could be determined with sufficient quality via XRD.

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Introduction

Heterogeneous vanadium based catalysts are used in the industrial synthesis of ethylene-propylene and ethylene-propylene-diene elastomers. Recently, highly active homogeneous vanadium based catalysts have been developed which attracted much interest in academia and industry [1]. On the one hand supported vanadiumoxide catalysts are employed for the oxidative dehydrogenation (ODH) of alcohols and alkanes [2], and for a couple of years we have been interested in molecular compounds, which can simulate the structure, reactivity and/or the spectroscopic properties of corresponding surfaces. For the construction of suitable models we are pursuing two approaches: oxovanadium units are attached on the one hand to deprotonated forms of calixarenes [3] or on the other hand to deprotonated forms of silsesquioxanes [4,5,6], both of which are capable of mimicking the oxidic environments, that vanadiumoxo moieties experience on the surface of oxidic support or bulk materials. This contribution focuses on oxovanada silsesquioxanes.

Silsesquioxanes (sil(icone) - sesqui(1.5) - ox(ygen) - (alk)ane) are characterised by the general formula $(RSiO_{1.5})_n$,

and their structures are differentiated between those of the ladder- and cage type. Some of these frameworks resemble the structures of crystalline forms of SiO_2 [7], and hence silsesquioxanes are also discussed as molecular sections of such or its amorphous form [8]. Consequently, if formally RSi^{3+} units are removed from a silsesquioxane cage and the resulting siloxide functions saturated by protons or if formally $Si-O-Si$ units are hydrolyzed, incompletely condensed silsesquioxanes are obtained, which are probably the most realistic low-molecular weight models for silica surface silanols as they possess both structural and electronic similarities [9]. Chart 1 shows, how such incompletely condensed silsesquioxanes ($H_3^R T_7$ and $H_2^R T_8$) can be derived from the silsesquioxane cage $R^R T_8$.

Chart 1. The completely condensed silsesquioxane $R^R T_8$ and incompletely condensed silsesquioxanes $H_3^R T_7$ and $H_2^R T_8$.

In turn, the reaction of incompletely condensed silsesquioxanes with transition metal precursors thus resembles the grafting process applied for the preparation of heterogeneous catalysts, and resulting compounds may be regarded as models for SiO_2 -supported metal surface sites.

F. J. Feher et al. were the first to systematically explore the coordination chemistry of deprotonated $H_3^R T_7$ (Chart 1) – also with respect to vanadium(V) centres [10]. They were able to synthesize a mononuclear complex $R^R I$ (with R = cyclo-hexyl), which crystallized in form of a dimeric version,

^RII, from solutions containing both complexes in equilibrium (see Chart 2).

Chart 2. Equilibrium between **^RI** and **^RII**.

While, derivatives of **^RI** with R = cyclo-pentyl and iso-butyl have also been synthesized [11], the complexes **^RI**/**^RII**, originally synthesized in 1991, remained the only known oxovanadium-silsesquioxane complexes until recently, when we described novel vanadium(V) derivatives (see **III** - **V** in Chart 3). Inter alia, these could be utilised as spectroscopic models to discuss certain assignments made in vibrational spectra of corresponding heterogeneous catalysts [4]. Moreover we managed to prepare polynuclear oxovanadium(IV) compounds (see for instance **VI**), which can be regarded as models for reduced aggregates formed on silica surfaces in course of the reduction of corresponding catalysts in contact with hydrocarbons and whose behaviour in contact with O₂ was thus investigated to simulate the reoxidation step for the real catalysts [5]. Very recently we have described the results of studies testing available oxovanadium(V) silsesquioxane complexes as functional models [6]. While the employed silsesquioxane complexes were found to be only slightly active as catalysts for the ODH of alcohols, in-depth studies showed that leaching caused by carboxylic acids (formed as products) leads to a very active catalyst, which was identified. In the end this led to the discovery of a novel, simple and easy to prepare, catalytic system for the ODH of alcohols.

Chart 3. Oxovanadium-silsesquioxane complexes.

Considering the known oxovanadium-silsesquioxane complexes **I** - **VI** depicted in Charts 2 and 3, it becomes obvious that their number and variety is still rather limited although a lot of valuable information has been derived from these published examples. Here we extend the palette by new representatives formed from different types of silsesquioxane ligands or vanadium-containing precursor

compounds. Two of those were tested as ethylene polymerisation catalysts.

Results and Discussion

While the syntheses of all known oxovanadium silsesquioxane complexes (apart from **III**) started from H₃^RT₇ or silylated derivatives thereof, we intended to explore the possibility of employing silsesquioxane-based silanol precursors different from that.

The complexes resulting from reactions of H₃^RT₇ or its mono-silylated derivatives with PPh₄VO₂Cl₂ have in common that a VO₂⁺ unit occupies the corner that is missing in comparison to the completely condensed ^RT₈ cage. Hence, the question occurred whether such a VO₂⁺ unit might also be capable of bridging two such corners, that is, whether it can be bound to a “hydrolysed edge” of the ^RT₈ cage, although at first sight sterics seem unfavourable.

Hence, the known silanol H₂^{c-C₅H₉}T₈ was reacted with one equivalent of PPh₄VO₂Cl₂ (Scheme 1) in the presence of excessive NEt₃. After work up, this yielded in pure PPh₄[^{c-C₅H₉}T₈VO₂], **1** (n = 56 %).

Scheme 1. Synthesis of **1**.

The results of a NMR spectroscopic investigation of **1** suggest, that in solution **1** adopts a structure with C_{2v} symmetry: The ²⁹Si NMR spectrum shows only three signals, and also the ¹³C NMR spectrum exhibits only three resonances for the tertiary C atoms, whose intensities indicate the presence of three chemically equivalent groups of atoms in the ratio 2:4:2. This is in agreement with results of a single crystal X-ray analysis (see below) which indicate a C_{2v} symmetric structure also for the solid state.

With the background of the successful synthesis of **1** despite sterical constraints, one may ask whether a VO₂⁺ unit can act as a bridge between two silsesquioxanes: In all reactions of PPh₄VO₂Cl₂ with silsesquioxane-based silanols investigated so far only 1:1 conversions occurred [4, 6], and there were never indications for the formation of products with two silsesquioxane ligands bound to one V centre. Hence, HOSi^{c-C₅H₉}T₇ containing only one silanol function was treated with 0.5 equivalents of PPh₄VO₂Cl₂ in the presence of excessive NEt₃ but this did not lead to a pure product. However, employing NBu₄VO₃ instead of PPh₄VO₂Cl₂/NEt₃ led to the facile formation and isolation of NBu₄[O₂V(OSi^{c-C₅H₉}T₇)₂], **2**, as a white solid in 40 % yield (Scheme 2).

Scheme 2. Synthesis of **2**.

The ^{29}Si -NMR spectrum of **2** dissolved in CDCl_3 showed 4 signals in the approximate ratio 1:3:3:1, while the ^{13}C -NMR spectrum showed 3 signals in the approximate ratio 1:3:3. This is what one would expect assuming a local C_{3v} symmetry for the $\text{OSi}^{\text{c-C}_5\text{H}_9}\text{T}_7$ ligands, i.e. a fast rotation of the $\text{Si}^{\text{c-C}_5\text{H}_9}\text{T}_7$ units around the Si-O bonds of the V-O-Si linkages on the NMR timescale in combination with an overall C_{2v} symmetry of the anion of **2**. Of both compounds **1** and **2** crystals could be grown, which were analyzed by X-ray diffraction. While the data obtained – due to insufficient crystal quality, which is often a problem in silsesquioxane chemistry – did not lead to solutions, whose qualities would allow for a detailed discussion of bond lengths and angles, the molecular structures of the anions constituting **1** and **2** are beyond doubt, and they are shown in Figures 1 and 2. Their symmetries are in agreement with the findings made investigating solutions by NMR spectroscopy. Furthermore, in case of **1** even without evaluation of atomic distances the severe distortion of the T_8 cage clearly becomes obvious. Undistorted cages are found in **2**; as expected they are oriented in a way that leads to a maximum distance and thus to a W conformation of the Si-O-V-O-Si unit. Of course, the latter reduces the model character of **2** to some extent, as corresponding configurations cannot be adopted on silica surfaces. In this regard **1**, **IV** or **V** are better suited as structural or spectroscopic mimicks.

Figure 1. Molecular structure of the anion of **1**. Figure 2. Molecular structure of the anion of **2**.

Among the early transition metal (Ti, Zr, Hf) silsesquioxane silanolates numerous representatives containing one or two cyclopentadienyl co-ligands were discussed as models for immobilized metallocene polymerization catalysts or even investigated as catalyst precursors for the polymerization of olefins [12]. Considering that silica-supported vanadium materials have proved to be efficient as heterogeneous catalysts for olefin polymerisations, too, and oxovanadium complexes with multipodal ligands were shown to catalyse such polymerisations homogeneously [1], it seemed worthwhile to attempt the preparation of the first organometallic oxovanadium silsesquioxane complexes.

Hence, ligand precursors $\text{H}_2(\text{R}')^{\text{c-C}_5\text{H}_9}\text{T}_7$ (R' : H or TMS) were reacted with OVCP^*Cl_2 in the presence of excessive NEt_3 (Scheme 3). After work up this yielded in a deep violet solid. Analytically pure compounds could be obtained by recrystallization of the raw materials from hexane. The crystals thus obtained were suitable for X-ray diffraction studies, and the molecular structures of $[\text{OVCP}^*(\text{H})^{\text{c-C}_5\text{H}_9}\text{T}_7]$, **3**, and $[\text{OVCP}^*(\text{TMS})^{\text{c-C}_5\text{H}_9}\text{T}_7]$, **4**, are shown in Figure 3 and 4; but due to the low crystal quality in case of **4** bond lengths and angles are not given for this complex.

Scheme 3. Synthesis of **3** and **4**. Figure 3. Molecular structure of **3**. Figure 4. Molecular structure of **4**.

Selected bond lengths and angles of **3** are given in Table 1.

Table 1. Selection of bond lengths [Å] and angles [°].

	3	Cp*VOCl ₂
V-O1	1.600(3)	1.576(8)
V-O2	1.844(3)	
V-O3	1.809(3)	
O2-Si1	1.627(3)	
O3-Si2	1.622(3)	
Si3-O4	1.621(3)	
Σ(V-C)/5	2.334	
O1-V-O2	103.62(14)	
O1-V-O3	105.22(14)	
O2-V-O3	103.21(13)	
V-O2-Si1	128.90(17)	
V-O3-Si2	134.88(17)	

A Cp* ligand which binds to a metal fragment in a η^5 -fashion usually needs three coordination positions, and occupation of the residual three (available to metals that undergo octahedral coordinations) leads to the so-called three-legged piano stool structures. Such a structural motif is also found for the vanadium atoms in **3** and **4**. Focusing on the silsesquioxane ligand only small differences can be made out between the molecular structure of **3** and the one of ^c-C₆H₁₁II. The V=O bond lengths of **3** and Cp*VOCl₂ are very similar, as can be seen in Table 1. The interpretation of the NMR data for **3** and **4** suggests that both compounds are characterised by a plane of symmetry in solution. This is probably the case because of fluctuations, which are fast on the NMR time scale. With regard to the motivation of the synthesis of **3** and **4** as outlined above, of course it seemed of interest to investigate their potential as homogeneous olefin polymerization catalysts (see Table 2).

Table 2. Results of ethylene polymerizations.^{a)}

procatalyst (amount)	co-catalyst V-Al-ratio	PE [mg] activity ^{b)}	melt. point ^{c)} crystallinity ^{d)}	M _w ^{e)} PDI ^{e)}
3 (9.3 μmol)	PMAO 1000	460 74	135.0 14 %	2.1 x 10 ⁶ 5.7
4 (8.7 μmol)	PMAO 1000	1106 190	134.7 6 %	1.9 x 10 ⁶ 5.8
3 (9.3 μmol)	EtAlCl ₂ 2000	670 115	142.2 42 %	6.8 x 10 ⁵ 2.9
4 (8.7 μmol)	EtAlCl ₂ 2000	520 84	140.3 52 %	6.2 x 10 ⁵ 2.9

^{a)} Polymerization conditions: ethylene pressure 1 bar; room temp.; polymerization time 40 min; ^{b)} in kg PE mol(V)⁻¹ h⁻¹; ^{c)} peak maximum of the second melting point; ^{d)} melting enthalpy relative to 100% crystalline PE^[13]; ^{e)} determined by GPC.

Vanadium based procatalysts can be activated by methylaluminoxane (MAO) or by alkyl aluminum chlorides. The advantage of chloro aluminum co-catalysts in case of some vanadium complexes probably has to do with the formation of catalytically active chloro-bridged V-Cl-Al-compounds [1b, 1c]. We tested the ability of **3** and **4** to act as procatalysts in combination with PMAO [14] and ethyl aluminumdichloride, respectively. Both complexes are active for the polymerization of ethylene at atmospheric pressure with no clear trend in activities between **3** and **4**. The influence of the co-catalyst on the activity is also small. However, the molecular weight of the produced

polyethylenes strongly depends on the co-catalyst: Whereas EtAlCl₂ leads to a weight averaged molecular weight (M_w) of 6 x 10⁵ g mol⁻¹, PMAO allows for the formation of ultra-high molecular weight polyethylene (UHMW-PE, M_w = 2 x 10⁶ g mol⁻¹). The polydispersity index (PDI) of 2.9 is in accordance with a single site catalyst. The UHMW-PE has a larger PDI (5.8) due to some PE in the range of 10⁴ to 10⁵ g mol⁻¹. The lower molecular weight PE produced with EtAlCl₂ are higher in crystallinity and have higher melting points than the UHMW-PE of the PMAO co-catalyzed reactions. The polymers produced with **3** or **4** have analogous properties. This shows that the active catalyst, derived from **3** and **4** are very similar or even identical.

While compounds **1–4** are all mononuclear and contain vanadium(V), naturally we are also interested in polynuclear compounds as well as in oxovanadasilsesquioxane complexes containing vanadium(IV), as they could model reduced species formed on V₂O₅/SiO₂ catalysts in course of hydrocarbon oxidation. Recently, we have reported the synthesis of trinuclear vanadium(IV)silsesquioxane complexes [5]. These compounds had been isolated after reaction of H₃^c-C^{SH9}T₇ with VCl₄(THF)₂ in the presence of excessive NEt₃ as the base followed by controlled exposure to water vapour. After removing of all volatiles under reduced pressure the residue had been extracted with hexane. Storage of the extract at room temperature had then afforded **VI**, with a maximum yield of 33 % in form of blue crystals. As we considered **VI** as an interesting model for reduced polynuclear vanadium species we have tried to further improve its synthesis. In course of the optimization studies we noted that under certain conditions work-up not only leads to light blue crystals of **VI** but also to small amounts of dark blue crystals, which were only soluble in hot toluene. This pointed to the formation of a product, which is different from **VI**. Crystals obtained were suitable for X-ray diffraction studies, and the result of a corresponding analysis is shown in Figure 5.

Figure 5. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: V1-O1 1.580(2), V1-O4 2.028(2), V1-O3 2.030(2), V1-O5 1.993(2), V1-O6 2.002(2), V2-O2 1.578(2), V2-O3 2.034(3), V2-O4 2.028(2), V2-O6 1.989(2), V2-O5 2.003(2), O1-V1-O4 110.86(10), O1-V1-O3 111.11(12), O1-V1-O6 111.74(10), O1-V1-O5 113.03(11), O4-V1-O3 74.50(9), O3-V1-O5 135.86(10), O3-V1-O6 87.29(9), O4-V1-O5 90.25(9), O2-V2-O6 112.81(11), O6-V2-O4 90.22(8), O2-V2-O4 110.68(10), O2-V2-O3 111.45(12), O4-V2-O3 74.40(9), O2-V2-O5 111.59(10), O6-V2-O5 76.40(8), V2-O3-V1 96.18(13), V2-O4-V1 96.46(9), V1-O5-V2 99.49(9), V1-O6-V2 99.68(9), O5-V2-O4 137.62(9), O6-V2-O3 135.75 (9), O5-V2-O3 87.51(9), O5-V1-O6 76.33(8), O4-V1-O6 137.27(9).

It revealed that beside **VI** a tetranuclear complex $[(OV)_4(OH)_2(^{c-CH_9}T_7)_2]$, **5**, is formed as a second product. Every vanadium atom in **5** is coordinated by five oxygen atoms, one of which is doubly bound; they occupy the corners of a square pyramid (see Figure 6).

Figure 6. Illustration of the vanadium coordinationspheres within **5**. The organic residues of the silsesquioxane ligand have been omitted.

Hydrogen atoms are difficult to detect by X-ray diffraction, and therefore it was hard to decide whether O3 and O3' correspond to oxo or hydroxo bridges. Due to the fact, that the bond lengths between the O-atom of the μ_2 -bridging silanolate functions and the vanadium atoms are almost identical to the ones between O3 (O3') and the transition metal centres, it is likely that the oxygen atoms O3 and O3' are part of hydroxo bridges. Moreover, the IR spectroscopic investigation showed an absorption band at 3546 cm^{-1} , which is in the typical region for OH stretching vibrations. Therefore we concluded that the four vanadium atoms in **5** are in the oxidation state +IV. To support this an EPR-measurement of **5** dissolved in toluene was performed at 77 K (see Figure 7).

Figure 7. EPR spectrum of **5** and its simulation. Simulation parameters: $S = 2$, $A_{xx} = A_{yy} = A_{zz} = 0.0\text{ G}$, $g_x = g_y = g_z = 2.00$, $D = 470\text{ G}$, $E = 30\text{ G}$ linewidth: x: 280 G, y: 350 G, z: 180 G.

The good agreement between the experimental EPR-spectrum and its simulation shows that there are indeed four vanadium(IV) centres in **5**. These could be coupled in various ways. To investigate that a variable-temperature SQUID measurement was performed (see Figure 8).

Figure 8. Plot of μ_{eff} versus temperature for **5**. The solid line represents the best curve fit.

Experimental magnetic data for **5** were simulated based on the appropriate Hamiltonian for isotropic exchange and Zeeman splitting ($S_1 = S_2 = S_3 = S_4 = 1/2$), which involves two isotropic exchange parameters J_1 and J_2 [15].

$$\hat{H} = -2J_1(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_3 \cdot \hat{S}_4) - 2J_2(\hat{S}_2 \cdot \hat{S}_3 + \hat{S}_1 \cdot \hat{S}_4) + \sum_{i=1}^4 g_i \mu_B B \hat{S}_{iz}$$

A Curie-behaved paramagnetic impurity (PI) with spin $S = 1/2$ and temperature-independent paramagnetism (TIP) was included according to $\chi_{\text{calc}} = (1 - PI) \cdot \chi + PI \cdot \chi_{\text{mono}} + TIP$. The calculated curve fit is shown as solid line in Figure 8. The fitting [16] of the experimental data led to $g = 1.96$, $J_1 = 16.1\text{ cm}^{-1}$, $J_2 = -0.56\text{ cm}^{-1}$, $TIP = 0.30 \cdot 10^{-4}\text{ cm}^3\text{K mol}^{-1}$ and $\rho = 0.1\%$ (fixed, $S = 0.5$). The presence of two different exchange pathways is rationalized by the differences in V-O-V angles between V1 and V2/V2'. Because the V1-O-V2' angles (96.18° and 96.46°) are closer to the orthogonality than V1-O-V2 (99.49° and 99.68°) we assume that the positive coupling constant J_1 is attributed to the exchange pathway between V1 and V2' and the small negative coupling constant J_2 to exchange between V1 and V2. A fitting model based on four equal exchange pathways does not reflect the experimental data.

Conclusions

Bearing in mind (i) the importance of silica-supported V_2O_5 -based catalysts, (ii) the definite need for molecular oxovanadium compounds that can be regarded as models for surface species of these catalysts and thus may aid their characterisation, and (iii) the fact that incompletely condensed silsesquioxanes are recognized as suitable low-molecular weight analogues of hydroxylated silica surfaces, the number of known oxovanadium silsesquioxane compounds is still surprisingly small; only the representatives shown in Charts 2 and 3 had been reported at the outset of this work, which now adds 5 new compounds to the portfolio, inter alia with ligands that hitherto have not been employed in this kind of chemistry. While **1** represents the first precedent case formally derived from Si-O-Si edge reactivity within the R_8T_8 cage, **3** and **4** are the first organometallic derivatives. The latter themselves were found to display moderate activities in the polymerization of ethylene. With **5** the first tetranuclear complex was synthesized and it attracts further interest through the fact

that the V centres are in the oxidation state +IV, which is rather rare in combination with silsesquioxane ligands

Experimental Section

All manipulations were carried out in a glove-box, or else by means of Schlenk-type techniques involving the use of a dry argon atmosphere. The ^1H , ^{13}C , ^{29}Si and ^{51}V NMR spectra were recorded on a Bruker AV 400 NMR or DPX-300 spectrometer at 20 °C. The ^1H NMR spectra were calibrated against the residual proton and natural abundance ^{13}C resonances of the deuterated solvent, the ^{29}Si NMR spectra against TMS, and the ^{51}V NMR spectra against VOCl_3 as standards. Coupling constants are given in Hz. Microanalyses were performed on a Leco CHNS-932 or HEKAtech Euro EA 3000 elemental analyzer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets with a Shimadzu FTIR 8400S spectrometer. Magnetic data were measured with a Quantum-Design MPMS-5S SQUID magnetometer at 0.5 T in the range from 2 to 295 K. The powdered sample was contained in a gel bucket and fixed in a nonmagnetic sample holder. Electron spin resonance (ESR) spectra were measured on an ERS 300 (ZWG/Magnettech GmbH, Berlin-Adlershof, Germany). DSC measurements: Mettler Toledo DSC821 (heating rate $10^\circ \text{ min}^{-1}$, 35°C to 180°C , the maximum of the second melt-peak was taken as melting point); GPC-measurements were performed at the Deutsches Kunststoffinstitut, Darmstadt (Germany) with a HT-GPC PL220 (Polymer Laboratories) equipped with 3 linear columns type Olexis and refractive index detector, temp. 150°C , solvent 1,2,4 trichlorobenzene, flow rate 1 ml min^{-1} , concentration 1 mg ml^{-1} , calibration (polynomial) with polystyrene standards. PMAO (7% solution in toluene) was supplied from Akzo Nobel. $\text{H}_3^{\text{c-CH}_9}\text{T}_7$ [17], $\text{H}_2(\text{TMS})^{\text{c-CH}_9}\text{T}_7$ [18], $\text{HOSi}^{\text{c-CH}_9}\text{T}_7$ [19], $[\text{PPh}_4][\text{VO}_2\text{Cl}_2]$ [20], $[\text{NBu}_4][\text{VO}_3]$ [21] and Cp^*VOCl_2 [22] were prepared according to the literature procedures. $\text{H}_2^{\text{c-CH}_9}\text{T}_8$ was supplied by Sigma Aldrich.

Synthesis of 1: A total of 0.50 g (0.51 mmol) $\text{H}_2^{\text{c-CH}_9}\text{T}_8$ and 0.26 g (0.53 mmol) $[\text{PPh}_4][\text{VO}_2\text{Cl}_2]$ were dissolved in 15 mL CH_2Cl_2 . The resulting solution was treated with 0.69 mL (4.98 mmol) NEt_3 . The grey reaction mixture was stirred overnight at room temperature. Subsequently, all volatiles were removed under reduced pressure. After drying of the residue for 3 h under a high vacuum, it was extracted with 10 mL of THF. All volatiles were removed from the extract, and the crude material was dried overnight under high vacuum. This yielded in 0.40 g, (0.28 mmol) **1** in form of a white powder ($\eta = 56\%$). Elemental analysis for $\text{C}_{64}\text{H}_{92}\text{O}_{15}\text{PSi}_8\text{V}$ (1408.0); C 55.07 (calc. 54.59); H 6.28 (6.59) %. **IR:** [KBr, cm^{-1}]: $\nu = 3057$ (vw), 2947 (s), 2864 (m), 1586 (vw), 1484 (w), 1438 (m), 1320 (vw), 1245 (m), 1105 (vs), 1035 (m), 997 (sh), 937 (s), 935 (s), 752 (w), 723 (m), 690 (m), 527 (m), 496 (m). **$^1\text{H-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 7.93$ – 7.89 (m, 4 H, PPh_4^+), 7.84 – 7.78 (m, 8 H, PPh_4^+), 7.68 – 7.61 (m, 8 H, PPh_4^+), 1.73 – 1.26 (m, 64 H, CH_2), 1.00 – 0.77 (m, 8 H, CH); **$^{13}\text{C}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 135.77$ (d, $^4\text{J}(\text{C,P}) = 3.0 \text{ Hz}$, PPh_4^+), 134.45 (d, $^3\text{J}(\text{C,P}) = 10.4 \text{ Hz}$, PPh_4^+), 130.83 (d, $^2\text{J}(\text{C,P}) = 12.9 \text{ Hz}$, PPh_4^+), 117.46 (d, $^1\text{J}(\text{C,P}) = 89.4 \text{ Hz}$, PPh_4^+), 27.84 , 27.53 , 27.55 , 27.30 , 27.16 , 27.11 , 27.06 , 27.03 (s, CH_2), 24.15 , 23.03 , 22.47 (s, CH); **$^{29}\text{Si}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -69.0$, -67.7 , -65.8 (s); **$^{51}\text{V}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -591$.

Synthesis of 2: A total of 0.30 g (0.32 mmol) $\text{HOSi}^{\text{c-CH}_9}\text{T}_7$ and 0.19 g (0.54 mmol) $[\text{NBu}_4][\text{VO}_3]$ were dissolved in 10 mL CH_2Cl_2 . The reaction mixture was stirred overnight at room temperature. Subsequently, all volatiles were removed under reduced pressure.

After drying of the residue overnight under high vacuum, it was extracted with 10 mL of hexane. All volatiles were removed from the extract, and the crude material was dried again overnight under high vacuum. This yielded in 0.28 g (0.13 mmol) **2** in form of a white powder ($\eta = 40\%$). Elemental analysis for $\text{C}_{86}\text{H}_{162}\text{NO}_{28}\text{Si}_{16}\text{V}$ (2158.5); C 48.14 (calc. 47.85); H 7.52 (7.56); N 0.72 (0.65) %. **IR:** [KBr, cm^{-1}]: $\nu = 3057$ (vw), 2951 (s), 2866 (m), 1457 (w), 1245 (w), 1110 (vs), 997 (s), 936 (m), 736 (vw), 665 (vw), 628 (vw), 577 (vw), 505 (m); **$^1\text{H-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 3.46$ – 3.33 (m, 8 H, N-CH_2) ppm, 1.71 – 1.45 (m, 128 H, CH_2), 0.99 – 0.89 (m, 26 H, 14 CH , 12 CH_3); **$^{13}\text{C}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 58.83$ (s, NCH_2CH_2), 27.39 , 27.27 , 27.00 (s, CH_2), 24.02 (s, NCH_2CH_2), 22.40 , 22.33 , 22.08 (s, CH), 19.68 (s, CH_2CH_3), 13.64 (s, CH_2CH_3); **$^{29}\text{Si}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -106.2$ (s, SiOV), -66.7 , -66.5 , -65.8 (s); **$^{51}\text{V}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -607$.

Synthesis of 3: A total of 0.70 g (0.80 mmol) $\text{H}_3^{\text{c-CH}_9}\text{T}_7$ and 0.22 g (0.80 mmol) Cp^*VOCl_2 were dissolved in 20 mL THF. The resulting solution was treated with 0.55 mL (3.60 mmol) NEt_3 . The brown reaction mixture was stirred overnight at room temperature. Subsequently, all volatiles were removed under reduced pressure. After drying of the violet residue for 3 h under high vacuum, it was extracted with 10 mL of hexane. The extract was concentrated to a volume of 3 mL and stored at -30°C . During 1 week, violet crystals precipitated. Separation and drying of the crystalline material under reduced pressure yielded 0.30 g (0.28 mmol) **3** in form of a violet solid ($\eta = 35\%$). Elemental analysis for $\text{C}_{45}\text{H}_{79}\text{O}_{13}\text{Si}_7\text{V}$ (1075.6); C 49.70 (calc. 50.25); H 7.43 (7.40) %. **IR:** [KBr, cm^{-1}]: $\nu = 2948$ (vs), 2864 (s), 1450 (w), 1380 (vw), 1321 (vw), 1246 (m), 1092 (vs), 1010 (m), 969 (s), 930 (s), 865 (m), 804 (vw), 726 (vw), 633 (vw), 586 (vw), 499 (m), 425 (w); **$^1\text{H-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 3.89$ (s, 1 H, OH), 2.13 (s, 15 H, $\text{C}_5(\text{CH}_3)_5$), 1.73 – 1.37 (m, 56 H, CH_2), 1.05 – 0.86 (m, 7 H, CH); **$^{13}\text{C}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 127.82$ (s, $\text{C}_5(\text{CH}_3)_5$), 27.87 , 27.72 , 27.44 , 27.36 , 27.26 , 27.14 , 27.11 , 27.04 (s, CH_2), 22.86 , 22.71 , 22.34 , 22.28 , 22.27 (s, CH), 11.81 (s, $\text{C}_5(\text{CH}_3)_5$); **$^{29}\text{Si}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -67.3$, -66.7 , -65.6 , -59.7 , -56.1 (s); **$^{51}\text{V}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -554$.

Synthesis of 4: A total of 0.40 mg (0.42 mmol) $\text{H}_2(\text{TMS})^{\text{c-CH}_9}\text{T}_7$ and 0.10 mg (0.37 mmol; 0.9 eq.) Cp^*VOCl_2 were dissolved in 30 mL THF. The resulting solution was treated with 0.60 mL (4.32 mmol) NEt_3 . The brown reaction mixture was stirred overnight at room temperature. Subsequently, all volatiles were removed under reduced pressure. After drying of the violet residue for 3 h under high vacuum, it was extracted with 20 mL of hexane. The extract was concentrated to a volume of 10 mL and stored at -30°C . Within 2 weeks, violet crystals precipitated. Separation and drying of the crystalline material under reduced pressure yielded 80 mg (0.07 mmol) **4** in form of a violet solid ($\eta = 19\%$). Elemental analysis for $\text{C}_{48}\text{H}_{87}\text{O}_{13}\text{Si}_8\text{V}$ (1147.8); C 50.68 (calc. 50.23); H 7.82 (7.64) %. **IR:** [KBr, cm^{-1}]: $\nu = 2950$ (vs), 2864 (s), 1450 (w), 1377 (w), 1322 (vw), 1250 (m), 1100 (vs), 1053 (m), 1043 (m), 983 (s), 937 (s), 906 (m), 895 (m), 861 (m), 841 (m), 753 (w), 732 (vw), 648 (vw), 586 (vw), 498 (m), 426 (w); **$^1\text{H-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 2.11$ (s, 15 H, $\text{C}_5(\text{CH}_3)_5$), 1.83 – 1.38 (m, 56 H, CH_2), 1.04 – 0.84 (m, 7 H, CH), 0.15 (s, 9 H, $\text{Si}(\text{CH}_3)_3$); **$^{13}\text{C}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = 126.97$ (s, $\text{C}_5(\text{CH}_3)_5$), 27.95 , 27.89 , 27.82 , 27.71 , 27.61 , 27.32 , 27.30 , 27.25 , 27.07 , 26.97 , 26.91 (s, CH_2), 25.15 , 23.62 , 22.69 , 22.30 (s, CH), 11.90 (s, $\text{C}_5(\text{CH}_3)_5$), 2.11 (s, $\text{Si}(\text{CH}_3)_3$); **$^{29}\text{Si}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -68.29$, -66.21 , -66.11 , -65.67 , -61.34 (s), -15.62 (s, SiMe_3); **$^{51}\text{V}\{-^1\text{H}\}\text{-NMR}$:** [CDCl_3 , RT, ppm]: $\delta = -593$.

Synthesis of **5**: A total of 0.50 g (0.57 mmol) of $\text{H}_3^{\text{c-CSH}^9}\text{T}_7$ and 192 mg (0.57 mmol) of $\text{VCl}_4(\text{THF})_2$ were dissolved in 15 mL of THF, and 0.40 mL (2.85 mmol) of NEt_3 was added. The red-brown reaction mixture was stirred overnight at room temperature. Afterwards, the reaction mixture was connected to a Schlenk tube filled with degassed distilled water and stirred for 1.5 h (transport of water through the gas phase). Subsequently, all volatiles were removed under reduced pressure. After drying of the residue for 3 h under a high vacuum, it was extracted with 20 mL of hexane. The resulting solution was filled into a test tube and stored in the glovebox. Within 1 week blue crystals were obtained by slow evaporation of the solvent. The crystalline material was separated and treated with 10 mL of THF, where most of it dissolved. The insoluble residue was washed with THF and Et_2O and dried under reduced pressure. The yield of **5** ranged from 1 to 5 %. Elemental analysis for $\text{C}_{70}\text{H}_{126}\text{O}_{20}\text{Si}_{14}\text{V}_4$ (1882.3); C 41.49 (calc. 41.12); H 6.17 (6.21) %. IR: [KBr, cm^{-1}]: $\nu_{\text{IR}} = 3546$ (w), 2952 (s), 2866 (m), 1450 (w), 1249 (w), 1110 (sh), 1090 (vs), 1026 (s), 874 (s), 734 (vw), 627 (vw), 586 (w), 570 (w), 551 (m), 502 (m), 489 (sh). Polymerization procedures: 10.0 mg of procatalyst (corresponding to 9.3 μmol (**3**) and 8.7 μmol (**4**) respectively) were dissolved in 30 mL of dry toluene and the co-catalyst solution was added. After 5 min the activated catalyst solution was transferred into a 250 mL flask which contained 100 mL of dry toluene. At atmospheric pressure ethylene gas (3.0) was passed in. The polymerization was stopped by addition of 60 mL of a mixture of hydrochloric acid/ CH_3OH (1:1). The polymers were collected with a frit and washed several times with water, subsequently with acetone and were dried at 80 °C for 5 h.

X-ray Diffraction Studies: Crystal data for **3** (CCDC 784560): $\text{C}_{45}\text{H}_{79}\text{O}_{13}\text{Si}_7\text{V}$, $T = 150(2)$ K, monoclinic, space group $\text{P } 2_1/c$, $a = 10.3925(16)$ Å, $b = 21.469(4)$ Å, $c = 23.916(5)$ Å, $\alpha = 90^\circ$, $\beta = 90.635(17)^\circ$, $\gamma = 90^\circ$, $U = 5335.7(18)$ Å³, $Z = 4$, $D_c = 1.339$ Mg/m³, $\mu = 0.402$ mm⁻¹; 9660 reflections measured, 9660 unique ($R_{\text{int}} = 0.0509$); Final R indices [$I > 2\sigma(I)$] $R = 0.0833$, $wR = 0.1495$. Crystal data for **5** (CCDC 784561): $\text{C}_{70}\text{H}_{128}\text{O}_{30}\text{Si}_{14}\text{V}_4$, $T = 100(2)$ K, $\lambda = 0.71073$ Å, triclinic, space group $\text{P } \bar{1}$, $a = 12.2801(3)$ Å, $b = 12.3899(3)$ Å, $c = 16.5440(7)$ Å, $\alpha = 69.208(3)^\circ$, $\beta = 86.137(3)^\circ$, $\gamma = 84.899(3)^\circ$, $U = 2342.17(13)$ Å³, $Z = 1$, $D_c = 1.451$ Mg/m³, $\mu = 0.640$ mm⁻¹; 29478 reflections measured, 8231 unique ($R_{\text{int}} = 0.0505$); Final R indices [$I > 2\sigma(I)$] $R = 0.0614$, $wR = 0.1398$. Cell parameters for **2**: triclinic, space group $\text{P } \bar{1}$, $a = 14.0402(7)$ Å, $b = 23.5728(10)$ Å, $c = 37.8852(17)$ Å, $\alpha = 83.194(3)^\circ$, $\beta = 85.098(4)^\circ$, $\gamma = 84.200(4)^\circ$, $U = 12352.3(10)$ Å³. Cell parameters for **4**: triclinic, space group $\text{P } \bar{1}$, $a = 14.321(3)$ Å, $b = 14.870(4)$ Å, $c = 15.694(4)$ Å, $\alpha = 84.27(3)^\circ$, $\beta = 78.36(3)^\circ$, $\gamma = 75.32(3)^\circ$, $U = 3162.4(13)$ Å³. The crystals were mounted on a glass fiber and then transferred into the cold nitrogen gas stream of the Stoe IPDS diffractometer using MoK α radiation. The structure was solved by direct methods (SHELXS-97) [23] and refined versus F^2 (SHELXL-97) [24] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined using a riding model.

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