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Well-Defined Silica-Supported Zirconium–Benzyl Cationic Species: Improved Heterogenization of Single-Site Polymerization Catalysts

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 $Zr(CH_2Ph)_4$ (1) was grafted onto a recently disclosed hybrid material based on amorphous silica that features unique phenol grafting sites {[(=SiO)₂(AlOC₆H₄OH)(Et₂O)] (H)}. A monopodal tribenzyl surface species, structurally similar to the silica-supported species previously disclosed [=SiOZr(CH₂Ph)₃] (2), was obtained and fully characterized as [(=SiO)₂(AlOC₆H₄OZr(CH₂Ph)₃)(Et₂O)] (3). The activation of both these species by B(C₆F₅)₃ proceeded by benzyl abstraction to yield the inner-sphere ion pairs [=SiOZr-(CH₂Ph)₂]⁺[(PhCH₂)B(C₆F₅)₃]⁻ (4) and [(=SiO)₂(AlOC₆H₄-OZr(CH₂Ph)₂)(Et₂O)]⁺[(PhCH₂)B(C₆F₅)₃]⁻ (5), respectively.

Introduction

The heterogenization of organometallic Ziegler–Natta type complexes has been one of the greatest challenges in the development of heterogeneous single-site polymerization catalysts.^[1] The hopes of transposing the high activities and selectivities obtained under homogeneous conditions to a process- and morphology-friendly catalyst have been thwarted by surface interactions that negatively affect the overall performances.^[2]

In the field of fundamental studies of olefin polymerization mechanisms, benzyl group 4 complexes have been instrumental. Since they were first prepared and crystallized at the end of the 1960s,^[3] they have been extensively studied as polymerization catalysts^[4] and are now commonly used both in academia and in patents with an extensive range of ligands, from biscyclopentadienyl,^[5] monocyclopentadiThese surface species were fully characterized by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, elemental analyses, and ¹H, ¹³C, ¹¹B, and ¹⁹F solid-state NMR spectroscopy. These isolated cationic catalysts displayed increased ethylene polymerization activity compared to the neutral species. Most importantly, the heterogenization of the cationic complex with the phenol spacer (**5**) led to a fourfold increase in productivity compared to that of the silica counterpart **4**, in agreement with reduced surface interactions and improved electrophilicity.

enyl,^[6] mono(pentamethylcyclopentadienyl)^[7] or metallocene-related constrained geometry catalysts^[8] [CGCs, Me₂-Si(C₅Me₄)*t*BuN] and their analogues,^[9] mixed cyclopentadienyl–guanidinate (Cp–guanidinate),^[10] nonbridged amido Cp^[11] or Cp with a linked ancillary ligand.^[12] A large number of benzyl complexes with diamine ligands have also been described.^[13] The benzyl ligands can adopt various coordination modes (η^1 , η^2 , or η^3) in the neutral complexes previously mentioned.

However, their popularity was derived from the rich structural characterizations of cationic precursors obtained following their reactivity with borane activators. This work was pioneered by the group of Zambelli, almost simultaneously to the advent of borane cocatalysts by Marks^[14] and Ewen,^[15] by investigating the alkyl abstraction effect of B(C₆F₅)₃ to produce cationic complexes from monocyclopentadienyl derivatives and homoleptic benzyl complexes of titanium and zirconium,^[16] which are active in ethylene, propylene, and styrene polymerization. Variable-temperature NMR studies^[16c] and crystallographic identification^[17] revealed in this case, as in many others, the stabilizing η^6 coordination mode of the benzyl group of the borate anion on the cationic zirconium center (Scheme 1, A). The reactivity of homoleptic benzyl zirconium or titanium complexes with the Brønsted acidic salt [Me₂NHPh][B(C₆F₅)₄]^[18] or

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with the tritylium salt $[Ph_3C][B(C_6F_5)_4]^{[5a,19]}$ were also studied. More cationic structures were later characterized and of particular interest to our study are alkoxy or phenoxy ligands, as they best approximate a putative silicagrafted benzyl group 4 complex.



Scheme 1. Homoleptic (A) and aryloxide (B) zwitterionic benzyl complexes of zirconium following benzyl abstraction by $B(C_6F_5)_3$.

Rothwell et al. structurally characterized mixed benzyl– aryloxide complexes $[(ArO)_x(MBn_{4-x})]$ (x = 1, 2; M = Ti, Zr; ArO = 2,6-di-*tert*-butylphenoxide,^[20] 2,6-diphenylphenoxide,^[21] or 2,6-diphenyl-3,5-dimethylphenoxide).^[22] Subsequent activation reactions with B(C₆F₅)₃ yielded zwitterionic complexes through benzyl abstraction (Scheme 1, **B**).

Similarly to what was observed for the homoleptic complexes, upon abstraction of a benzyl group, the borate anion remains in the coordination sphere of the metal through an η^6 coordination of the aromatic ring.^[22]

Other good silica models for benzyl complexes include the calix[4]arene-based complexes studied by Floriani et al.^[23] and the polysilsesquioxane complexes prepared by Duchateau et al.^[24] Cationic structures were obtained in some cases after reaction with $B(C_6F_5)_3$; however, these models suffered from either selectivity issues during the protonolysis steps or resulted in unwanted dimeric structures, which are the logical step in the thermodynamic stabilization of the complexes in the homogeneous phase and are indicative of the limits of molecular compounds as silica models.

On the other hand, studies related to the use of group 4 metal complexes with benzyl ligands as heterogeneous polymerization catalysts are scarce and have not reached the level of characterization obtained homogeneously. Their use is mostly described in patent examples, and they are most often used on activating supports.^[25] Patents for the heterogenization of benzyl group 4 complexes by reaction with silica or alumina surfaces have shown interesting polymerization activities when activated with organoaluminum compounds as far back as 1971^[26] and gained in importance with patent applications related to zirconium tetrabenzyl grafted on alumina.^[27] The groups of Ballard,^[28] Yermakov,^[29] and Giesemann^[30] conducted preliminary studies in surface organometallic chemistry by grafting the group 4 homoleptic benzyl complexes on silica and alumina. The silica-supported complexes displayed some surprising activity in polymerization, and the formation of active polymerization catalysts on alumina is to be expected owing to its dual role as both support and activator,^[31] which leads to cationic species by alkyl abstraction to surface aluminum sites. We very recently revisited the grafting of the organometallic complexes Ti(CH2Ph)4 and Zr(CH₂Ph)₄ on hydroxy-rich silica (SiO₂₋₂₀₀) and highly dehydroxylated silica (SiO₂₋₇₀₀). The resulting bipodal and monopodal surface species $[(=SiO)_2M(CH_2Ph)_2]$ and $[\equiv SiOM(CH_2Ph)_3]$ (M = Ti, Zr), respectively, were unambiguously characterized for the first time and presented an unexpected polymerization activity in the absence of any activating agent.^[32] We also recently demonstrated the highly beneficial influence of a new hybrid material H that was developed on amorphous silica and features a rigid phenol grafting site as a substitute for silica hydroxy groups and, thus, affords reduced steric and electronic interactions from the surface.^[33] In this publication, the influence of the phenol spacer will be studied on the grafting of Zr(CH₂Ph)₄, and the resulting surface species will be structurally compared to its silica-supported counterpart [=SiOZr(CH₂Ph)₃]. We will also explore and fully characterize the cationic surface species formed by reaction with $B(C_6F_5)_3$. The influence of both the new hybrid material and the cocatalyst will be assayed in ethylene polymerization.

Results and Discussion

The formation of the monopodal species $[\equiv SiOZr(CH_2Ph)_3]$ (2) was performed according to a literature procedure. The silica (Evonik Aerosil-200) used was previously dehydroxylated under vacuum (10⁻⁵ mbar) at 700 °C (SiO₂₋₇₀₀),^[32] as was the hybrid material featuring phenolic grafting sites, which was prepared by first reacting silica with isobutylaluminum-diethyl ether to yield an aluminum isobutyl site $[(\equiv SiO)_2Al(iBu)(Et_2O)]$ concomitantly with an adjacent [=Si(iBu)] fragment. This unique and reactive [Al(iBu)] species was then selectively reacted with a hydroquinone spacer to yield $[(\equiv SiO)_2(AlOC_6H_4OH)-$ (Et₂O)] (H).^[33] Zr(CH₂Ph)₄ was impregnated on this latter material and on SiO₂₋₇₀₀ by using an excess (1.3 equiv.) of complex in benzene at room temperature for 2 h. After multiple washings with benzene followed by evacuation of the volatiles, the materials 1-H and 1-SiO₂₋₇₀₀ were obtained as yellow powders.

Reactivity of $Zr(CH_2Ph)_4$ with the Phenolic Functionalities of the New Hybrid Material H

Compared to the spectrum of the phenolic material **H** (Figure 1, a), the diffuse reflectance infrared Fourier transform (DRIFT) spectrum of **1-H** (Figure 1, b) displays new bands in the 3000–3100 cm⁻¹ range attributed to v_{C-H} vibrations from aromatic rings. A new $v_{C=C}$ vibration band at 1600 cm⁻¹ is also observed, which arises from the benzyl aromatic ring stretching, whereas the one at 1495 cm⁻¹ overlaps with the intense $v_{C=C}$ band from the hydroquinone ring at 1510 cm⁻¹. The δ_{C-H} band observed at 1450 cm⁻¹ can be attributed to the methylene group. These bands are similar



to those observed in the DRIFT spectrum of the silicagrafted material $1-\text{SiO}_{2-700}$ (Figure 1, c) and confirm the presence of benzylic moieties.^[32] Concomitantly the wide and large band centered at 3300 cm⁻¹ previously attributed to the phenol function^[33] has disappeared completely, in agreement with the protonolysis of a benzyl ligand during the grafting reaction.



Figure 1. DRIFT spectra of (a) H, (b) 1-H, and (c) 1-SiO₂₋₇₀₀.

The amount of zirconium, as quantified by elemental analysis of **1-H** is 1.91 wt.-%, which accounts to Zr/Al = 0.8. On the other hand, the 8.15 wt.-% of carbon, corresponding to C/Zr = 32, is close to the expected total of 21 carbon atoms on the zirconium center (three benzyl ligands) plus the 10 carbon atoms from the hydroquinone ring and silicon isobutyl fragment (not taking into account the diethyl ether molecule, see Exp. Sect.). These data are in agreement with the protonolysis of one benzyl ligand by the phenol function, as evidenced by the disappearance of the v_{O-H} vibration from the DRIFT spectra and the presence of ca. one zirconium atom per spacer moiety.

Thus, a monopodal structure, similar to the one previously characterized on SiO_{2-700} (species 2 in Scheme 2),^[32] tethered to the phenolic moiety can be proposed (species 3 in Scheme 2) as the major species featured on 1-H.



Scheme 2. Formation of the monopodal species 2 and 3 following the grafting of 1 on SiO_{2.700} and H, respectively.

The ¹H magic-angle spinning (MAS) NMR spectrum of **1-H** (Figure 2, a) displays a broad signal at $\delta \approx 1$ ppm that encompasses the protons from the Si–isobutyl group and from the methyl groups of the ether molecule. Together with a sharp and intense signal at $\delta = 20$ ppm in the ¹³C crosspolarization/MAS (CP/MAS) spectrum (Figure 2, b), the narrow peak at $\delta = 2$ ppm is attributed to free toluene as previously assigned in a ¹H–¹³C heteronuclear correlation (HETCOR) experiment for **1**-SiO₂₋₇₀₀; its presence is attributed to slight thermal degradation of the surface species under NMR conditions.^[32] The methylenic protons from



Figure 2. ¹H MAS NMR spectra (500 MHz, 8 scans, relaxation delay: 2 s, spinning speed: 10 kHz) of (a) **1-H** and (a') **H**; ¹³C CP/MAS NMR spectra (125.7 MHz, 30000 scans, relaxation delay: 2 s, CP contact time: 2 ms, spinning speed: 10 kHz) of (b) **1-H** with 20% ¹³C isotopic enrichment of the methylenic benzyl carbon atom and (b') **H**; * spinning sidebands.



the benzyl ligands are expected to give rise to a signal centered at $\delta = 1.4$ ppm, in agreement with what was observed on SiO₂₋₇₀₀ (Figure S1); however, this signal cannot be resolved in the spectrum. The intense signal at $\delta = 6.9$ ppm is assigned to the aromatic protons of both the benzyl ligands and the hydroquinone spacer.

To improve the detection of the methylenic carbon atom during ¹³C solid-state NMR experiments, the 20% α -labeled Zr(¹³CH₂Ph)₄ complex was synthesized (see Exp. Sect.) and grafted on both H and SiO₂₋₇₀₀. The ¹³C CP/MAS NMR spectrum of 1-H (Figure 2, b) thus displays an intense signal centered at δ = 66 ppm assigned to the 20% enriched ¹³CH₂Ph carbon atoms from the benzyl ligands, similar to the signals for the complex on SiO₂₋₇₀₀ (Figure S1), as well as from the CH_2 carbon atoms from the diethyl ether molecule that is already present in H (Figure 2, b'). The signals at $\delta = 12$ and 25 ppm from the methyl group of the ether molecule and the various carbon atoms in the Siisobutyl fragment, respectively, are still present, centered around the signal from the methyl group of the free toluene at $\delta = 20$ ppm as identified in the ¹H NMR spectrum and as observed for the SiO₂₋₇₀₀ species.^[32] The aromatic carbon atoms from both the benzyl ligand and the hydroquinone spacer overlap between $\delta = 115$ and 130 ppm. Two signals at $\delta = 143$ and 155 ppm are observed. Although the signal at $\delta = 143$ ppm could be assigned to the *ipso* carbon atom from the benzyl ligands, it is also possible that the previously indistinguishable oxygen-bound carbon atoms in the hydroquinone ring are now sufficiently different in species 3 to give rise to two separate signals at higher field (δ = 143 ppm) and lower field (δ = 155 ppm) from the original signal (δ = 150 ppm in **H**, Figure 2, b').

The solid-state NMR spectroscopic data for the isotopically enriched complex thus confirms the proposed structure **3** and is in good agreement with the molecular models.^[34]

Activation of 2 and 3 with B(C₆F₅)₃

The activation of the surface species was performed by reacting the materials $1-\text{SiO}_{2-700}$ and 1-H with the abstracting agent tris(pentafluorophenyl)borane (1.5 equiv.) in benzene for 3 h at room temperature. After multiple washings followed by evacuation of the volatiles, the materials **1B-SiO**_{2-700} and **1B-H**, respectively, were obtained as light brown powders.

These new materials were first analyzed by DRIFT spectroscopy. The DRIFT spectrum of **1B**-SiO₂₋₇₀₀ (Figure 3, b) is moderately altered in the 2800–3200 cm⁻¹ range but displays new bands at 1645, 1575, 1520(s), and 1465(vs) cm⁻¹, characteristic of $v_{C=C}$ vibrations from the penta-fluorophenyl rings.^[35] Similar bands are observed when comparing the spectra of **1-H** and **1B-H** (Figure S2) and this confirms the presence of pentafluorophenyl moieties on the surface.



Figure 3. DRIFT spectra of (a) $1-SiO_{2-700}$ and (b) $1B-SiO_{2-700}$ after activation with $B(C_6F_5)_3$.

The zirconium loading on both materials determined by elemental analysis (2.34 wt.-% on 1B-SiO₂₋₇₀₀ and 1.75 wt.-% on 1B-H) did not change significantly, except to reflect the overall mass gain from the addition of $B(C_6F_5)_3$ on the surface. The amount of boron was determined to be 0.19 and 0.16 wt.-% for 1B-SiO₂₋₇₀₀ and 1B-H, respectively, which corresponds to B/Zr = 0.7 and 0.8. The presence of 0.8 B(C_6F_5)₃ units per zirconium center on **1B-H** is confirmed by the presence of 4.29 wt.-% fluorine (F/B = 15), and the carbon determination of 10.5 wt.-% (C/Zr = 45.6) confirms the proposed structure 5 (Scheme 3). Indeed, considering that there are 10 carbon atoms from the aromatic ring and silicon-isobutyl fragment plus 21 carbon atoms from the three benzyl ligands and 18×0.8 carbons from the borane activator, this leads us to a theoretical value of 45.5 for C/Zr, which is close to the observed value. These data are in agreement with the expected benzyl abstraction reaction previously observed that leads here to the cationic surface species 4 and 5 on SiO₂₋₇₀₀ and H, respectively (Scheme 3). Interestingly, the amount of boron on \mathbf{H} is 10% higher than on bare SiO₂₋₇₀₀, in agreement with the previously observed reduced steric hindrance at the metal cen-



Scheme 3. Formation of cationic surface species 4 and 5 following the activation of 3 and 4, respectively, by $B(C_6F_5)_3$.



ter owing to the larger distance to the surface enforced by the hydroquinone spacer.^[33]

The ¹H MAS NMR spectra of **1B**-SiO₂₋₇₀₀ and **1B**-H are quite uninformative (Figures S3 and S4, respectively). The resulting aromatic protons give rise to a very broad signal centered at $\delta = 7.0$ ppm. The methylenic protons from the [ZrCH₂Ph]⁺ moieties can be assigned to the $\delta = 1.4$ ppm signal of **1B**-SiO₂₋₇₀₀, whereas they are masked by other signals in the spectrum of **1B**-H. In both cases, the methylenic protons from the [BCH₂Ph]⁻ moiety, which are usually very broad, are not resolved.^[13m]

On the other hand, the ¹³C CP/MAS experiments were particularly useful to follow the activation reaction of the $20\% \alpha$ -labeled surface species 2 and 3. The aromatic carbon atoms gave rise to a broad signal centered at $\delta = 128$ ppm for 1B-SiO₂₋₇₀₀ (Figure 4, a) that encompasses the various carbon atoms from the benzyl ligands. For 1B-H, the benzyl and hydroquinone aromatic carbon atoms give rise to similar features before and after activation with broader signals at $\delta = 120, 128, 146, \text{ and } 156 \text{ ppm}$ (Figure 4, b). The signals at $\delta = 67$ ppm for both materials correspond to the labeled methylenic carbon atoms from the cationic [Zr¹³CH₂Ph]⁺ moieties; these signals are broader but at a similar chemical shift as that of the neutral [Zr¹³CH₂Ph] moieties prior to activation, in agreement with literature data.^[34] In the spectrum of **1B-H**, the other signals at $\delta = 13$, 20, and 25 ppm from the methyl group of the ether molecule, the free toluene molecule, and the various carbon atoms in the Si-isobutyl fragment, respectively, are unaffected. Most importantly, both spectra present a new signal at $\delta = 35$ ppm, which can be attributed to the labeled [B¹³CH₂Ph]⁻ anionic moiety, in agreement with previous studies.^[13m,17]



Figure 4. ¹³C CP/MAS spectra of (a) 1B-SiO₂₋₇₀₀ and (b) 1B-H.

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The presence of the [PhCH₂B(C₆F₅)₃]⁻ counterion can be confirmed by ¹¹B and ¹⁹F solid-state NMR spectroscopy. The ¹¹B spectra of **1B**-SiO₂₋₇₀₀ and **1B-H** display single signals at $\delta = -12.5$ and -12.8 ppm, respectively (Figure S5), previously attributed in homogeneous studies to the tetrahedral boron atom from the anionic [PhCH₂B(C₆F₅)₃]⁻ moiety.^[36] The ¹⁹F NMR spectra of **1B**-SiO₂₋₇₀₀ and **1B-H** each display three signals at $\delta \approx -131$, -163, and -167 ppm, more clearly defined by deconvolution of the spectra (Figure 5). The intensities and chemical shifts of these three signals are characteristic of the *ortho*, *para*, and *meta* fluorine atoms, respectively, of the [PhCH₂B(C₆F₅)₃]⁻ counterion, in agreement with literature data.^[13c,37]



Figure 5. ¹⁹F MAS NMR spectra (376.5 MHz, 64 scans, relaxation delay of 5 s, 28 kHz spinning speed) of **1B-SiO**₂₋₇₀₀ and **1B-**H (plain) with deconvolution fit (dashed) and fitted peaks (points).

By using deconvolution to extract the actual chemical shift values, the diagnostic difference between the chemical shifts of the *meta* and *para* fluorine atoms $[\Delta\delta(m,p-F)]$ was found to be 4.16 and 4.32 ppm for 4 and 5, respectively. The fact that these values are higher than 3.5 ppm are indicative of a tightly coordinated [PhCH₂B(C₆F₅)₃]⁻ counterion, as depicted in Scheme 3.^[13d,38]

Ethylene Polymerization Results

To assess the influence of the spacer between the silica surface and the zirconium complexes, these new catalysts were assayed in the polymerization of ethylene in an 80 mL autoclave in the absence of any other activating or scaveng-



ing agent. The results from the neutral catalysts and activated catalysts on both SiO_{2-700} and H are compiled together in Table 1.

Table 1. Ethylene polymerization results for neutral and cationic zirconium benzyl complexes grafted on SiO₂₋₇₀₀ and H.^[a]

	Catalyst	Yield [g]	Activity ^[b]	$M_{\rm n}^{\rm [c]}~(imes 10^5)$	$M_{\rm w}/M_{\rm n}$
1	1-SiO ₂₋₇₀₀	0.25	32	2.2	7.2
2	1B-SiO ₂₋₇₀₀	0.39	60	1.8	7.9
3	1-H	0.40	76	4.3	8.9
4	1B-H	1.05	220	1.3	8.5

[a] 30 min, 50 mg catalyst, 20 mL toluene, 10 bar, 40 °C, 300 rpm. [b] Average activity calculated over the whole polymerization time in kgPE mol_{Zr}⁻¹h⁻¹. [c] Masses in gmol⁻¹ determined by size-exclusion chromatography (SEC) in 1,2,4-trichlorobenzene at 150 °C, in polystyrene equivalents.

This table shows that the introduction of a surface spacer increases the polymerization activity. The polymerization activities of the neutral species 2 and 3, which are still the subject of intense scrutiny and will be the topic of a forthcoming article, were multiplied by a factor of 2.4 between the silica-grafted complex and its tethered counterpart. Similarly, the cationic analogues showed tremendous gain from this surface remoteness with an increase in the activity of almost fourfold to reach 220 kgPE $mol_{Zr}^{-1}h^{-1}$ in the absence of scavenger. All catalysts produce linear polyethylene, as illustrated by ¹³C CP/MAS NMR analysis of the polymer produced by 1-SiO₂₋₇₀₀ (Figure S6). The polymer was of high molecular weight and had a broad molecularweight distribution. Such high polydispersity is not typical of single-site catalysts and may result from an inefficient initiation step. A rough estimate of the number of growing chains per metal center in the catalyst gives an upper estimate of the active species, provided that no transfer occurs (which was previously confirmed by NMR analysis of the produced polyethylene that was devoid of olefinic signals). For the four systems presented in Table 1, this estimate corresponds to 8.3, 16.9, 8.9, and 84.2% respectively. This means that less than 10% of the neutral zirconium centers in 1-SiO₂₋₇₀₀ and 1-H are active. This result indicates that the initiation of the polymerization process is not efficient in those cases, because only a fraction of the organometallic centers induce chain growth.

Multiple parameters can explain the rise in activity induced by the hydroquinone material. The reduction in steric hindrance facilitates the $B(C_6F_5)_3$ activation reaction and leads to a slightly higher amount of cationic species. More importantly, it is believed that the hydroquinone ring reduces the interactions between the surface siloxane moieties and the metallic centers and, thus, improves the electrophilicity of the cationic complex.^[33] This is further illustrated by the high number of sites that were able to induce chain growth in **1B-H** (84%) compared to **1B-**SiO₂₋₇₀₀ (16.9%).

Conclusions

New heterogeneous polymerization catalysts have been developed by supporting $Zr(CH_2Ph)_4$ on silica and modi-

fied silica. These neutral species have been fully characterized and both displayed ethylene polymerization activity. The addition of $B(C_6F_5)_3$ led to the abstraction of a benzyl ligand to form the expected ion pairs, which have been isolated and fully characterized on the surface and which logically led to increased polymerization activity. Most notably, we have demonstrated that the previously developed hybrid material that features phenolic grafting sites as spacers and is easily prepared in two simple steps from cheap, commercially available reagents is an effective support for polymerization complexes. An almost fourfold gain in productivity was observed as a result of the surface separation of the cationic zirconium benzyl species; this further confirms the validity of our strategy towards reduced steric interactions and improved electronic effects for supported organometallic species for olefin metathesis, polymerization, and other future applications.

Experimental Section

General: All experiments were performed under a controlled atmosphere by using Schlenk and glove-box techniques for organometallic syntheses. For the synthesis and treatments of the surface species, the reactions were performed by using high-vacuum lines (ca. 1 mPa) and glove boxes. Benzene and pentane were distilled over NaK/benzophenone and degassed through freeze-pump-thaw cycles. Elemental analyses were performed at the Mikroanalytisches Labor Pascher, Remagen (Germany). It is noteworthy that molecules of diethyl ether were released during the elemental-analysis procedures in some cases, especially if the aluminum atom was bonded to three oxygen atoms. DRIFT spectra were recorded with a Nicolet 6700 FTIR spectrometer by using airtight cells. Solidstate ¹H MAS and ¹³C CP/MAS NMR spectra were recorded with a Bruker Avance 500 spectrometer with a conventional double-resonance 4 mm CP/MAS probe at the Laboratoire de Chimie Organométallique de Surface in Ecole Supérieure de Chimie Physique Electronique de Lyon. The samples were loaded under argon in a zirconia rotor, which was then tightly closed. ¹⁹F solid-state NMR spectra were recorded with a DSX400 instrument with a doubleresonance 2.4 mm CP/MAS probe at the Institut de Recherches sur la Catalyse et l'Environnement de Lyon. Rotation frequencies were set for 28 and 25 kHz to detect spinning sidebands, and the spectra were recorded with 64 scans with 2.8 µs 90° pulses and 5 s of relaxation time. The deconvolution of the solid-state ¹⁹F NMR spectra was performed by using the dmfit software.^[39] Chemical shifts are given with respect to tetramethylsilane (TMS) as external reference for ¹H and ¹³C NMR and to BF₃·OEt₂ for ¹¹B NMR. B(C₆F₅)₃ (Strem Chemicals >97%) was dried with Me₃SiCl,^[40] purified by vacuum sublimation, and controlled by ¹⁹F NMR before use.

The synthesis of tetrabenzyl zirconium was adapted from a patented protocol.^[41] The monopodal species [\equiv SiOZr(CH₂Ph)₃] (2) was prepared according to a literature procedure,^[32] as was the hybrid material featuring phenolic grafting sites **H**.^[33]

Preparation of 1-H: A benzene solution of $Zr(CH_2Ph)_4$ (155 mg, 0.340 mmol) and **H** (1 g) was stirred at 25 °C for 2 h in the absence of light. After filtration, the solid was washed three times with benzene. The resulting yellow powder was dried under vacuum (1.34 Pa) and stored in the glove box at -30 °C.

Preparation of 1B-SiO₂₋₇₀₀ and 1B-H: A benzene solution of $B(C_6F_{5)3}$ (1.5 equiv.) and either 1-SiO₂₋₇₀₀ or 1-H was stirred at



25 °C for 2 h in the absence of light. After filtration, the solid was washed three times with benzene. The resulting light brown powder was dried under vacuum (1.34 Pa) and stored in the glove box at -30 °C.

Benzylic Alcohol α -¹³C Labeled at 100%: A solution of benzoic acid α -¹³C labeled at 100% (5.000 g, 40.940 mmol, purchased from Euriso-Top) in dry tetrahydrofuran (THF, 100mL) was added dropwise to a solution of BH₃·Me₂S (82 mL, 81.900 mmol, 1 M in CH₂Cl₂) and B(OEt)₃ (14 mL, 81.900 mmol) in dry THF (300 mL). After H₂ evolution, the resulting solution was stirred overnight at reflux. When cold, the mixture was quenched with MeOH (100 mL) at 0 °C. After evaporation of the volatiles, the residue was dissolved again in MeOH (100 mL), and the solvents were evaporated. Without further purification, benzylic alcohol was obtained in quantitative yield as a clear oil (4.430 g). ¹H NMR (C₆D₆, 300 MHz, 298 K): δ = 4.06 (d, ¹J_{H,C} = 150 Hz, 2 H, CH₂), 7.00 (m, 5 H, Ar-H) ppm.

Benzyl Chloride α -¹³C Labeled at 100 %: Thionyl chloride (3.6 mL, 49.158 mmol) was added dropwise to a solution of benzylic alcohol (4.430 g, 40.94 mmol) in Et₂O (40 mL). Pyridine (0.15 mL) was then added, and the resulting mixture was stirred at reflux for 1 h. The same quantity of thionyl chloride and pyridine was added again. After another 1 h of stirring at reflux, the mixture was quenched with water and extracted with Et₂O (3 × 20 mL), and the resulting organic phases were washed with brine and dried with MgSO₄. The resulting benzyl chloride was obtained as a clear oil in quantitative yield. ¹H NMR (C₆D₆, 300 MHz, 298 K): δ = 4.67 (d, ¹J_{H,C} = 144 Hz, 2 H, CH₂), 7.40 (m, 5 H, Ar-H) ppm.

Benzylmagnesium Chloride α -¹³**C** Labeled at 20%: A benzyl chloride solution (unlabeled and α -¹³**C** labeled at 100% in an 8:2 ratio; 23.5 mL, 204 mmol) in Et₂O (50 mL) was added dropwise to Et₂O (100 mL) containing Mg turnings (30 g, 1235 mmol). The exothermicity of the reaction self-maintains the reflux of Et₂O. At the end of the addition, the resulting mixture was stirred at room temp. for 2 h and filtered to yield a yellowish clear solution. This solution (1 mL) was titrated with a solution of benzylic alcohol in dry xylene in the presence of 2,2'-biquinoline as indicator (turns red to yellow), which indicated a concentration of 1.05 M of the Grignard reagent.

Tetrabenzylzirconium *a*-¹³**C Labeled at 20**%: In the dark and at –33 °C, benzylmagnesium chloride *a*-¹³**C** labeled at 20% (49 mL, 51.493 mmol, 1.05 M in Et₂O) was added dropwise to a suspension of ZrCl₄ (3.000 g, 51.493 mmol) in toluene (20 mL) and Et₂O (10 mL). After 1 h of stirring at room temp., 1,4-dioxane (4.5 mL) was added, and the resulting mixture was stirred at room temp. for 1 h. The salts were removed by filtration, the volume of the resulting limpid orange solution was reduced, and the product crystallized at –30 °C over 2 d. Zr(¹³CH₂Ph)₄ was collected as orange crystals (4.700 g, 80%). ¹H NMR (C₆D₆, 300 MHz, 298 K): δ = 1.53 [d (20%) + s (80%), ¹J_{H,C} = 136 Hz, 8 H, CH₂], 6.37 (d, 8 H, Ar-H), 6.98 (m, 12 H, Ar-H) ppm.

Procedure for the Polymerization Experiments: Polymerization runs were performed in the absence of any activating agent. Typically, an accurate amount of the catalyst was loaded into an 80 mL autoclave within the glove box. Then, toluene (20 mL), previously distilled from sodium and further purified by freeze–pump–thaw cycles and stored over zeolite, was added. After the reactor had been set to the desired temperature, the polymerization was initiated by the introduction of ethylene previously purified over copper catalyst and zeolite. After stirring for 30 min with a magnetic stirrer, the reaction was quenched with methanol. Following its collection

by filtration, washing, and drying, the polymer produced was weighed.

Supporting Information (see footnote on the first page of this article): Additional spectroscopic data.

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