Preparation of a Well-Defined Silica-Supported Nickel-Diimine Alkyl Complex – Application for the Gas-Phase Polymerization of Ethylene

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The interaction of $[(\alpha-diimine)Ni(CH_2SiMe_3)_2]$ (1) $(\alpha-diimine = 2,3-dimethyl-1,4-[(2',6')-diisopro$ pylphenyl]-*N,N'* $-diazadiene) with the silanol <math>\equiv$ Si–OH groups of Aerosil SiO₂₋₍₇₀₀₎ leads to the formation of the surface complex [\equiv SiO–Ni(α -diimine)(CH₂SiMe₃)] (2) with the concomitant emission of 1 mol equiv of SiMe₄ (TMS). The surface complex characterized by IR, chemical and mass balance analyses, solid-state NMR, and EXAFS has been activated by gaseous BF₃ to give an active gas-phase ethylene polymerization catalyst. The polymers thus obtained present a highly branched structure. The activity is attributed to the formation of the putative surface ion pair [\equiv SiOBF₃]⁻[Ni(α -diimine)(CH₂SiMe₃)]⁺.

Introduction

The production of polyolefins, which is currently over 100 millions of tons per year,^{1,2} has been developed using mainly two catalytic systems found ca. 50 years ago: the Ziegler-Natta catalytic system,^{3,4} using TiCl₄ as precursor of the active species, and the "Phillips polymerization system",⁵ based on chromium oxide supported on silica. These catalysts have been modified over the last decades to improve their activity and steric control.^{2,6-8} An important breakthrough in the development of Ziegler-Natta catalysts was the activation of catalysts based on metallocenes by methyl aluminoxane (MAO), found in the 1980's by Kaminsky.⁹ However, the early transition metal-based metallocenes, although very active, do not allow the copolymerization of olefins with polar functionalities, whereas late transition metals are usually more tolerant for this type of monomers, but they are known to present a lower activity. In late transition metal chemistry and catalysis, imino ligands with bulky aryl substituents on the nitrogen atoms have provided a number of active polymerization catalysts.¹⁰ Brookhart et al. reported that aryl ortho-disubstituted α -diimine nickel(II) com-

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plexes in combination with different cocatalysts show remarkably high activities in the polymerization of ethylene.^{1,11} In addition, the microstructure of the polymers can be varied by changing the bulkiness of ortho substituents on the aryl rings or by changing reaction parameters.

A logical approach to develop catalysts for their use in gasphase processes is to immobilize them on a solid support.^{12–15} A typical approach with Ni(II) diimine is the treatment of the silica with MAO to form an ill-defined "surface-bound MAO", followed by reaction of this "surface-bound MAO" with halogenated Ni(II) precursors.^{16,17} Usually the activities reported for these catalysts are relatively low. The large molar excesses of MAO used might be responsible for the reduction of the nickel leading to catalyst deactivation.¹⁸

Recently, Brookhart et al. reported a new methodology for the covalent attachment of α -diimine nickel(II) complexes to a silica support: α -diimine nickel(II) complexes that contain an amino or hydroxy functionality on the α -diimine were reacted with a silica previously treated with AlMe₃, BCl₃, or SiCl₄ to afford the covalently linked catalysts.^{19,20} However, activation of these supported dibromo nickel precursors then requires an alkylaluminum cocatalyst to afford highly productive ethylene polymerization systems (the presence of an alkylaluminum can also be highly beneficial for the scavenging of impurities).

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One of the advantages of surface organometallic chemistry (SOMC) is the ability to create stable grafted complexes presenting coordinative unsaturation, in particular due to the impossibility of bimolecular deactivation.²¹ Catalytic systems derived from the SOMC approach also exhibit a very high percentage of active sites ("single sites"). One of the easiest ways to obtain such complexes covalently bound to silica is the reaction of M-C bonds of MR_n alkyl complexes with one surface silanol to form a SiO-M bond. In particular, with this approach, well-defined isolated (2,3-dimethyl-1,4-[(2',6')-diisopropylphenyl]-N,N'-diazadiene)(CH2SiMe3)Fe(II) centers grafted onto Aerosil silica were sythesized,²² and active Zr ethylene polymerization catalysts were obtained from well-defined zirconium complexes grafted onto alumina, silica-alumina, or activated silica supports. The activity observed for the Zr grafted complexes was attributed to the presence of some "cation-like" surface species,²³ which could be described as "floating cations"^{24,25} (e.g., $[Cp*Zr(Me)_2 \cdot NEt_2Ph]^+$) on a silica correctly activated by $B(C_6F_5)_3$.

Boennemann has shown that hydroxyl groups activated by the gaseous Lewis acid BF₃ on the surface of the support serve as effective anchoring sites for organometallic complexes of nickel cyclooctadienyl. The resulting species described as ${SiO_2}O-(BF_3)-Ni-(\eta^1,\eta^2-C_8H_{13})$ are active for the oligomerization of olefins.²⁶ We wish to report here a new method, which consists of grafting first the molecular complex [(α diimine)Ni(CH₂SiMe₃)₂] (1) (α -diimine = (2,6-Pr₂C₆H₄)-N=CMe-CMe=N(2,6-Pr₂C₆H₄)),²⁷ to obtain the well-defined [\equiv SiO-Ni(α -diimine)(CH₂SiMe₃)] supported onto Aerosil SiO₂. (700) by the SOMC method. The resulting surface organometallic complex can then be activated by BF₃ to form an active catalyst for the polymerization of ethylene, which may be a cationic α -diimine nickel species obtained by coordination of the strong Lewis acid on the oxygen bound to Ni.

Results and Discussion

During the reaction of a disk of SiO₂₋₍₇₀₀₎ (ca. 30 mg) with a benzene solution of $[(\alpha-diimine)Ni(CH_2SiMe_3)_2]$ (1), the solid turned blue. The sample was further washed twice with toluene and pentane, to remove the excess of complex, and then dried under vacuum (10⁻⁵ torr, 2 h). It can be observed by IR that the band attributed to isolated silanol groups, $\nu_{(O-H)}$ at 3747 cm⁻¹, disappeared almost completely (Figure 1). Concomitantly, other vibration bands appeared in the 3000–2700 cm⁻¹ (ν_2 to ν_4) and 1500–1300 cm⁻¹ (δ_6 to δ_{10}) regions, which are assigned, respectively, to $\nu_{(CH)}$ and $\delta_{(CH)}$ vibrations of the hydrocarbyl groups of the neosilyl and diimine ligands,²⁸ while the bands at 3070 cm⁻¹ (ν_1) and 1586 cm⁻¹ (ν_5) are only characteristic of the diimine ligand of the nickel-supported complex and assigned,



Figure 1. Infrared spectra of the grafting reaction of $[(\alpha \text{-diimine})\text{Ni}(\text{CH}_2\text{SiMe}_3)_2]$ (1) onto SiO₂₋₍₇₀₀₎ by impregnation: (a) silica partially dehydroxylated at 700 °C for 15 h; (b) the same sample, after reaction with 1 at 25 °C.

respectively, to the $\nu_{(sp2 C-H)}$ and $\nu_{(C=N)}$ vibration. Moreover, a broadband also appeared at 3695 cm⁻¹ (ν_0). This latter band, observed in the case of several supported complexes, is attributed to the interaction of residual silanols with the ligands coordinated to the metal.²⁹ The irreversible disappearance of free silanols and the appearance of $\nu_{(CH)}$, $\nu_{(C=N)}$, and $\delta_{(CH)}$ bands is in agreement with a chemical grafting of 1 and the formation of a (\equiv SiO-Ni) bond.

The reaction of $[(\alpha - \text{diimine})\text{Ni}(\text{CH}_2\text{SiMe}_3)_2]$ (1) and $\text{SiO}_{2-(700)}$ $(0.7 \text{ OH/nm}^2, \text{ i.e.}, 0.22 \pm 0.03 \text{ mmol OH/g of SiO}_{2-(700)})$ was also carried out in a benzene solution at 25 °C on a larger scale (ca. 1 g). After three washing cycles with benzene and drying under vacuum at 25 °C, a blue solid was obtained. The Ni loading was 0.76 wt %, according to elemental analysis (0.13 mmol Ni/g), which corresponds to a partial consumption of the surface silanols (ca. 60% of the 0.22 mmol OH/g of $SiO_{2-(700)}$). This is consistent with what has already been observed when monitoring this reaction by in situ IR spectroscopy (vide supra). During the grafting reaction, tetramethylsilane (SiMe₄) was evolved and quantified by GC analysis: 1.0 ± 0.1 SiMe₄/grafted Ni. This is consistent with the exchange of only one neosilyl group of the complex 1 by one siloxy group of SiO₂₋₍₇₀₀₎. Moreover, according to the elemental analysis of the sample, the resulting solid contained, respectively, 5.15 wt % C and 0.42 wt % N. This corresponds to 33 ± 3 C/Ni (expected 32 for 2) and 2.3 \pm 0.35 N/Ni (expected 2 for 2). All of these results are thus in full agreement with the formation of the surface species $[(\equiv SiO)Ni(\alpha - diimine)(CH_2SiMe_3)]_{SiO2-(700)}$ (2) (Scheme 1). According to a molecular modeling approach using the Tripos force field of the Sybyl program package, the maximum loading for this surface fragment due to its size is 0.17 mmol per g of SiO₂₋₍₇₀₀₎ support. This means that ca. 75% of this theoretical maximum surface coverage would be reached for this complex with the consumption of ca. 60% of the support surface silanols.

The ¹H MAS NMR spectrum of **2** displays broads signals, which were assigned by comparison with the spectrum of the molecular complex in solution (Figure S1 in the Supporting Information) to the aromatic protons (C3–*H* and C4–*H*, δ at ca. 7 ppm), the isopropylic methyne protons (C5–*H*, δ at ca. 3.5 ppm), the remaining surface silanols (\equiv SiO–*H*, δ at ca. 1.8 ppm), the protons of the methyl groups of isopropyls and of the methylene of neosilyls (C6*H*₃ and C9*H*₂, δ at ca. 0.3–1.5 ppm), and the protons of the methyl groups in α position of imines and of the neosilyls (C8*H*₃ and C10*H*₃, δ at ca. -0.5 to

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Scheme 1. Reaction of 1 with SiO₂₋₍₇₀₀₎



0.3 ppm). The ¹³C CP-MAS spectrum presents six resolved signals (Figure 2a), which can be assigned to the imine carbons, C7, at 165 ppm, to the aromatic carbons ipso C1 and ortho C2 at 140 ppm, to the aromatic carbons meta C3 and para C4 at 124 ppm, to the methyne of the isopropyl groups, C5, at 29 ppm, to the methyl of the isopropyl groups, C6, and to the methyl group sin α position to the imines, C8, at 23 ppm, and to the methyl group of the neosilyl, C10, at 0.5 ppm (Table 1). Note that the signal of the methylene carbon, C9, of the neosilyl group would be large and obscured in the tail of the C8 and C6 signals. This difficult observation of the signal of the carbon in α position of the metal has been commonly observed with



Figure 2. ¹³C NMR spectra of (a) the nickel(diimine) complex **2** grafted onto $SiO_{2-(700)}$ (CP-MAS NMR); and (b) the molecular complex **1** dissolved in C_6D_6 (marked signal: traces of C_6D_5H).

 Table 1. Comparison of the ¹³C NMR Chemical Shifts of the Carbon Atoms of 1 and 2



carbon atom	molecular complex 1 , ^{<i>a</i>} ppm	grafted complex 2 , ^{<i>b</i>} ppm
C1	147.0	140 (C1 + C2)
C2	140.1	140 (C1 + C2)
C3	124.2	124 (C3 + C4)
C4	127.0	124 (C3 + C4)
C5	28.7	29
C6	24.3 and 24.7	23 (C6 + C8)
C7	163.1	165
C8	22.9	23 (C6 + C8)
С9	-5.5	
C10	4.2	0.5

^a Dissolved in benzene. ^b Grafted onto SiO₂₋₍₇₀₀₎.

Table 2. EXAFS Parameters for the Supported Complex, 2^a

type of neighbor	number of neighbors	distance (Å)	σ^2 (Å ²)
<i>Ni</i> −OSi≡	1	1.86(2)	0.0044(16)
$Ni - \overline{C}H_2SiMe_3$	1	1.98(3)	0.008(3)
$Ni - \overline{N}Ar (= C <)$	2	2.06(2)	0.008^{b}
Ni-CH ₂ SiMe ₃ and Ni -OSi=	2	3.27(4)	0.013(5)

^{*a*} The errors generated by the EXAFS fitting program "RoundMidnight" are indicated in parentheses. Δk , [2.3 - 12.0 Å⁻¹] – ΔR , [0.8–3.3 Å]; $S_0^2 = 1.0$; $\Delta E_0 = -2.5 \pm 1.10$ eV (the same for all shells); fit residue, $\rho = 7.1\%$; quality factor, $(\Delta \chi)^2/\nu = 1.12$ ($\nu = 9/17$). ^{*b*} Shell constrained to the parameter above.

several other metals when they are grafted through one oxygen atom on an oxide support.^{30,31} These ¹³C solid-state NMR data features are reminiscent of those of the starting molecular complex **1** in solution (Figure 2b), with the above-mentioned exception of the **C9** signal.²⁷

The structure of the supported complex was further confirmed by the analysis of the Ni K-edge extended X-ray absorption fine structure (EXAFS) data (Table 2 and Figure S2 in the Supporting Information). The results are consistent with the following coordination sphere around Ni: one oxygen atom at 1.86(2) Å, in agreement with a σ -bonded siloxy, ^{32,33} one carbon atom at 1.98(3) Å, assigned to C9 of the neosilyl ligand, this distance is in good agreement with values obtained from crystallographic data of 1 (Ni-C at 1.955(2) Å),²⁷ and two nitrogen atoms at 2.06(2) Å, a distance that is longer than that found in complex 1 (Ni-N at 1.974(2) Å) but in the good range for such a Ni-N distance, which can reach up to 2.093-2.109(4) Å in $[{(2C_6F_5-C_6H_4)-N=C(Nap)-C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)=N-(2C_6F_5-C_6H_4)-N=C(Nap)+N=C(N$ C_6H_4]<u>Ni</u>Br₂] (Nap = 1,8-naphthidiyl).³⁴ Finally, the EXAFS data could be improved when the model included two silicon atoms at 3.27(4) Å, one corresponding to a remaining trimethylsilyl group (the two Ni--Si distances in Ni-CH₂-SiMe₃ are 3.286 and 3.228 Å in 1^{27}) and the other to the silicon of a surface siloxy group, Ni−O-Si≡.

In summary, the reaction of $[(\alpha \text{-diimine})\text{Ni}(\text{CH}_2\text{SiMe}_3)_2]$ (1) with SiO₂₋₍₇₀₀₎ leads to the formation of a well-defined surface complex $[(\equiv \text{SiO})\text{Ni}(\alpha \text{-diimine})(\text{CH}_2\text{SiMe}_3)]_{\text{SiO}_2-(700)}$ (2) (Scheme 1) in which the nickel atom is grafted to the surface via one covalent $\equiv \text{SiO}-\text{Ni}$ bond as evidenced by chemical and mass balance analyses, IR, solid-state NMR, and EXAFS.

Next, complex 2 was activated by gaseous BF_3 at -78 °C to room temperature, and no gas evolution occurred during the reaction. The elemental analysis of the resulting solid gave a

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Scheme 2. (a) Proposed Structure of 3, after Activation of 2 by BF₃; and (b) Strategies Used by Bönnemann et al.²⁶ To Obtain Active Sites for the Oligomerization of Olefins



Table 3. Summary of Ethylene Polymerization Data at 25 °C, Using 3 as Supported Catalyst

entry	Ni (µmol)	P (bar)	concentration (mol C ₂ H ₄ /L)	$\begin{array}{l} {\rm maximum} \\ {\rm activity}^a \\ ({\rm kg}_{\rm PE}/{\rm mol}_{\rm Ni} \times {\rm h}) \end{array}$	$\begin{array}{l} \text{productivity}^{b} \\ (\text{kg}_{\text{PE}}/\text{mol}_{\text{Ni}} \times \text{h}) \end{array}$	$M_{\rm w}^{\ c}$ (kg/mol)	$M_{ m w}/M_{ m n}{}^c$	SCB^d
1^e	6.1	0.53	0.022	12.9 (0.51 bar)	3.4 (9.0 h - 0.13 bar)	1282	4.73	128
2^{f}	9.3	22.5	1.07	1455 (18.4 bar)	370 (30 min - 7.8 bar)	477	4.10	74
3^g	28.5	4.0	0.62	1505 (4.0 bar)	860 (10 min - 4.0 bar)	281	2.85	71

^{*a*} From ethylene consumption, average pressure indicated in parentheses. ^{*b*} From the mass of polymer obtained after the quench of the reaction, time and final pressure are indicated in parentheses. ^{*c*} Obtained by SEC. ^{*d*} Branches/1000C, obtained by ¹H NMR. ^{*e*} Gas phase, 25 °C, no agitation. ^{*f*} Gas phase, autoclave filled with 20 g of Teflon powder, rpm = 900 during 30 min. ^{*s*} 25–30 °C, 4 bar, toluene (400 mL), stirring during 10 min.

C/Ni ratio of 31 ± 3 (th. 32 for **3**) and a N/Ni ratio of 2.3 ± 0.35 (th. 2 for **3**). The resulting species could not be observed by NMR, very likely due to the presence of paramagnetic species. We then suggest that the hard BF₃ Lewis acid reacted with the oxygen of the \equiv SiO-Ni bond rather than with the neosilyl carbon with the formation of a surface ion pair **3** (a in Scheme 2). Similarly, Bönnemann et al. reported that η^3 -allylnickel alkoxides { η^3 -C₃H₅NiOR}₂ (R = Me, Et, *i*-Pr, Ph, SiPh₃) may be activated by gaseous boron trifluoride (BF₃) to give active catalysts for the oligomerization of olefins in homogeneous phase (b in Scheme 2),²⁶ and, more recently, Lee and Bazan et al. have shown that B(C₆F₅)₃ could break a nickel-oxygen bond to create a cationic imino nickel complex.³⁵

The activated complex 3 has shown to be active for ethylene polymerization in an IR cell (533 mbar C₂H₄, 25 °C, entry 1 in Table 3) and produced a highly branched polymer with a value close to 128 branches per 1000 carbons (mainly methyl branches, ca. 83%; 6% ethyl branches, 2% propyl, 3% butyl, 1% amyl, and less than 5% of long branches $> C_5$), while in the same conditions complex 2 was not active. A polymerization test was then carried out with catalyst 3 in a batch reactor at 25 °C without solvent, starting with an ethylene pressure of 22.5 bar for a C_2H_4/Ni molar ratio of ca. 7700 (entry 2 in Table 3). The productivity of the catalyst, calculated by weighing the obtained polymeric product, was 370 kg_{PE}/mol_{Ni} \times h after a 30 min run. The polymer formed during this experiment was also characterized by ¹H and ¹³C NMR spectroscopy^{36,37} and size exclusion chromatography (SEC). It appears that the degree of branching of the polymer obtained is lower but relatively high for such an ethylene concentration, with a value close to 74 branches per 1000 carbons (mainly methyl branches, ca. 73%; 10% ethyl branches, 8% propyl, 3% butyl, 3% amyl, and less than 3% of long branches > C₅), with a $M_{\rm w}$ of 478 kg mol⁻¹ and a $M_{\rm n}$ of 116 kg mol⁻¹, which gives a $M_{\rm w}/M_{\rm n}$ ratio of 4.10

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 $(M_{\rm w}, {\rm weight average molecular weight; and } M_{\rm n}, {\rm number average}$ molecular weight). For comparison, a polymerization experiment was carried out with suspended particles of the supported catalyst 3 in toluene, allowing one to follow more conveniently the evolution of the temperature of the reaction medium (entry 3 in Table 3). It appeared that this temperature increased from 25 to 30 °C within ca. 30 s, due to the exothermicity of the reaction, and could be maintained at this level for the rest of the run. In these conditions, the initial rate of polymerization, 1505 kg_{PE}/mol_{Ni} \times h, and the degree of branching of the polymer, 71 branches per 1000 carbons (mainly methyl branches, ca. 77%; 8% ethyl branches, 5% propyl, 3% butyl, 3% amyl, and less than 4% of long branches $> C_5$), are similar to those obtained without solvent (entry 2), while the ethylene concentration is lower for the run in toluene than for the gas-phase run. In the gas-phase run, a higher local temperature of the catalyst particles, due to the highly exothermic polymerization reaction with the heat dissipation not as efficient as in toluene, may contribute to increase the branching of the polymer and decrease the catalyst lifetime and thus the turnover number.

The best productivity obtained with the supported diimine nickel catalyst **3**, 860 kg_{PE}/mol_{Ni} × h under 4 bar ethylene, that is, 215 kg_{PE}/(mol_{Ni} × h × bar) for a 10 min run in toluene at 30 °C, is rather low as compared to that obtained with soluble molecular diimine nickel complexes, for example, up to 4540 kg_{PE}/(mol_{Ni} × h × bar) for a 10 min run in toluene at 35 °C,³⁴ while the polymers obtained with this homogeneous catalytic system were also highly branched, from 24 branches per 1000 carbons under 200 psig ethylene (ca. 1.7 mol C₂H₄/L) to 106 branches per 1000 carbons under 1 atm (ca. 0.12 mol C₂H₄/L). Productivities higher than those observed for **3** were also reported in the case of supported diimine Ni complexes tethered to a silica support pretreated with trimethyl aluminum:^{19,20}

⁽³⁶⁾ Gottfried, A. C.; Brookhart, M. Macromolecules 2003, 36, 3085–3100.

⁽³⁷⁾ Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620–1625.

370–400 kg_{PE}/g_{Ni} at 30 °C and 284–820 kg_{PE}/g_{Ni} at 60 °C for 2 h runs under 150 psig ethylene, which are equivalent to around 950–1040 kg_{PE}/(mol_{Ni} × h × bar) at 30 °C and 730–2120 kg_{PE}/(mol_{Ni} × h × bar) at 60 °C. High productivities, 1190–7158 kg_{PE}/(mol_{Ni} × h × bar) at 50 °C under 5 bar ethylene pressure after a 1 h run (up to 11416 kg_{PE}/(mol_{Ni} × h × bar) for a 30 min run), have also been reported by Severn et al. for nickel complexes immobilized on a support of composition MgCl₂ · AlEt_{2.3}(OEt)_{0.7}, and the polymers produced presented 7 to 26 branches per 1000 carbons.³⁸

The activity of the supported nickel complex 3 seems thus rather low by comparison with the homogeneous or the most active supported nickel diimine systems reported in literature. Several explanations can be considered. It may be that an oxide surface too close to the cationic site is not a favorable environment for a polymerization catalyst. The surface would indeed occupy a significant portion of the coordination sphere, which may restrict the olefin coordination. The catalyst mobility may also be a factor: the lower mobility of these supported complexes as compared to their molecular analogs in solution probably results in a lower activity. It may be also that, in the case of this particular supported nickel diimine complex 3, the insertion of ethylene in the Ni-R polymer growing chain is less efficient, due to a metal environment (surface anion, ligands), which lowers the electrophilic character of the Ni cationic center. Considering all of these aspects, by comparing our results on the cationic complex 3 firmly anchored on the silica support with published results on other supported α -diimine nickel complexes, it seems to us that the design of a more efficient supported catalyst should include the formation of a cationic nickel complex with a better charge separation, and a weaker link with the surface to increase the nickel accessibility, mobility, and electrophilic character.

Conclusion

A new strategy has been designed to anchor a nickel α -diimine complex onto silica via surface organometallic chemistry. With such an approach, a very well-defined Ni surface compound has been synthesized, $[(\equiv SiO)Ni(\alpha$ diimine)(CH₂SiMe₃)]_{SiO2-(700)} (2) (α -diimine = (2,6-^{*i*}Pr₂C₆H₄)-N=CMe-CMe=N($2,6^{-i}Pr_2C_6H_4$)). This complex, covalently bonded to silica, was well characterized via chemical and mass balance analyses, infrared, solid-state NMR, and EXAFS. Complex 2 was then activated by gaseous BF₃ to give a still pair hypothetical surface ion $[\equiv SiO - BF_3]^-[Ni(\alpha$ diimine)(CH₂SiMe₃)]⁺ **3**, which is active for the gas-phase ethylene polymerization to produce polyethylene with a high degree of branching. The lower activity of this complex as compared to the most productive supported diimine nickel systems may be attributed to a lower mobility and electrophilic character of its nickel cationic center.

Experimental Section

General Procedure. All experiments were carried out by using standard Schlenk and glovebox techniques for the organometallic synthesis. Solvents were purified and dried according to standard procedures. C_6D_6 (SDS) was distilled over Na/benzophenone and stored over 3 Å molecular sieves. Other chemicals were used as received unless otherwise specified: 2,3-butanedione (97%, Aldrich), 2,6-diisopropylaniline (97%, Aldrich), formic acid (96%, Aldrich), Ni(Acac)₂ (99%, Strem, stored in the glovebox), and (trimethylsi-

lylmethyl)magnesium chloride (1.0 M in diethyl ether, Aldrich). Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and an Al₂O₃/KCl on fused silica column (50 m \times 0.32 mm).

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Elemental analyses were performed at the CNRS Central Analysis Department of Solaize, France, or at Pascher Mikroanalytisches Labor in Remagen, Germany. IR spectra were recorded on a Nicolet 5700-FT by using an IR cell equipped with CaF_2 windows, allowing in situ studies. Typically, 16 scans were accumulated for each spectrum (resolution, 2 cm⁻¹). Solution NMR spectra were recorded on an Avance-300 Brüker spectrometer. All chemical shifts were measured relative to residual ¹H or ¹³C resonance in the deuterated solvents: C_6D_6 , δ 7.15 ppm for ¹H, 128 ppm for ¹³C.

Preparation of [(α-Diimine)Ni(CH₂SiMe₃)₂], **1.** The molecular precursor [(α-diimine)Ni(CH₂SiMe₃)₂] **1** was prepared following the literature procedure²⁷ but starting from Ni(acac)₂, ^{11,39} with a 52% yield from Ni(acac)₂. ¹³C{¹H} NMR (100.6 MHz, C₆D₆): δ (ppm) -5.5 (CH₂SiMe₃), 4.2 (SiCH₃), 22.9 (*N*=CCH₃), 24.3, 24.7 (CH(CH₃)₂), 28.7 (CHMe₂), 124.2 (meta-*C*), 127.0 (para-*C*), 140.1 (ortho-*C*), 147.0 (ipso-C), 163.1 (N=CMe).

Preparation of SiO₂₋₍₇₀₀₎. Aerosil silica from Degussa with a specific area of 200 m² g⁻¹ was partially dehydroxylated at 700 °C under high vacuum (10^{-5} torr) for 15 h to give a white solid having a specific surface area of 190 m² g⁻¹ and containing 0.7 OH nm⁻².

Preparation of 2 by Impregnation of 1 onto SiO₂₋₍₇₀₀₎. A solution of [(α-diimine)Ni(CH₂SiMe₃)₂] (1) (300 mg, 0.49 mmol) in benzene (5 mL) and SiO₂₋₍₇₀₀₎ (1.014 g, 0.22 mmol \equiv SiOH) was stirred at 25 °C for 4 h. After filtration, all volatile compounds were condensed into another reactor (of known volume) to quantify the tetramethylsilane evolved during grafting. The solid was then washed five times with benzene and pentane, and the resulting blue powder was dried under vacuum (10^{-5} torr) to yield 1.070 g of 2. Analysis by gas chromatography indicated the formation of tetramethylsilane during the grafting (1.0 ± 0.1 TMS/Ni). Elemental analysis of 2: Ni 0.76 wt %; C 5.15 wt %; N 0.42 wt %. For the IR study, a disk of Aerosil silica (30 mg, 17 mm diameter, pressed at 800 kg/cm²) was calcined for 4 h in air at 700 °C in a quartz sample holder within a quartz tube. This tube was then connected to a vacuum line (10^{-5} mbar) and kept for 15 h at this temperature. Within an argon filled drybox the silica disk was then dipped into a toluene solution of **1** (70 mg, 0.11 mmol in 10 mL of toluene) for 4 h at room temperature and was further washed twice with 10 mL of toluene (1 h each time) to eliminate the excess of complex and washed twice with 10 mL of pentane to eliminate the adsorbed toluene. Elemental analysis: Ni 0.70 wt %; C 4.78 wt %.

Preparation of 3 by Treatment under BF₃ of the Supported Complex [(\equiv SiO)Ni(α -diimine)(CH₂SiMe₃)]_{SiO2-(700)}, 2. In a 375 mL reactor, 500 mg of [(\equiv SiO)Ni(α -diimine)(CH₂SiMe₃)]_{SiO2-(700)} (0.065 mmol of Ni) was treated under 100 mbar of BF₃ at -78 °C. The color of the solid turned from blue to green. After 30 min, the excess of gaseous BF₃ was removed under vacuum while the sample was allowed to warm slowly to room temperature. The thus obtained product, **3**, was directly used in ethylene polymerization.

¹H MAS and ¹³C CP MAS solid-state NMR spectra were recorded on a Brüker Avance-500 spectrometer with a conventional double-resonance 4 mm CP-MAS probe. The samples were introduced under argon in a zirconia rotor, which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz unless otherwise specified. Chemical shifts were given with respect to TMS as external reference for ¹H and ¹³C NMR.

X-ray absorption spectra were acquired at LURE in Orsay (France) on beam-line D44, at room temperature at the nickel

⁽³⁸⁾ Severn, J. R.; Chadwick, J. C.; Van Axel Castelli, V. *Macromolecules* **2004**, *37*, 6258–6259.

⁽³⁹⁾ Svoboda, M.; Tom Dieck, H. J. Organomet. Chem. **1980**, 191, 321–328.

K-edge, with a double crystal Si(111) monochromator detuned to reduce the higher harmonics of the beam. The spectra were recorded in the transmission mode between 8.2 and 9.2 keV. The samples were packaged within a dry glovebox in a double airtight sample holder equipped with kapton windows. The spectra analyzed were the results of four such acquisitions, and no evolution could be observed between the first and last acquisition. The data analyses were performed by standard procedures using the programs developed by Alain Michalowicz, in particular the new version of the EXAFS fitting program RoundMidnight.⁴⁰ As recommended by the Standards and Criteria Committee of the International XAFS Society,⁴¹ an improvement of the fit took into account the number of fitted parameters (decrease of the quality factor, $(\Delta \chi)^2/\nu$, where ν is the number of degrees of freedom in the signal).

Polymerization of Ethylene, General Procedure. All experiments were carried out by using standard air-free methodology. In particular, the reactors were filled within a dry argon atmosphere glovebox. Ethylene was dried over a deoxo catalyst (BASF R3-11 and 4 Å molecular sieves) prior to use.

Gas-Phase Polymerization Runs Followed by IR Spectroscopy. A precise mass of the activated catalysts [$(\equiv$ SiOBF₃][Ni(α diimine)(CH₂SiMe₃)] (3) was introduced into a break-seal reactor. The break-seal tube was then sealed and connected to an IR cell of ca. 310 mL equipped with CaF₂ windows. A pressure of dry ethylene (533 mbar) was introduced at ambient temperature, and a spectrum of the gas phase was recorded. The sealed reactor was then broken, and the consumption of ethylene was followed by recording the infrared spectrum of the gas phase at room temperature as a function of time. The maximum catalyst activity was observed between 5 and 10 min (average pressure of 506 mbar). The reaction was quenched after 9 h; the ethylene pressure inside the IR cell had then dropped from 0.53 to 0.13 bar (entry 1 in Table 3). The polymer formed was analyzed by SEC and ¹³C NMR.

Gas-Phase Polymerization Runs in an Autoclave. The activated supported catalyst [(\equiv SiOBF₃][Ni(α -diimine)(CH₂SiMe₃)] (**3**) was introduced into a 77 mL batch reactor (66 mL, with 11 mL Teflon) filled with Teflon powder (20 g, 400 μ m diameter particles). After the removal of argon under vacuum, the reactor was charged with 22.5 bar of ethylene at room temperature (entry 2 in Table 3). The polymerization activity was followed from the kinetic measurements of the pressure drop into the reactor with time (Figure S3). The maximum catalyst activity was observed between 3 and 4 min (average pressure of 18.4 bar). After 30 min, the pressure inside the reactor had dropped from 22.5 to 7.8 bar. The ethylene was then degassed, and the polymerization was quenched by the addition of methanol. The polymer was then purified by dissolution into 1,2,4-trichlorobenzene, using a Soxhlet. Finally, the polymer was

precipitated by adding methanol, filtered and washed with methanol, and dried for 5 h at 100 °C under vacuum. The activity, expressed in kilograms of PE per mole of Ni per hour, was represented as a function of time. Catalyst productivity (expressed in kilograms of PE per mole of Ni per hour) was calculated from the weight of polymer obtained.

Polymerization Runs in Toluene. The activated supported catalysts [(\equiv SiOBF₃][Ni(α -diimine)(CH₂SiMe₃)] (**3**), maintained in a sealed glass sphere, were introduced into a 500 mL roundbottom flask, and then charged with toluene and equipped with a mechanical stirrer and a thermometer (entry 3 in Table 3). The ethylene pressure in the reactor (4 bar) was kept constant during the reaction by supplying the monomer from a large volume reservoir through a control valve. The glass sphere containing the catalyst was broken with the stirrer, and the polymerization activity of the catalyst was followed from the kinetic measurements of the pressure drop into the ethylene reservoir. The temperature of the reactor was initially stabilized at 25 °C but rapidly rose to 30 °C within ca. 30 s and could be maintained by cooling with a cool water circulator for the rest of the run. The maximum catalyst activity was observed between 1 and 2 min. The reaction time for a polymerization experiment was 10 min, and then unreacted ethylene was vented and the polymerization product was stirred with methanol to quench the polymerization. Finally, the polymer was filtered and washed with toluene and methanol and dried for 5 h at 100 °C under vacuum.

Characterization of the Polymers. High temperature SEC analyses were performed using a Waters Alliance GPCV 2000 chromatograph equipped with three columns (2 Styragel HT6E and 1 Styragel HT2). Samples (1 mg mL⁻¹) were eluted with trichlorobenzene with a flow rate of 1 mL min⁻¹ at 150 °C. Online detection was performed by refractometry and viscosimetric measurements using Waters equipments. The polymers were characterized by ¹H and ¹³C NMR spectroscopy in a 5/1 mixture of 1,2,4-trichlorobenzene and C₆D₆ at 105 °C (378 K). The branching numbers for PE were determined by ¹H NMR spectroscopy using the ratio of number of methyl groups to overall number of carbons and were reported as branches per thousand carbons.³⁶ ¹³C NMR spectroscopy was used to examine the types of branches and determine their proportions in the polymers.^{37,42}

Supporting Information Available: ¹H NMR spectrum of the nickel(diimine) complex **2** grafted onto $SiO_{2-(700)}$ (MAS NMR); nickel K-edge k^3 -weighted EXAFS and corresponding Fourier transform with comparison to simulated curves for silica supported complex **2**; and evolution of the pressure with time during a gasphase polymerization test (entry 2 in Table 3).This material is available free of charge via the Internet at http://pubs.acs.org.

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