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A Well-Defined Silica-Supported Lanthanum Bis(phosphinimino)methanide

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Grafting of the bis(phosphinimino)methanide complex [La{CH(PPh$_2$NSiMe$_3$)$_2$}{N(SiHMe$_2$)$_2$}$_2$] (**1**) onto dehydroxylated silica (SiO$_2$-700) affords material **2**. Full characterization of this material by infrared spectroscopy, elemental analysis, and multinuclear, multidimensional solid-state NMR spectroscopy showed formation of well-defined bis(phosphinimino)methanide amido surface species, [(≡SiO)La{CH(PPh$_2$NSiMe$_3$)$_2$}{N(SiHMe$_2$)$_2$}], along with [≡SiOSiHMe$_2$] sites.

Introduction

Immobilization of organometallic catalysts is an attractive entry into the design of cleaner processes. In view of obtaining highly selective catalytic systems, a most promising approach is the synthesis of heterogeneous systems bearing a single type of active site, behaving in a well-understood fashion.[1] Such well-defined supported catalysts may be obtained through reaction of organometallic species with a conveniently prepared inorganic support.[1b] Indeed, we have recently shown that this may be efficiently carried out with rare-earth metals grafted onto silica, as use of a partially dehydroxylated silica support leads to selective formation of a material bearing a single type of surface species:[2] This stems from the reaction of isolated silanol groups with a single Ln–N bond of homoleptic [Ln{N(SiMe$_3$)$_2$}$_3$] to afford selectively the [(≡SiO)Ln{N(SiMe$_3$)$_2$}$_2$] surface species. Bearing in mind that controlled grafting of lanthanide amide species may be envisioned by following this approach, we aimed at the immobilization of amido derivatives of rare-earth metals bearing the bulky, monoanionic bis(phosphinimino)methanide ligand.[3] Indeed, according to our observations on selective grafting of homoleptic lanthanide tris(amido) derivatives,[2] we considered that [Ln{L}{NR$_2$}$_2$] species [where L is a bis(phosphinimino)methanide ligand] should react with isolated silanols in a similar way, namely by selectively affording monografted species of the type [(≡SiO)La{L}{NR$_2$}] through protonolysis of a single metal–nitrogen bond. Complexes bearing this ligand have been demonstrated to behave as efficient catalysts in a variety of reactions.[4] We describe in this communication our preliminary results on the grafting of a lanthanum bis(phosphinimino)methanide derivative, its characterization, and its reactivity in hydroamination/cyclization and hydrosilylation reactions.

Results and Discussion

A toluene solution of the bis(silylamide) complex [La{CH(PPh$_2$NSiMe$_3$)$_2$}{N(SiHMe$_2$)$_2$}$_2$] (**1**) was added to a toluene suspension of silica dehydroxylated at 700 °C (SiO$_2$-700), which only bears isolated silanols as protic surface groups (Scheme 1). Monitoring the supernatant composition by ^{1}H NMR spectroscopy demonstrated that a fast reaction took place, with release of HN(SiHMe$_2$)$_2$, in a similar manner to our observations for the reaction of [Ln{N(SiMe$_3$)$_2$}$_3$] with SiO$_2$-700.[2b] The resulting material **2** was repeatedly washed with toluene and dried under vacuum. Elemental analyses indicate a La content of 2.55 (wt.-%), which corresponds to a surface density of 0.32 La atoms per nm^2. The loading does not reach the maximal value (about 0.9 La atoms per nm^2), which may be not only because of the bulkiness of the incoming complex, but also to a silylation side-reaction of the silanols as already observed in comparable systems: the tetramethyldisilazane released in the grafting reaction reacts with surface silanols to afford ≡SiOSiHMe$_2$ groups.[5] N/La and P/La ratios of 3.0 and 2.0, respectively, indicate the formation of a surface

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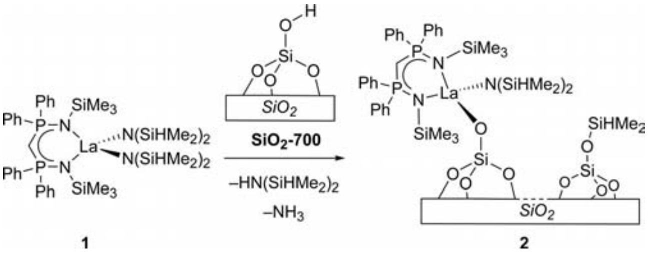
species that can be formulated as [(≡SiO)La{CH-$(PPh_2NSiMe_3)_2$}{$N(SiHMe_2)_2$}] (in accordance with theoretical values of 3 and 2 for N/La and P/La, respectively). Furthermore, the amount of silanols capped by $SiHMe_2$ groups can be estimated from the percentage of carbon (%C = 8.18): this result indicates that about one third of the silanols initially present are involved in SiOLn bonding and two thirds are silylated.



Scheme 1. Synthesis of material **2**.

Infrared spectra of SiO_2-700 and material **2** are compared in Figure 1. Disappearance of the sharp isolated silanol peak at 3947 cm^{-1} indicates full reaction of the surface silanols, either with the grafted complex or with tetramethyldisilazane. Such a completely hydrophobic surface may be advantageous for catalysis.[6] Elongation vibrations of aromatic (3080–3012 cm^{-1}) and aliphatic (2954–2900 cm^{-1}) C–H bonds are consistent with grafting of **1** onto silica. Furthermore, ν(Si–H) bands are also detected at 2150 and 2065 cm^{-1}. Comparatively, a material bearing ≡$SiOSiHMe_2$ groups [obtained from reaction of SiO_2-700 with $HN(SiHMe_2)_2$] gives rise to a band centered at 2150 cm^{-1} (Figure 1). For comparison, **1** exhibits bands at 2147 and 2044 cm^{-1}.[4c] Anwander and co-workers demonstrated that the ν(SiH) band may be used as a sensitive probe for distinguishing SiH bonding situations.[7] The spectral features of **2** in the SiH stretching region thus indicate both the presence of surface ≡$SiOSiHMe_2$ groups and of SiH groups interacting with the metal center. Further bands comprise C–C deformation bands at 1590, 1576, 1486, and 1438 cm^{-1}. The minor shifts compared to **1** do not allow us to draw conclusions regarding the evolution of the bonding situation in **2**. Interestingly, no coordinated ammonia originating from the silylation of silanols by $HN(SiHMe_2)_2$ was detected.[2b]

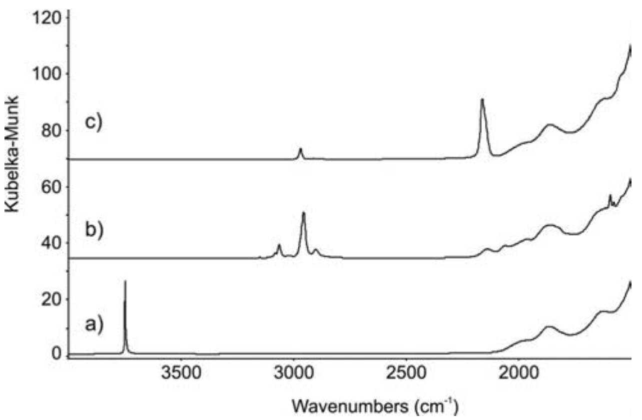


Figure 1. Diffuse reflectance infrared spectra of (a) SiO_2-700, (b) **2**, and (c) $SiHMe_2$-derivatized SiO_2-700.

Solid-state NMR spectroscopy is proven to be a powerful tool for analysis of grafted species.[8] More precisely, to get a deeper insight into the structure of surface species, we can rely on bidimensional solid-state NMR spectroscopy. The ^1H MAS NMR spectrum of **2** features broad signals in the aromatic region, at 7.1 ppm (with a shoulder at 7.5 ppm), a signal at 5.0 ppm accounting for SiH groups, and an intense peak at 0 ppm (SiMe) with a shoulder at 1.9 ppm (Figure 2a). This last signal may be assigned to the methanide proton, as it resonates at δ = 2.35 ppm in the case of **1** (C_6D_6). Bidimensional ^1H-^1H double-quanta MAS NMR spectroscopy, which gives information about spatial proximities of protons through observation of dipolar coupling exchange, was used in order to refine these assignments and confirm the proposed structure (Figure 2b). Three major off-diagonal interactions are observed: correlations A, B, and C involve the pairs of signals at 5.0/0.0, 7.1/–0.1, and 7.5/1.9 (ppm/ppm), respectively. Interaction A stems from the $SiHMe_2$ groups. The two other interactions involve protons located within the bis(phosphinimino)methanide ligand: *ortho* and *meta* aromatic and methylsilyl protons (B), and *ortho* aromatic and methanide protons (C) are observed. As expected from isolated protons, the SiH and CH protons do not afford an on-diagonal signal.

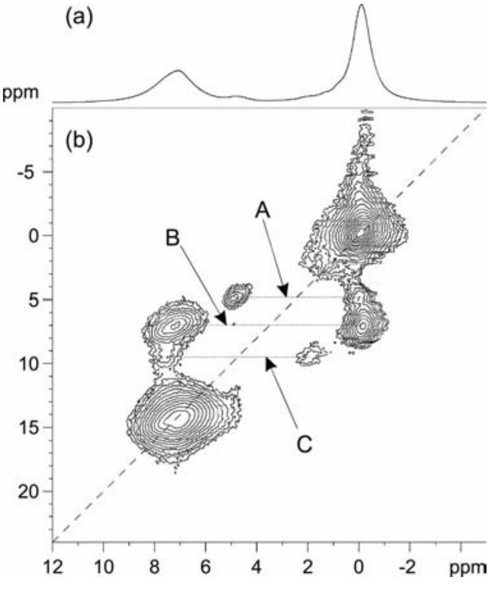


Figure 2. ^1H (a) and ^1H-^1H DQ (b) MAS spectra of **2**.

The ^{13}C CP MAS spectrum comprises signals at 130.6, 127.0 (aromatics), 16.6 (CH), and 1.4 ppm (broad, SiMe groups) [Supporting Information]. The *C*H located between the two phosphorus atoms gives rise to a weak signal, and – despite extended acquisition times – no ^{13}C-^1H correlation was detected between the signal of this carbon atom and the one assigned to the methanide C*H* (δ =1.9 ppm) in the ^{13}C-^1H CP HETCOR spectrum (see Supporting Information).

The ^{31}P-^{1}H CP MAS spectrum consists of a single signal centered at δ = 15.6 ppm, with a half-height width of 700 Hz, which compares well to the spectroscopic data of **1** (δ = 17.1 ppm in C_6D_6).[4c] The ^{31}P-^{1}H HETCOR spectrum allowed the further confirmation of the assignment of the C*H* signal (Figure 3). By using a mixing time of 2 ms, the ^{31}P signal was shown to correlate with signals at 7.1, 1.9, and 0.0 ppm. The aromatic and methylsilyl groups obviously account for the first and third of these spots, respectively, while the correlation at 1.9 ppm is the interaction of the C*H* of the *N*,*N* ligand with the two close phosphorus nuclei. Indeed, shortening the mixing time to 0.5 ms, and thereby decreasing the distance probed around the ^{31}P nuclei, resulted in the observation of a single correlation spot, at 1.9 ppm, confirming the assignment of this signal as the one corresponding to the methanide proton.

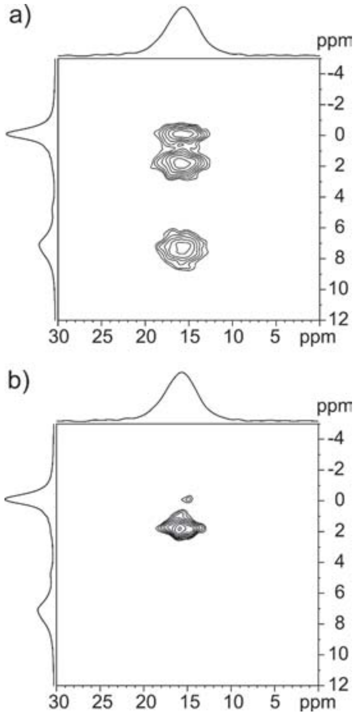


Figure 3. ^{31}P-^{1}H CP HETCOR NMR spectrum of **2**, with a mixing time of (a) 2 ms and (b) 0.5 ms.

In contrast to the nonsupported compound **1**, which shows remarkable activity as catalyst in the hydroamination/cyclization and the hydrosilylation reactions, no activity was observed when material **2** was used as catalyst in these reactions. Attempts to cyclize 2,2-diphenylpent-4-en-1-amine and [1-(pent-2-ynyl)cyclohexyl]methanamine at 120 °C in the presence of **2** failed. Also, the reaction of 1-hexene with $PhSiH_3$ did not result in any hydrosilylation product. Obviously, the activity of the homogeneous catalyst **1** is significantly influenced upon grafting. Although it is a frequently reported observation that grafting a homogeneous catalyst slows down its activity, further efforts will be devoted to the investigation of this point, by studying the fate of the grafted species under the considered reaction conditions.

Conclusions

In this work, we have demonstrated that well-defined sites of rare-earth species bearing a bis(phosphinimino)methanide ligand can be efficiently introduced onto a silica surface. The residual metal–amido function may be used for further functionalization or for applications other than the reported catalytic use, as bis(phosphinimino)methanide-based metal complexes have demonstrated a significant potential in this field. Investigations are under way to check these issues.

Experimental Section

General Considerations: Manipulations were carried out under an argon atmosphere in an M-Braun glove-box or by using Schlenk techniques. Solvents were dried by using conventional reagents and stored in the glove-box over 3Å molecular sieves. Complex **1** was prepared by following literature procedures.[4c] Liquid-state NMR spectroscopic analyses were run with a Bruker Avance 300 spectrometer. Solid-state MAS NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{31}P: 161.2 MHz). For ^{1}H experiments, the spinning frequency was 20 kHz, the recycle delay was 5 s, and 64 scans were collected with a 90° pulse excitation of 3 µs. The two-dimensional homonuclear experiment (DQ-MAS) was obtained at a spinning frequency of 20 kHz by using excitation and reconversion pulse blocks of two rotor periods each (100 µs). The 90° pulse length was 3 µs, the recycle delay was 5 s, and 16 scans were collected for each slice. The ^{31}P spectra were acquired at a spinning frequency of 14 kHz, the recycle delay was 30 s, and 64 scans were collected. During acquisition, the proton-decoupling field strength was set to 83 kHz. The ^{31}P-^{1}H CP HETCOR experiments were performed at a spinning frequency of 10 kHz, with a recycle delay of 5 s, and 1024 scans were collected. For the CP step, a ramped radio frequency (RF) field centered at 50 kHz was applied on protons, while the ^{31}P RF field was matched to obtain an optimal signal. The contact times were set to 2 and 0.5 ms. Chemical shifts are given with respect to TMS and phosphoric acid (85%) as external references for ^{1}H-^{13}C and ^{31}P NMR spectroscopy, respectively. Diffuse reflectance infrared spectra were collected with a Harrick cell on a Nicolet Avatar spectrometer fitted with a MCT detector. Elemental analyses were carried out at the Service Central d'Analyse du CNRS (metals and phosphorus) and in the Service d'Analyse Elémentaire, LSEO, Université de Bourgogne (C, H, N). Aerosil 380 silica (Degussa, specific area 380 m^2g^{-1} prior to heat-treatment) was subjected to heating under secondary vacuum (10^{-6} Torr) at 500 °C over 15 h followed by 4 h of heating at 700 °C and stored in a glove-box.

Synthesis of 2: In the glove-box, a double-Schlenk apparatus was loaded with molecular precursor **1** (370 mg, 0.385 mmol) dissolved in toluene (15 mL) in one compartment and with silica dehydroxylated at 700 °C (1.0 g) suspended in toluene (25 mL) in the other compartment. The complex solution was added to the support by filtering through the sintered glass separating the two Schlenk tubes, and the reaction mixture was stirred for 15 h at room temperature. The supernatant liquid was then separated by filtration into the other compartment, from which toluene was transferred in the gas phase by trap-to-trap distillation back into the compartment containing the modified support in order to wash away the residual molecular precursor. This operation was repeated twice.

The resulting white powder **2** was then dried under secondary vacuum (3×10^{-6} Torr) at 60 °C for 6 h. Elemental analysis: La 2.55, C 8.18, H 1.13, N 0.77, P 1.13.

Supporting Information (see footnote on the first page of this article): ^{13}C-^{1}H CP MAS and ^{13}C-^{1}H HETCOR CP MAS spectra of **2**.

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