Novel Zirconocene Hydride Complexes in Homogeneous and in SiO₂-Supported Olefin-Polymerization Catalysts Modified with Diisobutylaluminum Hydride or Triisobutylaluminum

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Reactive species in SiO₂-supported, zirconocene-based olefin-polymerization catalysts have been characterized by comparison of their UV-vis spectra with those of related, NMR-spectroscopically identified catalyst species in homogeneous solution. Neutral zirconocene dihydride complexes are found to arise in hydrocarbon solutions as well as on SiO₂ supports when catalyst systems that contain *rac*-Me₂Si(ind)₂ZrCl₂ and methylaluminoxane (MAO) are modified by addition of diisobutylaluminum hydride or triisobutylaluminum. These complexes, tentatively formulated as adducts with Lewis-acidic alkylaluminum species AlR₂X, *rac*-Me₂Si(ind)₂ZrH₂ · {*n*AlR₂X}, are reconverted into the initial reactive zirconocene cations upon addition of isobutene to these reaction systems.

Introduction

For most of their practical applications, zirconocene catalysts for the polymerization of olefins have to be 'heterogenized' by adsorption onto solid support materials, to allow their use as 'drop-in' substitutes for hitherto

commonly used solid-state catalysts in existing industrial production plants. Silica-gel support materials are most frequently used for this purpose, since they are easily fragmentized and furnish polyolefin resins with controlled spherical morphology, which contain the minute mass fraction of their catalyst ingredients as sub-micrometer-sized, visually undetectable fragments.^[1] For these SiO₂-supported catalysts, reactive catalyst species and their essential reaction paths are tacitly assumed to be the same as for their homogeneously dissolved analogs, for which many reaction steps have been elucidated in detail, mainly by NMR spectroscopic methods.^[2] In fact, however, SiO₂-supported polymerization catalysts are still eluding a comparably satisfactory characterization at the molecular level, despite serious efforts toward this goal.^[3] An impediment in this regard appears to be the difficulty to obtain adequate solid-state NMR spectra from the

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small fraction of organometallic compounds which these supported catalysts contain.

In view of the practical importance of 'heterogenized' catalyst systems, we have set out to approach their further characterization by parallel NMR and UV-vis spectroscopic studies. In previous studies it has been shown that reactions of zirconocene complexes can be monitored by UV-vis spectroscopy, even when these complexes are adsorbed on solid SiO₂ supports.^[3d,3e] In order to utilize this feat for a structural characterization of SiO₂-supported catalyst species, we have first followed reactions of methylaluminoxane (MAO)-activated zirconocene catalyst systems in homogeneous solutions by recording, in parallel, their NMR and UV-vis spectra. These data were then correlated with UV-vis spectroscopic changes of the corresponding supported catalysts in order to transfer the structural information obtained for homogeneously dissolved catalysts to their heterogenized counterparts.

To document the feasibility of such an approach, which would circumvent the necessity of solid-state NMR measurements, we have chosen as an example MAO-activated *rac*-Me₂Si(ind)₂ZrCl₂ (SBIZrCl₂). In a previous study it had been noticed that modification of this catalyst system by added triisobutylaluminum (Al^{*i*}Bu₃) induces, apart from cations of the type SBIZr(μ-Me)₂Al(^{*i*}Bu)₂⁺, also a partial conversion into a hitherto unrecorded type of zirconocene hydride.^[2n] The aims of our present work are to characterize these hydride species with regard to the conditions of their formation, their composition, and their reactivity and to compare, at the same time, homogeneously dissolved and SiO₂-supported catalyst systems in these regards by combined NMR and UV-vis studies, as outlined above.

Experimental Part

All experiments were carried out under an atmosphere of dry nitrogen or argon, using either Schlenk or glovebox techniques. Benzene-d₆, toluene, and decalin were dried over molecular sieves (4 Å) prior to use; decalin and toluene were then distilled from sodium metal and stored under argon. SBIZrCl₂ was prepared according to published procedures.^[4] Samples of the industrially used zirconocenes, *rac*-Me₂Si(2-Me-4-Ph-ind)₂ZrCl₂ and *rac*-Me₂Si(2-Me-benzind)₂ZrCl₂,^[5] were obtained as gifts from BASSELL Polyolefine GmbH.

Aluminum Alkyl Reagents

An MAO solution in toluene (1.8 M in Al, Al₂Me₆ content ≈30%), obtained as a gift from Chemtura (Bergkamen), was evaporated to dryness under vacuum at room temperature and then kept in a dynamic vacuum at 50 °C for 3 h, to give free-flowing solid MAO. Of this solid, 1.37 g were dissolved in 9 mL of C₆D₆, to give a MAO solution with [Al]_{MAO} = 2.0 M, based on an Al content of 36 ±

1 wt.-% of solid MAO prepared in this manner.^[3f] From solutions of triisobutyl aluminium (Al^{*i*}Bu₃, 1 M in toluene) and diisobutyl aluminium hydride (HAl^{*i*}Bu₂, 1.0 M in toluene), purchased from Aldrich, toluene was evaporated under vacuum and the respective residues were redissolved in C₆D₆ to give the same volume as the original solutions.

SiO₂/MAO Support

Following a method given in ref.^[1f], a sample of 9.0 g of silica gel (Grace XPO 2326, dehydroxylated under vacuum (10 mbar) at 180 °C for 8 h, donated by BASSELL GmbH), was suspended in 73 mL of toluene under an Ar atmosphere. To this suspension, 44.2 mL of a commercial toluene solution of MAO ([Al]_{tot} = 1.8 M, 30% of it as Al₂Me₆, which corresponds to 8.8 mmol of Al per g of silica) were added over a period of 30 min at room temperature and shaken for 2 h. The solid was then collected by filtration and dried in a stream of Ar for 5 h to give ≈15 g of a free-flowing powder, for which we estimated a content of 14.5 wt.-% Al or 5.3 mmol Al per g of the SiO₂/MAO support, based on a complete adsorption of all MAO added and the associated weight gain of 6 g.

SiO₂/MAO Supported Zirconocene Catalysts

Of the dried SiO₂/MAO support thus obtained, 7.50 g were suspended in 25 mL of a toluene solution of 16.7 mg (35 μmol) of SBIZrCl₂ under an argon atmosphere and shaken for 3.5 h, at which time the supernatant solution had become completely colorless. The solid was then collected by filtration and dried in a slow stream of argon for ≈4 h until a free-flowing, orange-colored powder was obtained. Based on complete adsorption of all SBIZrCl₂ used, a Zr content of ≈4.3 μmol per g of support, which corresponds to a ratio of [Al]_{MAO}/[Zr] ≈ 1 200, was assumed.

NMR Spectroscopy

¹H NMR spectra were recorded on a Varian INOVA-400 spectrometer at 22 °C in standard 5 mm NMR tubes. ¹H NMR operating conditions: spectrometer frequency 399.76 MHz, spectral width 6.4 kHz, pulse width 5.2 μs (45°), 6.74 s delay between pulses, 80–600 transients. ¹³C NMR parameters: spectrometer frequency 100.53 MHz, spectral width 28 kHz, pulse width 4.9 μs (45°), 5.3 s delay between pulses, broad-band decoupling, 4 000–25 000 transients. To determine chemical shifts, C₆D₆ solvent peaks were taken as 7.15 (¹H) and 128.00 ppm (¹³C). [Al]_{MAO}/[Zr]_{tot} ratios were determined by comparing the combined integral of the Si-CH₃ signals at 1.54, 1.7, and 1.8 ppm with the combined integrals of the broad CH₃ signal of MAO centered at -0.2 ppm and of the CH₃ signal of Al₂Me₆ at -0.33 ppm.

UV-Vis Studies of Homogeneous Catalyst Systems

A well-dried (105 °C, 16 h) Schlenk vessel was set up for UV-vis measurements with a double-septum inlet and with an immersion probe with 10 mm path length, connected by fiber-optics to a Cary 50 spectrometer.^[6] To this set-up were added, after

evacuation for 1h and subsequent protection by an argon atmosphere, 10 mL of a 2.0 M solution of MAO in C_6D_6 and then ≈ 15 mg (31 μ mol) of solid $SBIZrCl_2$. Integration of the 1H NMR signals of Al-bound CH_3 groups and of zirconocene ligand protons yielded a $[Al]_{MAO}/[Zr]$ ratio of ≈ 600 for this solution. As described before,^[2n] UV-vis spectra were recorded before and after addition of small increments of 1 M C_6D_6 solutions of HAi^iBu_2 or Al^iBu_3 . Whenever significant UV-vis spectroscopic changes were observed, 0.5 mL of the reaction mixture were transferred under argon to NMR tubes to obtain 1H NMR spectra.

Titration Experiments

UV-vis spectra of a 5×10^{-3} M solution of $SBIZrCl_2$ in toluene were recorded in a similar set-up with an immersion probe with 1 mm path length, at 25 °C, before and after additions of 0.05 mL increments of a 1 M solution of HAi^iBu_2 in toluene.

Reactions with Isobutene

10 mL of a toluene solution that contained 2 mg (4 μ mol) of $SBIZrCl_2$, 310 mg of solid MAO (4.1 mmol Al, $[Al]/[Zr] \approx 1000$), and 0.1 mmol of HAi^iBu_2 ($[HAi^iBu_2]_{add}/[Zr] = 25$) was treated with increments of a 1 M solution of isobutene in toluene and measured with an immersion probe with 10 mm path length (Supporting Information).

UV-Vis Studies of Supported Catalyst Systems

Into a Schlenk vessel that contained a UV-vis immersion probe with a path length of 1 mm, 2.5 g of the SiO_2 /MAO-supported catalyst was placed under argon. 10 mL of dry decaline were added and the mixture was shaken to remove all gas bubbles.

Small increments of toluene solutions of HAi^iBu_2 or Al^iBu_3 were added by way of a double-septum inlet.^[6] Before and after each addition, spectra were recorded after shaking the suspension for ≈ 1 min. From each of the spectra thus obtained, a base-line spectrum was subtracted, which was obtained from an analogous reaction mixture that contained a suspension of the SiO_2 /MAO support in decalin without any zirconocene addition.

Results and Discussion

Solution NMR Studies

In order to generate the zirconocene hydride complexes in question in higher proportions than previously obtained by addition of Al^iBu_3 , $SBIZrCl_2$ /MAO reaction mixtures were reacted with diisobutylaluminum hydride, HAi^iBu_2 . As in previous experiments,^[2n] solutions that contain $SBIZrCl_2$ and MAO in a $[Al]_{MAO}/[Zr]$ ratio of ≈ 600 (see Experimental) show a set of relatively sharp signals at 6.22, 5.05 and -1.30 ppm in their 1H -NMR spectra in C_6D_6 (Figure 1) attributable to the heterodinuclear cation $SBIZr(\mu-Me)_2AlMe_2^+$ (species III) and another set of broader signals at 5.7 to 6.0, 5.1 to 5.2, and -1.6 to -1.8 ppm, which

Figure 1. 1H NMR spectra of C_6D_6 solutions of $SBIZrCl_2$ (3.8×10^{-3} M) that contain MAO ($[Al]_{MAO}/[Zr] \approx 600$) and increasing proportions of HAi^iBu_2 ; top: ligand CH and $Zr-(\mu-CH_3)-Al$ regions; bottom: aluminum alkyl and hydride regions.

indicate that $\approx 10\%$ of the zirconocene units are present in the form of the contact ion pairs $\text{SBIZrMe}^+\cdots\text{Me-MAO}^-$ (species IV).^[2e] When such a solution is mixed with successive increments of HAL^iBu_2 , we observe a conversion of the initially predominant cation $\text{SBIZr}(\mu\text{-Me})_2\text{AlMe}_2^+$ to the previously seen zirconocene hydride species, which is characterized by two broad singlets at 5.54 and -1.97 ppm and a sharper one at 6.51 ppm (denoted by $\text{I}_{\text{H,H}}$ in Figure 1, top); this conversion is practically complete when HAL^iBu_2 is added in a ratio of $[\text{HAL}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}] = 40$.

Before analyzing the characteristics of this zirconocene hydride in more detail, we consider briefly the NMR signals of these reaction systems in the aluminum alkyl and hydride regions (Figure 1, bottom): The characteristic hydride signals of HAL^iBu_2 (3.3, 3.07, and 2.9 ppm in d^6 -benzene solution) are not discernible in these reaction systems. Instead, a relatively sharp hydride signal appears at 3.75 ppm at $[\text{HAL}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}]$ ratios above 20. We also observe this signal in MAO-free solutions of HAL^iBu_2 , which contain an excess of Al_2Me_6 or Al^iBu_3 . It is thus likely to be a result of hydride-bridged alkyl aluminium dimers of the type $\text{R}_2\text{Al}(\mu\text{-R})(\mu\text{-H})\text{AlR}_2$ with $\text{R} = \text{Me}$ or ^iBu . All of the available hydride units would thus appear to occupy bridging positions in these dimeric alkyl aluminum species.

The alkyl aluminium hydride signal at 3.75 ppm becomes discernible only at relatively high $[\text{HAL}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}]$ ratios. At lower $[\text{HAL}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}]$ ratios we observe (together with a rather sharp signal at 1.86 ppm, attributable to the ^iBu residues of mixed trialkyl aluminium dimers of the type $\text{Al}_2(\mu\text{-Me})_2\text{Me}_{4-x}^i\text{Bu}_x$, and a broader signal at ≈ 2 ppm, previously assigned to ^iBu residues of isobutylated MAO clusters, $^i\text{Bu-MAO}^{[2n]}$) two broad features at 3.6 and 4.1 ppm, which increase in parallel to the amounts of added HAL^iBu_2 . We assign these signals to hydride derivatives of MAO, referred to as H-AO, which appear to be generated by exchange of hydrides

from HAL^iBu_2 against Me groups from MAO (Equation (1)):

where H-AO and Me-AO are MAO clusters with exchangeable hydride and Me groups, respectively.

MAO clusters thus appear to have an unexpectedly high tendency to absorb hydride units in exchange for methyl groups. This is in contrast with their low tendency to accept ^iBu in exchange for Me groups.^[2n] The affinity of MAO clusters for various exchangeable entities thus appears to follow the sequence $^i\text{Bu} < \text{Me} \ll \text{H}$. This gradation is probably related to different propensities of these entities to occupy bridging positions in the MAO cluster framework and might be connected to changes in the Lewis acidity of the resulting modified MAO clusters.^[2l]

The zirconocene hydride complex, which predominates in these reaction systems at elevated $[\text{HAL}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}]$ ratios, yields an intensity ratio of 2:2:2 of its ligand and hydride signals, and the positions of its ligand signals are closer to those of the neutral complexes SBIZrCl_2 and SBIZrMe_2 than to the cationic species listed in Table 1. These signals must thus be due to a neutral zirconocene dihydride, SBIZrH_2 . The negative chemical shift of its Zr-hydride units, however, sets this species apart from other zirconocene hydrides with a positive chemical shift, which is typical for terminal Zr-H units.^[7] Previous observations strongly suggest that the negative chemical shift of the Zr-H units of the present zirconocene dihydride is a result of their placement in bridging positions,^[8] most likely in Zr-H-Al bridges that involve Lewis-acidic AlR_2X species present in the reaction medium.

This assignment is supported by further experiments. Treatment of a solution of SBIZrCl_2 in d^6 -benzene first with a ≈ 10 -fold excess of Al_2Me_6 , so as to generate equal proportions of $\text{SBIZr}(\text{Me})\text{Cl}$ and $\text{Al}_2(\mu\text{-Me})(\mu\text{-Cl})\text{Me}_4$,^[9] and then with slightly more than 2 equiv. of HAL^iBu_2 , leads to

Table 1. ^1H NMR signals of $\text{rac-Me}_2\text{Si}(\text{ind})_2\text{Zr}$ (SBIZr) derivatives (δ in ppm).

Derivative	H(3)	H(2)	Zr-Me	AlMe_t	Zr-H
SBIZrCl_2	6.80	5.74	—		
SBIZrMe_2	6.69	5.68	-0.97		
$\text{SBIZr}(\mu\text{-Me})_2\text{AlMe}_2^+$	6.20	5.03	-1.34	-0.62	
$\text{SBIZrMe}^+\cdots\text{MeMAO}^-$	5.7 to 6.0	5.1 to 5.2	-1.6 to -1.8		
$\text{SBIZrH}_2 \cdot \{2\text{AlMe}_3\}^{\text{a)}$	6.63	5.73	—		$-1.39^{\text{b)}$
$\text{SBIZrH}_2 \cdot \{2\text{AlMe}_2\text{Cl}\}$	6.64	5.70	—		$-1.54^{\text{b)}$
$\text{SBIZrH}_2 \cdot \{x(\text{AlMeO})_n\}$	6.51	5.55	—		$-1.95^{\text{b)}$

^{a)} Prepared by use of SBIZrMe_2 instead of SBIZrCl_2 ; ^{b)} Broadened signals with $\Delta\nu_{1/2} \approx 30$ Hz.

Figure 2. ^1H NMR spectra (ligand CH and Zr-H regions) of C_6D_6 solutions that contain SBIZrCl_2 ($3.8 \times 10^{-3} \text{ M}$), ≈ 10 equiv. of Al_2Me_6 , ≈ 2.5 equiv. of HAl^iBu_2 , and increasing amounts of MAO (high-field part shown with doubled intensity).

the quantitative generation of a set of signals that comprise a broad singlet at -1.53 ppm, a somewhat sharper one at 5.70 ppm, and a partly resolved doublet at 6.64 ppm, again with a 2: 2: 2 ratio (Figure 2), which we assign to a species $\text{SBIZrH}_2 \cdot \{2\text{AlMe}_2\text{Cl}\}$, in which the terminal hydrides of SBIZrH_2 are complexed to AlMe_2Cl , the strongest Lewis acid present in the reaction medium.

Addition of successive increments of MAO to this reaction system leads to a monotonous shift of all three signals to higher fields, together with an increased broadening. At the highest attainable MAO concentration, the appearance of this signal set is closely similar to that represented in Figure 1. We assume that at this point more strongly Lewis-acidic Al centers of some $(\text{AlMeO})_n$ clusters present in MAO solutions displace AlMe_2Cl from its interaction with the zirconocene dihydride.

The appearance in Figure 2 of hydride signals with intermediate shifts for increasing MAO concentrations implies that exchange between different Lewis acid adducts is fast on the NMR time scale. This raises the question of whether the symmetric appearance of the ZrH_2 signal is a result of complexation of both terminal hydrides with one AlR_2X entity each, or of a fast interchange of only one AlR_2X entity between both hydrides. The latter possibility would appear particularly reasonable for the presumably rather large $(\text{AlMeO})_n$ clusters present in MAO solutions. For simple alkylaluminum compounds, such as AlMe_3 , ClAlMe_2 , and HAl^iBu_2 (summarily referred to as AlR_2X), however, we would assume that each dihydride SBIZrH_2 is complexed to two AlR_2X units, when these are present in sufficient excess.

Similar observations as for the $\text{SBIZrCl}_2/\text{MAO}$ system pertain to reaction systems that contain the highly active catalysts $\text{rac-Me}_2\text{Si}(2\text{-Me-4-Ph-ind})_2\text{ZrCl}_2/\text{MAO}$ and rac-

Scheme 1. Structures proposed for AlR_2X adducts of zirconocene hydrides in previous studies (left and middle),^[8,10] and the structure proposed in the present study for the zirconocene dihydride complexes of the type $\text{SBIZrH}_2 \cdot \{n\text{AlR}_2\text{X}\}$ (right).

$\text{Me}_2\text{Si}(2\text{-Me-benzind})_2\text{ZrCl}_2/\text{MAO}$.^[5] Here, addition of HAl^iBu_2 causes ^1H signals attributable to ZrH_2 groups to appear at -1.6 and -1.67 ppm, respectively (Supporting Information). For the system $\text{rac-Me}_2\text{Si}(2\text{-Me-benzind})_2\text{ZrCl}_2/\text{MAO}$, the signals attributable to the hydride complex already appear after addition of the lowest HAl^iBu_2 proportions, being complete far before the appearance of the signal of the hydride-bridged alkylaluminum dimers. In this reaction system hydride complexes of the type discussed above thus appear to be even more highly favored than in any of the other zirconocene reaction systems studied.

For the adducts of zirconocene dihydrides with Lewis-acidic organoaluminum compounds, two types of structures have previously been proposed, namely species of the type $\text{Cp}_2\text{Zr}(\text{H})(\mu\text{-H})_2(\text{Al}_2\text{R}_4\text{X})$ ($\text{Cp} = \text{C}_5\text{H}_5$), formally derived from monomeric Cp_2ZrH_2 and species of the type $(\text{Cp}_2\text{ZrH} \cdots \text{AlR}_2\text{X})_2(\mu\text{-H})_2$, formally derived from its dimer (Scheme 1).^[8,10] All of these species have been reported, however, to yield two separate hydride NMR signals, since their individual Zr-H , Zr-H-Zr , and Zr-H-Al units give rise to distinct signals.

The Lewis-acid adducts observed in our study, on the other hand, give rise to a single ZrH_2 signal for the 2H atoms per zirconocene unit, which is not compatible with either of these structures. Clarification of the geometry of the hydride complexes in question by a crystal structure determination would be most desirable. Given the difficulties to obtain crystalline products from MAO-containing catalyst systems, however, we tentatively propose at this time the structure shown in Scheme 1 (right) for the AlR_2X -complexed zirconocene dihydrides observed in this study, as this would most directly explain the NMR data presented above.

At any rate, it is worth noting that HAl^iBu_2 should convert the cationic zirconocene species that prevail in the HAl^iBu_2 -free reaction systems to a neutral hydride rather than to one of the mononuclear^[11] or the dinuclear^[12] cationic hydride species known to arise through hydride abstractions from zirconocene hydrides by Lewis acids such as $\text{B}(\text{C}_6\text{F}_5)_3$ or by $\text{Ph}_3\text{C}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$. Apparently, hydride-saturated MAO clusters of the type H-AO , which arise in the present reaction systems by hydride transfer

according to Equation (1), are less Lewis-acidic than their hydride-free MAO counterparts and thus not sufficiently strong 'cationization' reagents to bring about hydride abstraction from a relatively stable neutral zirconocene dihydride.

UV-Vis Studies in Solution and on SiO₂ Support

In parallel to the NMR measurements just described, the reactions induced by addition of HAl^iBu_2 to solutions that contain SBIZrCl_2 and MAO were monitored by recording the concomitant UV-vis spectroscopic changes. After addition of each HAl^iBu_2 increment to a solution of SBIZrCl_2 and MAO, UV-vis spectra were recorded before samples were drawn from the reaction mixtures for NMR measurements.

The initial SBIZrCl_2 /MAO reaction mixture gives rise to an absorbance maximum at 490 nm, which is closer to that of the cationic trimethyl aluminum adduct III at 496 nm than to that of the contact ion pair IV at 456 nm (Figure 3).^[6] Deconvolution of the spectrum indicates that species III accounts for $\approx 80\%$ and species IV for $\approx 20\%$ of the total Zr content, in line with the NMR data presented above.

When HAl^iBu_2 is added to these SBIZrCl_2 /MAO reaction mixtures, the absorbance band at 490 nm is reduced in height and shifted towards 496 nm. These changes progress in proportion to the $[\text{HAl}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}]$ ratio and go to completion, at each stage, within 10–20 min. In accord with the NMR spectra in Figure 1, addition of HAl^iBu_2 appears to first remove species IV and then also species III from these systems. At ratios of $[\text{HAl}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}] > 20$, both of these species have practically vanished. Together with the absorbance decrease at 490–496 nm, an absorbance increase is observed at ≈ 380 –390 nm, which must be due to the complex $\text{SBIZrH}_2 \cdot \{x(\text{AlMeO})_n\}$, observed to form under these conditions by NMR spectroscopy. The proximity of the UV-vis band of this species to that of the dimethyl complex SBIZrMe_2 , observed at 387 nm,^[6b] supports its assignment to a neutral rather than to a cationic complex.

Each addition of HAl^iBu_2 to the SBIZrCl_2 /MAO reaction mixtures also yields, in addition to the absorbance increase at 380 nm, a transient absorbance increase in the region of 560–600 nm. Possible explanations for this phenomenon, which cannot be due to the hydride complex $\text{SBIZrH}_2 \cdot \{x(\text{AlMeO})_n\}$, since it essentially vanishes again at ratios of $[\text{HAl}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}] \geq 40$ where the hydride complex is fully developed, are to be discussed further below.

When a toluene solution of SBIZrCl_2 is treated with HAl^iBu_2 , in the absence of MAO or any other reagent, a decrease of its absorbance band at 443 nm is observed (Figure 4, top) This must be a result of the formation of the

Figure 3. UV-vis spectra of SBIZrCl_2 /MAO reaction mixtures before and after addition of increasing proportions of HAl^iBu_2 . Top: SBIZrCl_2 (3.8×10^{-3} M) in a C_6D_6 solution that contains MAO ($[\text{Al}]_{\text{MAO}}/[\text{Zr}] \approx 600$); bottom: $\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2$ on a solid SiO_2 /MAO support ($[\text{Al}]_{\text{MAO}}/[\text{Zr}] \approx 1200$) in a decaline suspension (for details see Experimental part).

hydride complex $\text{SBIZrH}_2 \cdot \{2\text{Al}^i\text{Bu}_2\text{Cl}\}$, seen before in the NMR spectra in Figure 2. This formulation of the hydride complex is corroborated by a plot of the remaining absorbance of SBIZrCl_2 at 443 nm as a function of increasing $[\text{HAl}^i\text{Bu}_2]_{\text{add}}/[\text{Zr}]$ ratios (Figure 4, bottom), which shows that 2 equiv. of HAl^iBu_2 are required for the consumption of each SBIZrCl_2 and that a slight excess of HAl^iBu_2 is necessary to complete this reaction (Equation (2)).

The absorbance increase at 380 nm, associated with the formation of the $\text{Al}^i\text{Bu}_2\text{Cl}$ adduct $\text{SBIZrH}_2 \cdot \{2\text{Al}^i\text{Bu}_2\text{Cl}\}$

Figure 4. UV-vis absorption spectra of a 5×10^{-3} M toluene solution of SBIzrCl₂ and of the same solution after addition of 1 to 8 equiv. of HAlⁱBu₂ (top), and the fraction of the initial SBIzrCl₂ concentration that remains after each addition, determined from the absorbance decrease at 443 nm (bottom).

(Figure 4), is significantly smaller than that due to the formation of the MAO adduct SBIzrH₂·{x(AlMeO)_n} (Figure 3). The nature of the alkylaluminum Lewis acid bound to the zirconocene hydride thus appears to affect not only the chemical shift of the ZrH₂ signal (Figure 2), but also the molar absorptivity at 380 nm of the resulting adduct.

Spectroscopic changes very similar to those described above are observed when increasing proportions of AlⁱBu₃, instead of HAlⁱBu₂, are added to SBIzrCl₂/MAO reaction mixtures. Here again, the absorbance band at 490 nm is reduced in height and shifted toward 496 nm (Figure 5). In this case, however, a residual absorbance at 496 nm remains at ≈30% of its initial value at the highest [AlⁱBu₃]_{add}/[Zr] ratios studied. Concomitant with the absorbance decrease at 490–496 nm, we observe an absorbance increase at ≈380 nm, which levels off, again, at less than half of the increase observed at this wavelength upon addition of HAlⁱBu₂.

These data, together with the NMR spectroscopic observations presented above, leave no doubt that additions of HAlⁱBu₂ and of AlⁱBu₃ produce the same kind of zircono-

Figure 5. UV-vis spectra of SBIzrCl₂/MAO reaction mixtures before and after addition of increasing proportions of AlⁱBu₃. Top: SBIzrCl₂ (3.8×10^{-3} M) in a C₆D₆ solution that contains MAO ([Al]_{MAO}/[Zr] ≈ 600). Bottom: Me₂Si(ind)₂ZrCl₂ on a solid SiO₂/MAO support ([Al]_{MAO}/[Zr] ≈ 1200) in a decaline suspension (for details see Experimental Part).

cene hydride species in SBIzrCl₂/MAO reaction mixtures, with AlⁱBu₃ acting as a source of HAlⁱBu₂ under release of isobutene (Equation (3)). Deuterium scrambling experiments with DAlⁱBu₂ (Supporting Information) show that the reaction according to Equation (3) is accelerated in the presence of the catalyst SBIzrCl₂/MAO, such that it approaches equilibrium with a half-life of 20–30 min.

The observation that about 30% of the total zirconocene content remains in the form of the cation

SBIZr(μ -Me)₂AlMe₂⁺, even in the presence of a large excess of AlⁱBu₃, must thus be due to the effect of the isobutene by-product, which remains in the reaction medium and keeps the conversion of AlⁱBu₃ into HALⁱBu₂ from going to completion.

In accord with this notion, we observe that addition of excess isobutene almost completely reverses the loss of absorbance at 490 nm and the absorbance increase at 380 nm (Figure 3), caused in SBIZrCl₂/MAO reaction mixtures by addition of HALⁱBu₂ (Supporting Information). Isobutene thus appears to reconvert the hydride complexes SBIZrH₂ · {x (AlMeO)_n} here into the cationic species SBIZr(μ -Me)₂AlMe₂⁺ and/or SBIZrMe⁺...Me-MAO⁻. This observation demonstrates that Zr-bound alkyl units, formed by insertion of isobutene into Zr-H bonds, are more easily abstracted in this reaction medium than Zr-bound hydride units.

During the course of these reverse reactions, a very strong transient absorbance at 560–600 nm is reproducibly observed (see Supporting information), which had also been seen, albeit to a lesser degree, in the ‘forward’ reactions induced by addition of HALⁱBu₂ described above.

Having at least preliminarily characterized, by mutually supportive and/or complementary NMR and UV-vis data, the zirconocene hydride species that occur in homogeneously dissolved SBIZrCl₂/MAO catalyst systems, we now turn to our goal of utilizing these insights to describe on a molecular level the ‘heterogenized’ catalyst systems adsorbed on a solid support. As outlined in our introduction, we approach this task by following, through UV-vis spectroscopy, reactions induced by HALⁱBu₂ in otherwise analogous catalyst systems that contain SBIZrCl₂ adsorbed on a MAO-pretreated SiO₂-gel.

In order to minimize the spectroscopic noise caused by density fluctuations in stirred catalyst suspensions,^[6b] we have resorted to measuring transmission spectra of unstirred, gravitationally settled catalyst suspensions, using hydrocarbon media with a refractory index as close as possible to that of the catalyst grains under consideration. After studying several solvent mixtures, we found that a highly suitable suspension medium for UV-vis studies with this support system is decalin, which is commercially available as a mixture of its *cis*- and *trans*-isomers. UV-vis spectra of suspensions of MAO-treated SiO₂ thus obtained, which are almost identical to those of decalin alone down to $\approx$ 340 nm, were used as baselines and subtracted from the spectra of supported catalysts that contained the zirconocene species of interest.

Exposure of a MAO-treated SiO₂ support to a toluene solution of SBIZrCl₂, decantation of the practically colorless supernatant, and drying of the solid under vacuum gave a free-flowing, orange-colored catalyst powder (Experimental part). UV-vis spectra of a suspension of this material in decalin, before and after addition of increasing amounts of

HALⁱBu₂ (Figure 3, bottom), are rather similar in appearance to those discussed above for the analogous homogeneous catalyst system (Figure 3, top); some differences are to be noted, however:

Instead of the absorbance band at 490 nm observed for HALⁱBu₂-free catalyst systems in homogeneous solution, the absorbance maximum of its SiO₂-supported counterpart is found at 460 nm, as observed before for similar catalyst systems by diffuse reflectance spectroscopy.^[3e] A maximum close to 460 nm is characteristic of the contact-ion pair SBIZrMe⁺...Me-MAO⁻ (species IV).^[6] Most of the zirconocene catalyst thus appears to be adsorbed on the MAO-containing SiO₂ support in the form of such a contact ion pair, rather than in the form of the AlMe₃ adduct [SBIZr(μ -Me)₂AlMe₂]⁺ (species III). Possibly, less ‘free’ AlMe₃ is available in the supported system than in the homogeneous system to form this adduct; alternatively, Me-MAO⁻ anions formed under these conditions might be less easily displaced from the contact-ion pairs IV than those formed in homogeneous solutions.

Nevertheless, addition of HALⁱBu₂ causes a similar diminution of the absorbance at 460 nm in the supported system, as for the band at 490 nm in the homogeneous case, which is essentially complete at ratios of [HALⁱBu₂]_{add}/[Zr] > 50. At the same time, the residual maximum is continuously shifted to higher wavelengths, until it reaches an end value close to 490 nm, which indicates, as before, a preponderance of species III. Again, HALⁱBu₂ appears to remove first species IV and then species III from the SiO₂-supported reaction system.

Concomitant with the absorbance decrease at 460–490 nm, an increase in absorbance, very similar to that seen in the homogeneous system, is observed at $\approx$ 380 nm. We can thus conclude that similar hydride species as discussed above are also formed in SiO₂-supported zirconocene catalysts by treatment with HALⁱBu₂.

Addition of AlⁱBu₃ instead of HALⁱBu₂ to a SBIZrCl₂/MAO reaction systems adsorbed on a SiO₂-gel support likewise yields a partial conversion to the hydride complex, which is rather similar again to that observed in homogeneous solution (Figure 5), albeit somewhat less complete. It would thus appear that, in addition to the identity of the catalyst species formed, equilibrium parameters, e.g., with regard to Equation (3), are also comparable in SBIZrCl₂/MAO catalyst systems in solutions and on SiO₂ supports. Very similar UV-vis spectroscopic observations pertain also to the formation of zirconocene hydride complexes in the industrially employed catalysts *rac*-Me₂Si(2-Me-4-Ph-ind)₂ZrCl₂/MAO and *rac*-Me₂Si(2-Me-benzind)₂ZrCl₂/MAO upon addition of HALⁱBu₂ or AlⁱBu₃, both in hydrocarbon solutions and on SiO₂ supports (Supporting Information).

Finally we note that a transient absorbance increase at 560–600 nm arises at intermediate [HALⁱBu₂]_{add}/[Zr] levels also in the SiO₂-supported SBIZrCl₂/MAO catalyst system,

as had been observed for the analogous homogeneous reaction system and, to a more pronounced extent, during the reconversion of the zirconocene dihydride $\text{SBIZrH}_2 \cdot x(\text{AlMeO})_n$ to the cationic species $\text{SBIZr}(\mu\text{-Me})_2\text{AlMe}_2^+$ and $\text{SBIZrMe}^+ \cdots \text{Me-MAO}^-$ by addition of isobutene.

With regard to the origin of this absorbance we note that Zr^{IV} hydride complexes appear to be intrinsically free of such colorations, but tend to form, presumably by loss of H_2 , deeply colored products,^[13] which probably contain some Zr^{III} species.^[14] Chirik et al., for example, have isolated a trinuclear complex, $\{(\text{Me}_2\text{Si})_2(\text{C}_5\text{H}_5)_2\text{Zr}\}_3(\mu_3\text{-H})_2(\mu_2\text{-H})_3$ from related reaction systems,^[15] which formally contains two Zr^{IV} centers and one Zr^{III} center.

Formation of mixed-valence clusters of this type, which tend to have rather high molar absorbance coefficients, might thus cause the appearance of this 'blue' absorbance. Alternatively, coordinatively unsaturated species with high molar absorptivity in this spectroscopic region might occur as fleeting intermediates in reactions in which isobutene is either lost from or reinserted into a zirconocene hydride species. In view of a possible participation of these transient species in the mechanisms of catalyst activation and/or deactivation, further efforts to characterize these unstable intermediates would appear worthwhile.

Conclusion

Our results document that the types and relative amounts of the main complex species formed in SiO_2 -supported zirconocene-based polymerization catalysts and, by implication, in other supported catalyst systems can be determined by comparison of the transmission UV-vis spectra of their hydrocarbon suspensions with those of their homogeneously dissolved, NMR spectroscopically characterized counterparts.

In this manner, SiO_2 -supported $\text{SBIZrCl}_2/\text{MAO}$ catalyst systems are found to differ from their homogeneously dissolved counterparts by the presence of much larger fractions of contact-ion pairs of type IV instead of the cationic alkyl aluminum adducts of type III, which predominate in solution. These observations are in line with results previously obtained by Panchenko et al. by diffuse reflectance spectroscopy,^[3e] and might be connected to activity differences between otherwise analogous catalyst systems in solution and on solid supports and to the effects of alkyl aluminum reagents on such catalyst systems.^[16]

Neutral zirconocene dihydride complexes of the type $\text{SBIZrH}_2 \cdot \{n\text{AlR}_2\text{X}\}$ arise, in the form of their adducts with some Lewis-acidic alkyl aluminum species AlR_2X , in homogeneous as in SiO_2 -supported $\text{SBIZrCl}_2/\text{MAO}$ cata-

lysts, and likewise in other metallocene catalyst systems, when these are modified by addition of HAl^iBu_2 or of Al^iBu_3 . More extensive studies on the role of these zirconocene hydride species in 'working' zirconocene-based catalysts for the polymerization of α -olefins will be the subject of further reports from our laboratories.

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