ORGANOMETALLICS

Volume 21, Number 20, September 30, 2002

Communications

The Lanthanide Ziegler−Natta Model: Aluminum-Mediated Chain Transfer

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Received June 3, 2002

Summary: C_2-symmetric tetraalkylaluminate complexes rac-[$Me_2Si(2\text{-}Me\text{-}C_9H_5)_2$]Y($\mu$-R)$_2AlR_2$ and terminal alkyl complexes rac-[$Me_2Si(2\text{-}Me\text{-}C_9H_5)_2$]YR(THF) (R = Me, Et, iBu) are quantitatively formed via a special silylamide elimination reaction. The "reversibility" of tetraalkylaluminate coordination gives access to the first mixed-alkyl lanthanidocene complexes, which can be discussed as models for polymer chain transfer in organoaluminum-dependent Ziegler−Natta catalysts.

Lanthanidocene alkyl complexes are excellent models for clarifying the active sites of Ziegler−Natta catalysts via emulation of the major initiation, propagation, and termination steps.[1] In the course of these studies key features such as olefin coordination,[2] olefin insertion (propagation),[3,4] β-hydrogen elimination,[3,4] and β-alkyl elimination[5] could be spectroscopically and structurally proven. Group 4 metallocene complexes are known to be efficiently activated for olefin polymerization by alkylalumoxanes,[6] in particular methylalumoxane (MAO), to form base-free cationic complexes of the general formula $[Cp_2M{-}R]^+$ (R = alkyl, M = Ti, Zr, Hf).[7] The commercially employed MAO cocatalyst contains a considerable amount of free and coordinated trimethylaluminum, $AlMe_3$ (up to 15 wt %),[8] the presence of which was ascribed to a deactivating and chain-transferring action.[7,9] Recently, Bochmann et al. were able to spectroscopically identify cationic group 4 tetramethylaluminate complexes of the type $[\{Me_2Si(C_9H_6)_2\}Zr(\mu\text{-}Me)_2AlMe_2][B(C_6F_5)_4]$ as dormant species ("resting states").[10]

We report the synthesis of indenyl-derived *ansa*-lanthanidocene alkylaluminate complexes[11] via a special silylamide elimination reaction and the reversibility of

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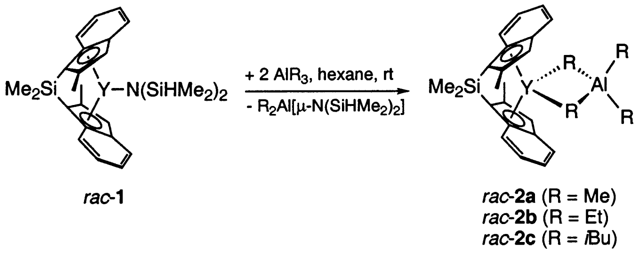
10.1021/om020440u CCC: $22.00 © 2002 American Chemical Society
Publication on Web 08/30/2002

Scheme 1[a]



[a] For *rac*-**1** and *rac*-**2** only one enantiomer is depicted.

the alkylaluminate coordination in the presence/absence of coordinating donor molecules. The reversibility of this process was exploited to synthesize mixed-alkyl aluminate complexes as models for alkylaluminum-mediated chain transfer processes.

The *ansa*-yttrocene silylamide complex [Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y[N(SiHMe$_2$)$_2$] (*rac*-**1**)[12] reacts with an excess of trialkylaluminum reagent, AlR$_3$ (R = Me, Et, *i*Bu), to yield the corresponding tetraalkylaluminate complexes *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y(*μ*-Me)$_2$AlMe$_2$ (**2a**), *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y(*μ*-Et)$_2$AlEt$_2$ (**2b**), and *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y(*μ*-*i*Bu)$_2$Al*i*Bu$_2$ (**2c**) in high yield and purity (Scheme 1).[13] This amide→alkyl transformation is driven by the elimination of a thermodynamically favored aluminum silylamide complex, {Me$_2$Al[*μ*-N(SiHMe$_2$)$_2$]}$_2$,[14] and, according to NMR spectroscopy, does not underlie any epimerization process.

Scheme 2

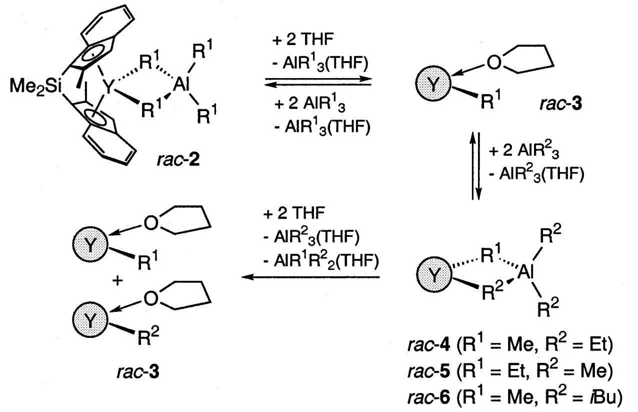


Table 1. ^{1}H NMR Spectroscopic Shifts (ppm) of Metal-Bonded Alkyl Moieties[a]

complex[b]	δ(*μ*-CH$_3$)	δ(*μ*-CH$_2$)	δ(t-CH$_3$)	δ(t-CH$_2$)
LY(*μ*-Me)$_2$AlMe$_2$ (*rac*-**2a**)	−1.32		−0.48	
LY(*μ*-Et)$_2$AlEt$_2$ (*rac*-**2b**)		−1.02/−2.08		0.20
LY(*μ*-*i*Bu)$_2$Al*i*Bu$_2$ (*rac*-**2c**)		−1.39/−1.75		0.25
LYMe(THF) (*rac*-**3a**)	−1.35			
LYEt(THF) (*rac*-**3b**)		−1.10		
LY*i*Bu(THF) (*rac*-**3c**)		−1.06/−1.46		
LY(*μ*-Me)(*μ*-Et)AlEt$_2$ (*rac*-**4**)	−1.38	−0.98/−1.05/ −2.10/−2.25		0.19
LY(*μ*-Et)(*μ*-Me)AlMe$_2$ (*rac*-**5**)	−1.31	−1.36	−0.42	
LY(*μ*-Me)(*μ*-*i*Bu)Al*i*Bu$_2$ (*rac*-**6**)	−1.36	−1.30/−1.88		0.18

[a] In C$_6$D$_6$ at 25 °C. [b] L = *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$].

Complexes **2** can easily be converted to terminal alkyl derivatives *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]YR(THF) (**3**) by addition of >2 equiv of THF (Scheme 2).[11e,13] Interestingly, this donor-induced aluminate cleavage is a *reversible* process; i.e., treatment of the isolated complexes **3** with 2 equiv of AlR$_3$ (R = Me, Et, *i*Bu) re-forms the tetraalkylaluminate derivatives **2**. According to this strategy the first mixed-alkyl aluminate lanthanidocene complexes *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y(*μ*-Me)(*μ*-Et)AlEt$_2$ (**4**), *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y(*μ*-Et)(*μ*-Me)AlMe$_2$ (**5**), and *rac*-[Me$_2$Si(2-Me-C$_9$H$_5$)$_2$]Y(*μ*-Me)(*μ*-*i*Bu)Al*i*Bu$_2$ (**6**) were obtained.[13] The methyltriethylaluminate complex **4** and the ethyltrimethylaluminate derivative **5** could be isolated in almost quantitative yield, while methyltriisobutylaluminate complex **6** formed in yields of only <10% (NMR scale experiment!), reflecting the enhanced steric bulk of the isobutyl group.

The ^{1}H NMR spectroscopic characterization of the various homo- and hetero-bridged alkylaluminate complexes revealed some interesting features. The protons of the bridging (*μ*) alkyl groups experience a considerable upfield shift of ca. 1 ppm compared to the terminal (t) aluminum-bonded alkyl ligands (Table 1), most likely due to the geometric proximity of the extended aromatic ligand system. Additionally, no exchange between bridging and terminal alkyl ligands, which appear in the correct integral ratios, is observed at ambient temperature. Although the rigidity of a heterobridged bimetallic arrangement has a beneficial effect for the assignment of the various alkyl groups, this implies complex signal patterns, particularly for the bridging ethyl and isobutyl moieties.[15]

X-ray structure analysis of the heterobridged complex **4**[16] proved the absence of any bridging → terminal alkyl

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[13] Representative synthesis of *rac*-**2a**, *rac*-**3a**, and *rac*-**4**: in an argon-filled glovebox, addition of 3 equiv of AlMe$_3$ in hexane (5 mL) to a suspension of *rac*-**1** (343 mg, 0.54 mmol) in hexane caused a clear solution after several minutes at ambient temperature. During 16 h of stirring *rac*-**2a** formed as a slightly yellow precipitate (303 mg, 95%), which was recrystallized from toluene at −45 °C. Anal. Calcd for C$_{26}$H$_{34}$AlSiY: C, 63.66; H, 6.99. Found: C, 63.07; H, 7.11. *rac*-**3a** formed upon addition of ca. 0.8 mL of THF to a solution of *rac*-**2a** (383 mg, 0.78 mmol) in hexane/toluene (10:1). Evaporation of the solvent after 5 min and recrystallization from hexane gave 250 mg (77%) of product. Anal. Calcd for C$_{27}$H$_{33}$OSiY: C, 66.11; H, 6.78. Found: C, 65.23; H, 6.01. Addition of 0.60 mmol of AlEt$_3$ to a solution of *rac*-**3a** (250 mg, 0.60 mmol) in hexane/toluene (10:1) and recrystallization of the product at −45 °C gave *rac*-**4** (275 mg, 86%). Anal. Calcd for C$_{29}$H$_{40}$AlSiY: C, 65.40; H, 7.57. Found: C, 64.60; H, 8.30. For another example of a mixed-alkyl Ln(III) complex, see: van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 1459−1467.

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[15] Complex signal patterns are caused by the overlap of $^2J_{Y,H}$ and $^3J_{H,H}$ coupling and by the presence of diastereotopic bridging methylene groups, as well as by the formation of various isomers due to hindered rotation of the bridging higher alkyl moieties; "2LY(*μ*-R)(*μ*-R)AlR$_2$ ⇄ LY[(*μ*-R)AlR$_2$(*μ*-R)]$_2$YL" equilibria[11g,j] can be excluded, as evidenced by variable-temperature NMR studies in the range from +30 to −90 °C.

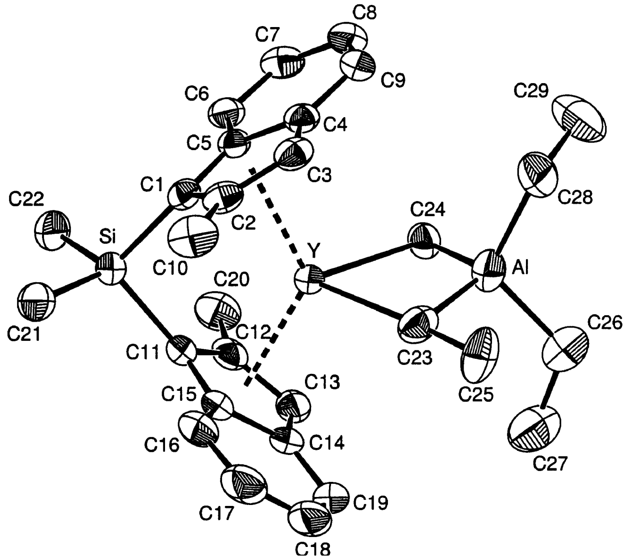

Figure 1. PLATON drawing of the complex *rac*-[Me_2Si-(2-Me-$C_9H_5)_2$]Y(μ-Me)(μ-Et)$AlEt_2$ (**4**). Atoms are represented by atomic displacement ellipsoids at the 50% level. Bond distances (Å) and angles (deg) include the following: Y−Al, 3.045(1); Y−C, 2.557(3), 2.561(3); Y−(Ind), 2.568(3)−2.769(3) (average 2.668); Al−C_μ, 2.093(3), 2.094(3); Al−C_t, 1.969(3), 1.995(4); Cg(1)−Y−Cg(2), 124.83(5); C(1)−Si−C(11), 99.0(1); Y−C(23)−C(25), 177.4(3); C(24)−Y−C(23)−Al, 7.20(9). Cg is the center of the five-membered ring.

group scrambling in the solid state (Figure 1). Moreover, the C_2 symmetry of the ansa-bridged bis(indenyl) ligand remains during the various manipulations at the metal center, as indicated by the NMR spectroscopic investigations. As a consequence of the optional attack of $AlEt_3$ on the yttrium center in **3a** from two different sides, the ethyl ligand occupies the bridging positions in a 2:1 ratio, causing disorder in the solid-state structure (not shown in Figure 1). The structural parameters of complex **4** lie within the expected range.[16]

Donor (THF)-induced cleavage of the heterobridged alkylaluminate complexes, performed on an NMR preparative scale by adding d_8-THF, revealed the intrinsic coordination capability of the differently sized alkyl moieties. Not surprisingly, the methyl-/ethyl-bridged derivatives **4** and **5** each gave an approximate 1:1 mixture of the terminal methyl (**3a**) and ethyl complexes (**3b**), respectively. However, the preferred formation of complex **3a** compared to **3c** (ca. 6:1 ratio) from **6** suggests that the bulkier alkyl group, which mimics a *polymer chain*, is preferentially transferred to the aluminum alkyl. Our studies reinforce that high concentrations of trimethylaluminum considerably affect both olefin precoordination and polymerization. Furthermore, due to their markedly decreased coordination capability, organoaluminum compounds carrying bulkier, *branched* alkyl groups comparatively increase polymerization activity.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fond der Chemischen Industrie, and Prof. W. A. Herrmann for financial support.

Supporting Information Available: Text giving full experimental and spectroscopic details for complexes *rac*-**2**−*rac*-**6** and tables of atomic coordinates, atomic displacement parameters, bond distances and angles, and disorder model for *rac*-**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[16] Compound **4** ($C_{29}H_{40}AlSiY$) crystallizes from toluene in the triclinic space group *Pbca* with $a = 16.2681(1)$ Å, $b = 13.8952(1)$ Å, $c = 24.5341(2)$ Å, $V = 5545.90(7)$ Å^3, and $D_{calcd} = 1.2756(1)$ g cm^{-3} for $Z = 8$. Data were collected at 193 K on a Nonius Kappa-CCD system. Least-squares refinement of the model based on 3537 reflections ($I > 2\sigma(I)$) converged to a final R1 = 3.39% (wR2 = 7.99%). The disorder of the bridging ethyl and methyl groups and one terminal ethyl group is desribed in the Supporting Information. For comparison, the Y−C_μ bond distances in cyclopentadienyl-derived aluminate complexes are 2.58 Å in $(C_5H_5)_2Y(\mu\text{-Me})_2AlMe_2$[11c] and 2.66 Å in $[(C_5Me_5)_2Y(\mu\text{-Me})_2\text{-}AlMe_2]$.[11g]