One Ligand Fits All: Cationic Mono(amidinate) Alkyl Catalysts over the Full Size Range of the Group 3 and Lanthanide Metals

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Cationic d^0 group 4 metal alkyl complexes have been the subject of intensive investigations over the past decade and a half, mainly because of their high efficiency in catalytic olefin polymerization.[1] In contrast, cationic alkyl species of trivalent group 3 and lanthanide metals have become available only very recently.[2-8] For transition-metal catalysts, the influence of the electronic configuration of the metal on the availability of accessible metal-centered valence orbitals causes a specific ancillary ligand type to yield active catalysts only for a limited range of metals. Due to the noninvolvement of the 4f electrons in ligand or substrate bonding, this is not a limiting factor for the group 3 and lanthanide metals. The relative reactivity of these compounds is expected to be determined mainly by the metal ionic radius. These range from 0.89 Å for the smallest metal in the series (Sc^{3+}) to 1.17 Å for the largest metal (La^{3+}).[9] Thus far, a comparison of catalytic properties of such cationic alkyl complexes over the whole range of metal ion sizes has been precluded by the fact that the trialkyl complexes $M(CH_2SiMe_3)_3$-$(THF)_x$ ($x = 2, 3$), used as precursors for the various derivatives, are only available for a limited set of metals (Sc–Dy),[6d,10] thus excluding the largest metals of the series. Nevertheless, early results by Okuda et al. on $M(alkyl)_n(THF)_m$ cations showed that the metal ionic radius strongly affects the reactivity of these species.[6d]

Recently, we described the synthesis of the mono(amidinate) yttrium dialkyl complexes $(NCN)Y(CH_2SiMe_3)_2(THF)_q$ (NCN = $PhC(NAr)_2$; Ar = 2,6-diisopropylphenyl; $q = 1, 2$), which could be converted to a cationic monoalkyl species that catalyzes the polymerization of ethene.[11] Here we report that, using an in situ alkylation procedure, these compounds can now be obtained over the full size range of the group 3 and lanthanide metals. From single-crystal X-ray structure determinations, it is seen that the cationic monoalkyl derivatives $[(NCN)M(CH_2SiMe_3)(THF)_r]^+$ bind an increasing number of THF molecules ($r = 2-4$) with increasing metal size. Their activities in catalytic ethene polymerization were found to be highly dependent on the metal ionic radius, with best activities being obtained for intermediately sized metals.

Following the procedure described previously for Y,[11] the reaction of the known trialkyl complexes $M(CH_2SiMe_3)_3(THF)_2$ (M = Sc, Lu)[10a] with the amidine $PhC(NAr)(NHAr)$ yielded the corresponding amidinate dialkyl complexes $(NCN)M(CH_2SiMe_3)_2$-(THF) (M = Sc, Lu; Scheme 1). These were characterized by elemental analysis, NMR spectroscopy, and a crystal structure determination for M = Sc. For the larger lanthanides Gd, Nd, and La, suspensions of $MX_3(THF)_p$ (M = La: X = Br, $p = 4$; M = Gd, Nd: X = Cl, $p = 3$) in THF were stirred with 3 equiv of Me_3SiCH_2Li for several hours, followed by addition of 1 equiv of the amidine (Scheme 1). Subsequent extraction with and crystallization from pentane yielded the salt-free amidinate dialkyl complexes $(NCN)M(CH_2SiMe_3)_2(THF)_2$ (M = Gd, Nd, La) as analytically pure crystalline solids in moderate yields (from 33% for La to 61% for Gd). A crystal structure determination for M =

Nd showed that these are essentially isostructural to the yttrium dialkyl bis-THF adduct reported previously,[11] with the alkyl groups occupying axial positions relative to the (amidinate)M plane. This in situ alkylation procedure can also be applied to the smaller metals, e.g., for Sc, which afforded the dialkyl complex in 70% yield, as compared to 76% when starting from the trialkyl precursor.

These neutral dialkyl complexes could be converted to their cationic monoalkyl derivatives $[(NCN)M(CH_2SiMe_3)(THF)_r]$ $[BPh_4]$ (M = Sc, $r = 2$; M = Lu, Y, Gd, $r = 3$; M = Nd, La, $r = 4$) by reaction with $[PhNMe_2H][BPh_4]$ in THF solvent, followed by crystallization from THF/alkane mixtures (Scheme 1). The compounds were characterized by elemental analysis, NMR spectroscopy (for the diamagnetic derivatives), and crystal structure determinations (M = Sc, Y, Gd, Nd, La). The structures of the Sc, Gd, and La derivatives are shown in Figure 1, illustrating the increasing coordination number of the metal by the binding of additional molecules of THF with increasing metal ionic radius. In all complexes, the remaining alkyl group occupies an axial position relative to the (amidinate)M plane, which can accommodate up to three molecules of THF (in the case of Nd and La). The increased steric crowding with increasing the number of bound THF molecules is also reflected in the alkyl $M-CH_2-Si$ angle, which increases from 135.26(10)° for Sc to 155.98(17)° for Nd. In the ^{13}C NMR spectra of the cations, the alkyl CH_2 resonance is found downfield from that in the neutral dialkyls and shows a smaller $^1J_{CH}$ (for La, δ 70.7 ppm and $^1J_{CH}$ 90 Hz, versus 52.9 ppm and 102 Hz in the dialkyl).

Thus, the dialkyl complexes $(NCN)M(CH_2SiMe_3)_2(THF)_q$ and their monoalkyl cations are now accessible for the full range of group 3 and lanthanide metals. This allows for the first time a comparison of the performance of cationic group 3 metal and lanthanide alkyls in catalytic ethene polymerization over this full metal size range. Ethene polymerization experiments were performed at 30 °C and 5 bar ethene pressure, in toluene solvent, by reacting the dialkyls $(NCN)M(CH_2SiMe_3)_2(THF)_q$ ($q = 1$ for Sc and Lu, $q = 2$ for the other metals) with the Brønsted acid activator $[PhNMe_2H][B(C_6F_5)_4]$[12] in the presence of 20 equiv of isobutyl alumoxane (TIBAO) scavenger. The results (Table 1) show that the catalyst activity is strongly dependent on the metal ionic radius. Whereas the smallest (Sc) and largest (La) metals in the series show very low activity, activities in the order of 3000 kg mol^{-1} h^{-1} bar^{-1} are observed for the metals of intermediate size (Y, Gd). The polyethene produced by these catalysts has a high molecular weight ($M_w \approx 1.5 \cdot 10^6$) and a $M_w/M_n \approx 2$, characteristic for single-site catalyst behavior. For the Y system, ethene polymerization in the absence of alkylaluminum scavengers was found to have living character, as seen by the very narrow polydispersities (1.1–1.2).[11] The present data indicate that alkyl transfer to Al is the main chain transfer mechanism in operation here. In this respect it is of interest that the smallest metal to show reasonable activity (Lu) produces
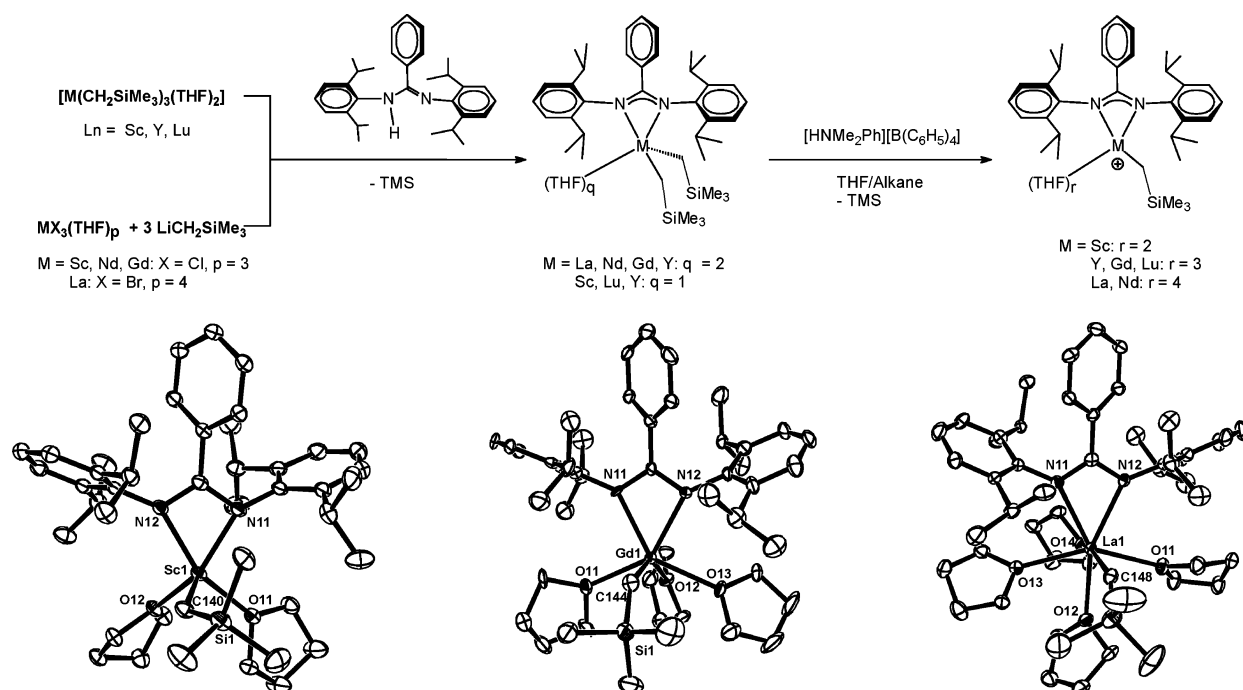
Scheme 1

Figure 1. Representative molecular structures of [(NCN)M(CH₂SiMe₃)(THF)ᵣ] cations (Sc, $r = 2$, left; Gd, $r = 3$, middle; La, $r = 4$, right).

Table 1. Ethene Polymerization with [(NCN)M(CH₂SiMe₃)₂(THF)_q]^a

M	R (Å)	yield (g)	productivity[b]	M_w (x 10^{-3})	M_w/M_n
Sc	0.89	0.20	24	93	1.6
Lu	1.00	2.82	342	496	1.4
Y	1.04	24.80	3006	1666	2.0
Gd	1.07	23.50	2848	1753	2.1
Nd	1.12	16.40	1988	1596	2.2
La	1.17	0.12	14	470	2.5

^a [PhNMe₂H][B(C₆F₅)₄] as an activator in the presence of TiBAO. Conditions: 5 μmol M; activator/M = 1:1, Al/M = 20, $T = 30$ °C, $p = 5$ bar, $t = 20$ min, toluene solvent (250 mL). ^b kg(PE) mol⁻¹ h⁻¹ bar⁻¹.

polyethene with a relatively narrow polydispersity even in the presence of TIBAO ($M_w/M_n = 1.4$). This suggests that the relatively small size of the metal makes the chain transfer process more difficult relative to that with the larger metals.

In conclusion, by using a sterically demanding amidinate ancillary ligand and an in situ metal alkylation procedure, we have prepared and structurally characterized a series of neutral dialkyl and cationic monoalkyl complexes for metals spanning the full size range of the trivalent ions of the group 3 and lanthanide metals. The catalytic activity of the cationic alkyl species in ethene polymerization was found to vary by over 2 orders of magnitude with the size of the metal ion. The availability of such a series of compounds also opens up the possibility to investigate in a systematic fashion the various reactivity aspects of cationic group 3 and lanthanide metals, e.g., in other catalytic reactions such as hydrogenation, hydrosilylation, and hydroamination, or in C−H activation reactions.

Supporting Information Available: Text giving full experimental and characterization data; crystallographic data for the dialkyl complexes of Sc and Nd and ionic monoalkyl complexes of Sc, Y, Gd, Nd, and La, as well as positional and thermal parameters and bond distances and angles (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) NMR tube-scale reactions of the diamagnetic metal dialkyls with [PhNMe₂H][B(C₆F₅)₄] in THF-d_8 showed clean conversion to the monoalkyl cations.

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