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Preliminary Communication

Alkylation of lanthanide alkoxides: synthesis of $[Ln(\mu\text{-}OBu^t)_3(\mu\text{-}Me)_3(AlMe_2)_3]$ (Ln = Pr, Nd or Y)

Paolo Biagini, Gabriele Lugli and Luigi Abis

Istituto Guido Donegani, EniChem Sp. A, via Fauser 4, 28100 Novara (Italy)

Roberto Millini

Eniricerche Sp. A, via Maritano 26, 20097 San Donato Milanese (Italy)

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Abstract

The alkylation of $Ln(OBu^t)_3$ with $AlMe_3$ leads to the mixed-bridged alkyl–alkoxy octahedral complexes $[Ln(\mu\text{-}OBu^t)_3(\mu\text{-}Me)_3(AlMe_2)_3]$ (Ln = Pr, Nd or Y). The neodymium derivative was characterised by single-crystal X-ray diffraction. The ^1H and ^{13}C NMR spectra of the diamagnetic yttrium complex showed the presence in solution of both *fac* and *mer* isomers.

Key words: Praseodymium; Neodymium; Ytterbium; X-ray structure; Alkoxides; Alkyl

The lanthanide-catalysed polymerisation of conjugated dienes is a well known process [1]. Generally the catalytic system is prepared by alkylation of a lanthanide derivative with an aluminium alkyl compound. Halides [2], carboxylates [3] and alkoxides [4] of all the elements of the lanthanide series have been successfully used as catalytic precursors.

Despite the wide use of these elements in catalysis very little is known about the nature of the catalytic species involved; presumably they are formed by an alkylated Ln^{III} derivative complexed with the aluminium compound [1,5]. The bimetallic complex $[Al_3Nd_6(\mu\text{-}Cl)_6(\mu_3\text{-}Cl)_6(\mu\text{-}Et)_9Et_5(OPr^i)]_2$ [6], obtained from the system $Nd(OPr^i)_3/AlEt_3/AlEt_2Cl$, is the only compound isolated and structurally characterised which represents a possible intermediate in the lanthanide-catalysed polymerisation of conjugated dialkenes.

While studying the alkylation of the lanthanide alkoxides we were able to isolate and characterise some mixed-bridged alkyl–alkoxy lanthanide complexes, namely $[Ln(\mu\text{-}OBu^t)_3(\mu\text{-}Me)_3(AlMe_2)_3]$ (Ln = Pr, **1**; Nd, **2**; Y, **3**). From the reaction of $AlMe_3$ with $Ln(OBu^t)_3$ in toluene at room temperature, complexes **1–3** were obtained pure after recrystallisation from pentane solution according to eqn. (1).

$$Ln(OBu^t)_3 + 3\,AlMe_3 \longrightarrow [Ln(\mu\text{-}OBu^t)_3(\mu\text{-}Me)_3(AlMe_2)_3] \quad (1)$$

(Ln = Pr, Nd or Y)

The complexes (**1–3**) are extremely soluble in aliphatic and aromatic solvents; they react vigorously with dioxygen and water and show good thermal stability. Complex **2** was sublimed at 100–120°C and 0.01 mmHg with about 50% decomposition.

Complex **2** was characterised by single-crystal X-ray diffraction, its molecular structure is shown in Fig. 1. The Nd atom, located on a three-fold axis (2/3, 1/3, *z*), is bonded to three crystallographically equivalent moieties $\{(\mu\text{-}OBu^t)\ (\mu\text{-}Me)\ (AlMe_2)\}$ giving rise to a highly distorted octahedral coordination. The structural features of complex **2** are quite similar to those recently reported for the yttrium analogue [7] obtained as minor product from the reaction between $[Y_3(OBu^t)_7Cl_2(THF)_2]$ and $AlMe_3$.

The ^1H NMR spectra of complex **3** were run at variable temperature in toluene-d_8. The room temperature spectrum was dominated by broad signals because of the fluxional behaviour of the ligands, but at 213 K the spectrum resolved into several sharp lines. Four singlets (δ = 1.28, 1.26, 1.24, 1.19 ppm; 27H) were assigned to $-OBu^t$ ligands; four doublets, two of which partially overlapped (δ = 0.12, 0.04, −0.02, −0.04 ppm, $J(^1H-^{89}Y) = 4.3$ Hz; 9H), were assigned to methyl ligands bridging aluminium and yttrium; finally a complex multiplet (δ = −0.2 to −0.5 ppm; 18H) was assigned to the methyl groups bonded terminally to the aluminium atoms.

The four $-OBu^t$ signals and four doublets for the bridging methyls is consistent with the presence in solution of both *fac* **3a** and *mer* **3b** isomers. Regarding **3a**, the C_3 symmetry axis makes all ligands on the yttrium equivalent, so that for this isomer one signal for $-OBu^t$ groups and one doublet for bridging methyl ligands are expected. In the case of **3b**, owing to the

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Correspondence to: Dr. G. Lugli.

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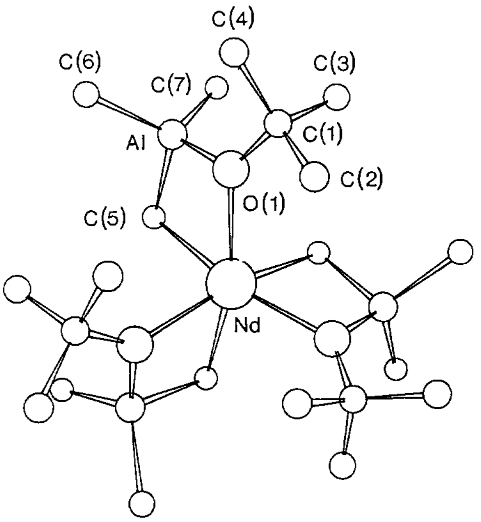

Fig. 1. PLUTO [10] plot of **2**. Selected bond lengths (Å) and angles (°): Nd–O(1) 2.303(7); Nd–C(5) 2.784(11); Al–O(1) 1.871(7); Al–C(5) 2.052(15); Al–C(6) 1.960(16); Al–C(7) 1.969(22); O(1)–Nd–O(1a) 111.5(2); O(1)–Nd–C(5) 71.6(3); O(1a)–Nd–C(5) 88.8(3); O(1b)–Nd–C(5) 154.8(3).

lack of any symmetry elements, all ligands are magnetically inequivalent so that such an isomer generates three different signals for each group: singlets for -OBu^t doublets for bridging methyls.

The methyl ligands terminally bonded to the aluminium atoms should give six in equivalent signals for **3b** but only two for **3a** because of the absence of any symmetry plane perpendicular to the C_3 axis. However, overlap of the resonances prevents resolution of the multiplicity.

The ^{13}C NMR spectra of **3**, in toluene-d_8 at 223 K, showed an analogous distribution of the signals. Four singlets (δ = 78.7, 78.5, 77.8, 77.1 ppm) for the quaternary carbons of $-OC(CH_3)_3$ and four doublets (δ = 11.6, 8.9, 8.7, 6.4 ppm $J(^{13}C-^{89}Y) = 13.6$ Hz) for methyl ligands bridged between yttrium and aluminium, correlate well with the presence of the *fac* and *mer* isomers. A complex signal stemming from the methyl groups of $-OC(CH_3)_3$ was observed at (δ = 34.5–32.5 ppm). Moreover, as already discussed, the pair of methyl groups terminally bonded to the aluminium should give six different resonances for **3b** and two for **3a**, but only seven signals are detected at (δ = −2.8, −2.9, −3.1, −3.5, −3.9, −4.2, −4.5 ppm). Overlap of two resonances probably occurs.

Experimental details

Preparation of [Nd(μ-OBu^t)$_3$(μ-Me)$_3$(AlMe$_2$)$_3$] (2)

To a solution of $Nd(OBu^t)_3$ (9.1 g, 25.0 mmol) in toluene (120 ml), 30 ml of a 2.5 M solution of $AlMe_3$ in toluene were added. The resulting pale blue solution was stirred at room temperature for 1 h, then the solvent was removed under reduced pressure and the solid residue dissolved in the minimum amount of pentane at room temperature. The solution was cooled slowly to −20°C and the pale blue crystals that separated were recovered by filtration and dried *in vacuo* to give 6.3 g of complex **2**. Another crop of crystals, 2.4 g (60% total yield) was obtained on cooling the mother liquor to −78°C.

Complexes **1** and **3** were obtained in a similar manner.

X-Ray structure determination of 2

A selected pale blue crystal ($0.4 \times 0.5 \times 0.7$ mm^3 in size) was introduced into a Lindemann glass capillary and sealed under an argon atmosphere. Data collection was carried out with a Siemens AED four-circle diffractometer and MoKα radiation ($\lambda = 0.71069$ Å). Trigonal space group P31c (No. 159), $a = 16.226(2)$ Å, $c = 8.219(1)$ Å, $V = 1874.0(4)$ Å^3, $Z = 2$ for $C_{21}H_{54}Al_3NdO_3$ (579.84 g mol^{-1}), $\rho_{calc} = 1.028$ Mg m^{-3}, μ 14.72 cm^{-1}. In total, 7150 reflections were collected in $\theta/2\theta$ scans, up to $\theta = 25°$, 1200 unique ($R_{int} = 0.0241$) and 1022 with $I > 3\sigma(I)$ were observed. The structure was solved using the MULTAN-80 direct method [8] and refined by full-matrix least squares (SHELX-76) [9]; the function minimized was $\Sigma_w[|F_o| - |F_c|]^2$, with $1/w = \sigma^2(F)$. The refinement converged (H atoms riding model with fixed isotropic $U = 0.05$ Å^2, all other atoms anisotropic) at $R = 0.0375$ and $R_w = 0.0420$. The remaining difference Fourier analysis was featureless. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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