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Synthesis and X-Ray Structure Analysis of Novel Ethyl-Bridged Ytterbium-Triethylaluminum Complex; $(\eta\text{-}C_5Me_5)_2Yb\cdot Al(C_2H_5)_3(THF)$

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A series of novel ytterbium-organoaluminum complexes has been prepared by the reaction of $YbCp^*_2(THF)$ ($Cp^*=\eta\text{-}C_5Me_5$) with AlR_3. The X-ray structure analysis of the triethylaluminum complex, $YbCp^*_2\text{-}Al(C_2H_5)_3(THF)$, revealed the presence of unusual $Yb\text{-}(\mu\text{-}C_2H_5)\text{-}Al$ linkage. The complex catalyzes the polymerization of ethylene, methyl methacrylate and styrene in toluene.

One of the prominent class of reactions in lanthanide chemistry is the complexation with main group organometallics to afford either alkylated mononuclear metal compounds or heterobimetallic compounds. These reactions are pivotal steps in a large variety of important catalytic and stoichiometric processes, including Ziegler-Natta type polymerizations of olefins,1) C-H activations of hydrocarbons2) and Grignard type insertion reactions of electrophiles.3)

Groups 3A and 4A metallocene compounds are known to extensively provide heterobimetallic complexes bearing double alkyl,4) halogeno5) or hydrido6) bridges such as $Cp_2M(\mu\text{-}CH_3)_2AlR_2$(M=Ti, Sm, Y, Gd, Dy, Ho, Yb),4) $Cp_2Ti(\mu\text{-}Cl)_2AlR_2$,5) $Cp_2Ti(\mu\text{-}H)_2BH_2$,6) and $Cp_2Ti(\mu\text{-}Cl)(\mu\text{-}R)AlR_2$7)($Cp=\eta\text{-}C_5H_5$) as the result of reactions with main group organometallic compounds. The complex with a single alkyl bridge is known only in the case of $Cp^*_2Yb(\mu\text{-}CH_3)BeCp^*$.8)

We report here the first example of the single ethyl bridged lanthanide(II)-aluminum(III) complex, $YbCp^*_2(\mu\text{-}C_2H_5)Al(C_2H_5)_2(THF)$(1) obtained by a facile method. One equiv. of $Al(C_2H_5)_3$ readily react with $YbCp^*_2(THF)$ in toluene at 25°C in argon. The recrystallization of the product in hexane at -20 °C gave the complex 1 as highly air sensitive green crystals in ca. 50% yield (Eq. 1). In a similar manner,

$$Cp^*_2Yb(THF) + AlR_3 \xrightarrow[\text{in toluene}]{30\,^\circ C,\ 30\ min} Cp^*_2Yb\cdot AlR_3(THF) \qquad (1)$$

1: $R=C_2H_5$
2: $R=CH_3$
3: $R=i\text{-}C_4H_9$

the corresponding adducts, $YbCp^*_2(\mu-CH_3)Al(CH_3)_2(THF)$(2) and $YbCp^*_2(\mu-i-C_4H_9)Al(i-C_4H_9)_2(THF)$(3), were also obtained as violet and green crystals in good yields by the addition of $Al(CH_3)_3$ and $Al(i-C_4H_9)_3$, respectively, as confirmed by the ^1H NMR studies.[9)] The EIMS spectra of 1-3, however, show only the signals of $YbCp^*_2$ together with AlR_3, indicating that these complexes exhibit rather weak bond between the two metal components.

In order to establish the exact molecular structure, the X-ray structure analysis has been carried out.[10)] Crystal data of 1: $C_{30}H_{53}OAlYb$, M=629.8, orthorhombic, space group $P2_12_12_1$, a=13.345(2), b=19.629(3), c=12.372(2) Å, V=3240.8(8) Å^3, Z=4, D_c=1.290 g/cm^3, μ(Mo$K\alpha$)=30.8 cm^{-1}. A total of 5218 independent reflections was collected up to 2θ=60° by the θ-2θ scan method, of which 3621 were observed reflections [$|F_o|>3\sigma(F_o)$]. The crystal structure was solved by the conventional heavy atom method and was refined by the full matrix least-squares (XRAY-76).[11)] The final $R(R_w)$ index is 0.077(0.079). The weighting scheme applied was $w=[\sigma^2(F_o)+0.003(F_o)^2]^{-1}$.

Figure 1 shows an ORTEP diagram of the complex 1 with the numbering scheme of selected atoms. The molecule consists of $YbCp^*_2$ and $Al(C_2H_5)_3(THF)$ components. Thus, $Al(C_2H_5)_3$ pulled out the THF molecule from $YbCp^*_2(THF)$ during the reaction. The ytterbium atom is tri-coordinated if the Cp* ligand is considered to occupy one coordination site and the ethyl group is bound to Yb only at the CH_2 position. The aluminum atom shows a distorted tetrahedral geometry since a tetrahydrofuran molecule is coordinated to the metal. The most intriguing structural feature of 1 lies in the mode of its Yb-(μ-C_2H_5)-Al linkage. The Yb-C(1) distance of 2.854(18) Å is the longest among the bonds reported for alkylytterbium complexes,

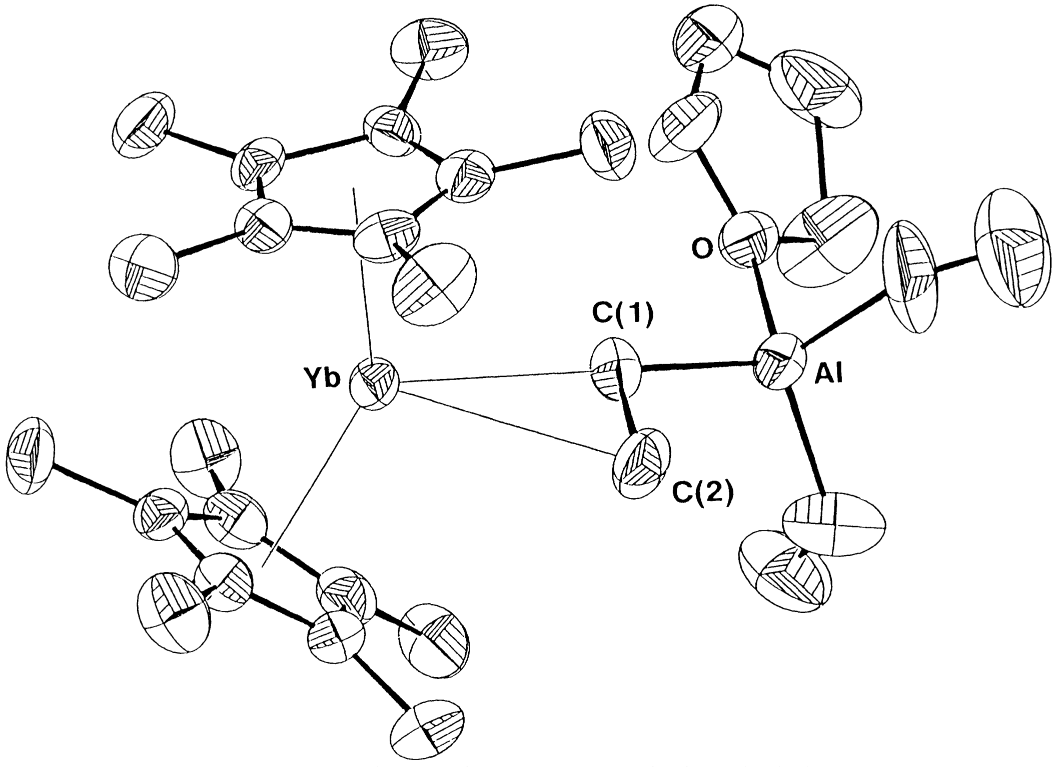

Fig. 1. Molecular structure of $(C_5Me_5)_2Yb\cdot Al(C_2H_5)_3(THF)$ (1) drawn by the thermal ellipsoids for nonhydrogen atoms at 20% probability level.

i.e. $Cp^*_2Yb(\mu\text{-}CH_3)BeCp^*$(2.766(4) Å),[8] $[Cp_2Yb(\mu\text{-}CH_3)]_2$(2.51 Å),[12] and $Cp_2Yb(\mu\text{-}CH_3)_2\text{-}Al(CH_3)_2$(2.609(23) Å).[4] The Yb-C(2) distance(2.939(21) Å) is slightly longer than the Yb-C(1) distance but is still within the bonding range. The close proximity of C(2) to Yb may arise from the electron deficient bonding of the C(1) carbon bridging over Yb and Al atoms. The Yb-C(1)-C(2) angle of 76.6° is significantly small even compared with the corresponding angles (85-88°) reported for typical complexes with agostic interaction.[15] The Yb-C(1)-Al angle(177.7°) is comparable to the corresponding angle observed for $Cp^*_2Yb(\mu\text{-}CH_3)BeCp^*$(177.4°). The four atoms, Yb, C(1), C(2), and Al are nearly coplanar and the dihedral angle between Yb-C(1)-C(2) and Al-C(1)-C(2) planes is 2.1°. A slight lengthening of the C(1)-C(2) bond (1.628(27) Å) as compared with the conventional non-bridged ethyl C-C bonds in $K[Al(C_2H_5)_3]_2F$(1.523(22) Å)[13] and $LiAl(C_2H_5)_4$(1.523(12) Å)[14] is suggestive of the presence of negligibly weak agostic interaction between the Yb and the C(2) methyl group, because the agostic interaction generally brings about the shortening of the ethyl C-C bond(by 0.06-0.08 Å).[15] The result of low temperature ^1H NMR studies also supports this concept. The Al-C(1)-C(2) angle(105°) is significantly smaller than the conventional $AlCH_2CH_3$ angle observed, for example, in $LiAl(C_2H_5)_4$(109°),[14] but is comparable with the value reported for $Cp^*_2Sm(\mu\text{-}C_2H_5)_2Al(C_2H_5)_2$(104°).[16] The Yb-C(Cp*) distances(av. 2.679(17) Å) and (Cp*-centroid)-Yb-(Cp*-centroid) angle(142.8°) are identical with those reported for Cp^*_2Yb(donor) adducts.[17]

The variable temperature ^1H NMR studies are ineffective in differentiation of the signals of the bridged ethyl groups from those of non-bridged terminal ethyl groups even at -100 °C in toluene-d_8. Three ethyl groups are magnetically equivalent at temperatures from 60 °C to -100 °C. Only upfield shift of ethyl and Cp* methyl resonances and downfield shift of the THF signals were observed on lowering the temperature. This means that three ethyl groups exchange rapidly in the NMR time scale presumably through dissociation of the complex 1 into $YbCp^*_2$ and $Al(C_2H_5)_3$(THF) in a solution reflecting the weak bonding interaction between these fragments. Actually the addition of one or two equiv. of ether, THF or pyridine to 1 readily induced the cleavage of the Yb-C_2H_5 bond to give $YbCp^*_2$(donor)[17] together with AlR_3(donor) in quantitative yield. This behavior differs greatly from that of double alkyl bridged complexes, $Cp^*_2M(\mu\text{-}CH_3)_2Al(CH_3)_2$(M=Y, Dy, Yb, Sc), which produce $[Cp_2M(CH_3)]_2$ or $Cp_2M(CH_3)$(donor) molecule upon the addition of donors.[12]

During our preliminary investigations of the reactivity of complexes 1-3, we have observed good catalysis of 1 in polymerization of ethylene in toluene. For example, 400 equiv. of ethylene is converted to polyethylene(Mw=7 000) in 98% yield at 25 °C in 8 h under atmospheric pressure. A mixture of $YbCp^*_2$(THF) with $Al(C_2H_5)_3$(1:1) also exhibits the similar catalytic activity. However, an increase of the Al/Yb ratio brings about lowering of the catalytic activity, i.e. the $YbCp^*_2(THF)/Al(C_2H_5)_3$(1:3) system exhibits only a half activity (regarding the yield) as compared with 1 and the $YbCp^*_2(THF)/Al(C_2H_5)_3$(1:5) system shows no activity under all conditions studied. Polyolefins such as poly(methyl methacryrate)(76% syndiotactic, Mw=960 000) and polystyrene(atactic, Mw=20 000) were also obtained using the isolated complex 1 (10^{-3} equiv. in toluene) as catalyst.

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9) 1: mp 115 °C(dec.) ^{1}H NMR (C_6D_6, at 30 °C, 100 MHz) δ 0.06 (q, J=8.0 Hz, 6H, Al-$C\underline{H}_2$-), 1.16 (t, J=8.0 Hz, 9H, -$C\underline{H}_3$), 2.09 (s, 30H, $C_5(C\underline{H}_3)_5$), 1.14 (m, 4H, THF), 3.48 (m, 4H, THF).
2: mp 143 °C(dec.) ^{1}H NMR (C_6D_6, at 30 °C, 100 MHz) δ -0.28 (s, 9H, Al-$C\underline{H}_3$), 2.21 (s, 30H, $C_5(C\underline{H}_3)_5$), 1.50 (m, 4H, THF), 3.60 (m, 4H, THF).
3: mp 48 °C(dec.) ^{1}H NMR (C_6D_6, at 30 °C, 100 MHz) δ 0.41 (d, 6H, J=7.0 Hz, -$C\underline{H}_2$-), 1.28 (d, J=6.2 Hz, 18H, -$C\underline{H}_3$), 1.49 (m, 3H, -$C\underline{H}$-), 1.99 (s, 30H, $C_5(C\underline{H}_3)_5$), 0.96 (m, 4H, THF), 3.34 (m, 4H, THF).

10) The X-ray diffraction data were collected on a Rigaku automated four-circle diffractometer using a suitable crystal sealed in a thin-walled glass capillary tube under argon. The ORTEP diagram was obtained using the "ORTEP-II" program; C. K. Johnson, Report ORNL-5138, Oakridge National Laboratory, Oakridge, TN (1974).

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