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Multiple C−H Bond Activation in Group 3 Chemistry: Synthesis and Structural Characterization of an Yttrium−Aluminum−Methine Cluster

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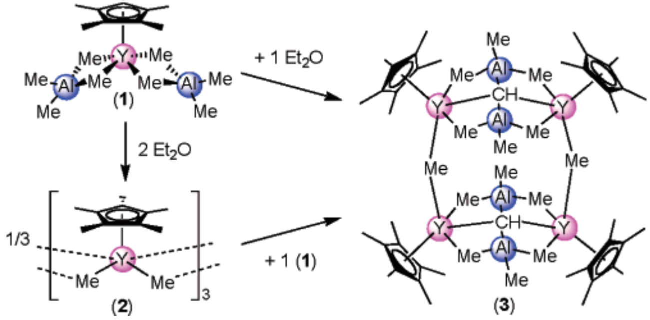
Metal-assisted C−H bond activation displays a crucial reaction pathway in many catalytic tranformations, be it in the field of homogeneous, heterogeneous, or enzyme catalysis.[1−4] Depending on the nature of the metal center, the key mechanistic steps involve oxidative addition of alkanes (late transition metals) or σ-bond metathesis (early transition and main group metals), with alkane addition across M═N bonds featuring a peculiar variant of the latter.[5] Multiple hydrogen abstraction from metal-bonded alkyl ligands has been discussed as a delicate case of C−H bond activation in organogroup 4-Al heterobimetallic chemistry.[6−10] "$AlMe_3$ inhibits the catastrophic decomposition of Cp_2TiMe_2, and dictates the abstraction of hydrogen from methyl rather than Cp groups." This was one of the concluding sentences when the *Tebbe reagent* $[Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Al(CH_3)_2]$ was reported for the first time in 1978.[6] Later, multiple hydrogen abstraction was structurally evidenced by cluster compounds such as $[(Cp^*M)_3Al_6Me_8(CH)_5(CH_2)_2]$ (M = Zr, Hf)[7] and $[(tBu_3PN)Ti(\mu\text{-}Me)(\mu_4\text{-}C)(AlMe_2)_2]_2$[8] featuring 1,2,3,4,5-pentamethylcyclopentadienyl and phosphinimide ancillary ligands. Particularly, the kinetic studies performed by Stephan et al. on the reactivity of $(tBu_3PN)_2TiMe_2$ with $AlMe_3$ proved divergent reaction pathways and their relevance to define deactivation in polymerization catalysis.[8] However, such organoaluminum-assisted multiple C−H bond activation reactions affording methylene, methine, and carbide species are rare and have been observed only at Ti, Zr, Hf, and Cr metal centers.[6−10]

In this communication, we demonstrate the feasibility of such a multiple hydrogen abstraction in organogroup 3-Al heterobimetallic complexes. The interactivity of well-defined $[Cp^*Y(\mu_2\text{-}Me)_2]_3$ and $Cp^*Y(AlMe_4)_2$ in the absence of any "free" $AlMe_3$ suggests that precoordination of $AlMe_3$ via tetraalkylaluminate formation is also a key step in group 4/6-promoted multiple C−H bond activation. Once more, the "lanthanide model"[3,11] seems to be applicable for studying reaction pathways involving highly reactive, intrinsically labile group 4 metal−ligand bonding.

Recently, we have described a convenient high-yield synthesis of $[Cp^*Y(\mu_2\text{-}Me)_2]_3$ (**2**) via donor (THF)-induced alkylaluminate cleavage of $Cp^*Y(AlMe_4)_2$ (**1**) (two-equiv reaction, Scheme 1).[12] We have now succeeded in obtaining single crystals of this simple halflanthanidocene bis(hydrocarbyl) complex (Figure 1), the trimetallic composition of which has been correctly postulated on the basis of its distinct J_{YH} coupling.[12,13] The X-ray structure analysis of **2** reveals a molecule with high molecular symmetry: C_{3h}. The yttrium atoms are coordinated by four μ_2-bridging methyl groups (Y−C = 2.539(3), 2.550(3) Å) and one Cp* ligand adopting a tetragonal pyramidal geometry. Structurally evidenced bridging Y−Me−Y motifs are limited to a few metallocene complexes including $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Y(\mu\text{-}Me)]_2$, and $[(\eta^5\text{-}C_5H_4SiEt_3)_2Y(\mu\text{-}Me)]_2$ with Y−C bond distances ranging from 2.511(4) to 2.61(2) Å.[14,15]

Scheme 1. Competing Donor-Induced Tetraalkylaluminate Cleavage and Multiple C−H Activation in Halflanthanidocene Complexes



Surprisingly, treatment of **1** with 1 equiv of diethyl ether in hexane, toluene, or mixtures thereof at −35 °C did not lead to instant precipitation of compound **2**. Instead, the yellowish solutions reproducibly gave pale yellow rhombic crystals of a new compound **3** (10−30% yields) after 3 days at ambient temperature. In aromatic solvents, metalation of 1,2,3,4,5-pentamethylcyclopentadienide in **2** is a competitive reaction pathway as indicated by transient black-colored solutions.[16] Unfortunately, **3** is insoluble in benzene-d_6 and toluene-d_8 and dissolved only slowly in refluxing THF-d_8 under decomposition which impeded its NMR spectroscopic characterization. The kinetically induced formation of compound **3** was corroborated by an NMR-scale reaction in toluene revealing the formation of a white precipitate and complexes **1**, **2**, and $AlMe_3\cdot OEt_2$ as the only traceable soluble components. The molecular composition of **3** was unequivocally proven by three independent X-ray crystallographic studies to be $[Cp^*_4Y_4(\mu_2\text{-}CH_3)_2\{(CH_3)Al(\mu_2\text{-}CH_3)_2\}_4(\mu_4\text{-}CH)_2]$, a heterooctametallic Y−Al−methylidine cluster (Figure 2), with two independent molecules per unit cell exhibiting an inversion center. Four yttrium atoms build a rectangle (90.2, 89.8 and 91.3, 88.7°) of 4.46 (4.45) by 5.23 (5.25) Å,

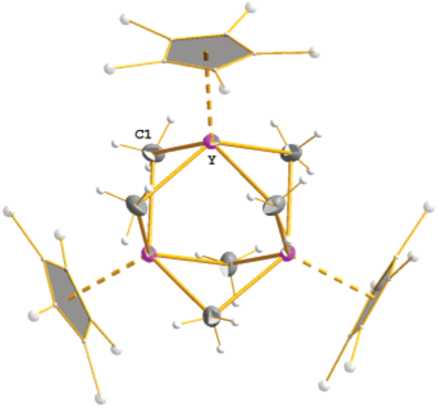


Figure 1. Molecular structure of $[Cp^*Y(\mu_2\text{-}Me)_2]_3$, **2**; the central part is shown with atomic displacement parameters at the 50% level and refined H atoms. Atoms in the Cp* groups are shown isotropically with an arbitrary radius and without H atoms.

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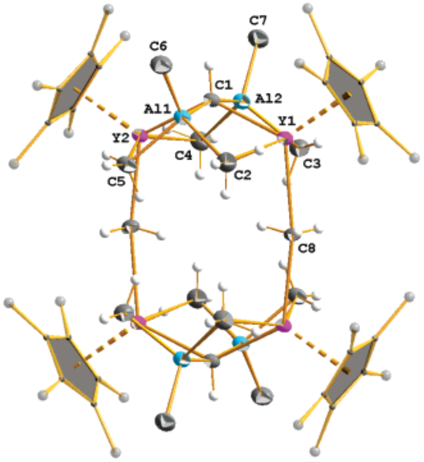

Figure 2. Molecular structure of $[Cp^*_4Y_4(\mu_2\text{-}CH_3)_2\{(CH_3)Al(\mu_2\text{-}CH_3)_2\}_4\text{-}(\mu_4\text{-}CH)_2]$, **3** (first molecule of two); the central part is shown with atomic displacement parameters at the 50% level and refined H atoms (terminal $AlMe_3$ are without H atoms). Atoms in the Cp* groups are shown isotropically with an arbitrary radius and without H atoms.

respectively. Each yttrium is surrounded by a Cp*, three methyl ligands, and a methylidine group, creating a markedly distorted tetragonal pyramid. The four carbon atoms of the methylidine and yttrium-bridging methyl groups together with the four yttrium atoms form a planar eight-membered ring. The cagelike structure can be also described as two butterfly arrangements, each composed of two Cp*Y groups linked via $[(AlMe_3)_2(\mu_4\text{-}CH)]$ moieties, being connected by the two bridging methyl groups. In contrast to halfyttrocene complex **2** and doubly methyl-bridged metallocenes, the Y_4 cage shows large $Y-CH_3-Y$ angles (167.8(1)° and 168.0(1)°) and significantly different $Y-C(CH_3)$ bond lengths (2.577(3)/2.687(3) and 2.579(3)/2.702(3) Å) comparable to the unsolvated asymmetric lanthanidocene methyl complexes $[Cp^*_2Sm(CH_3)]_3$ (Sm−C−Sm, 176.2(3) and 162.2(2)°) and $[Cp^*_2Lu(CH_3)]_2$ (Lu−C−Lu, 169.5(2)°).[16,17]

The $Y-CH_3-Y$ homometal-bridged arrangement in **3** features a typical "linear symmetry" being characterized by a flattened CH_3 group.[18] The carbon atoms of the bridging methyl group are displaced on average by 0.15(2) Å from the hydrogen atom plane (cf. 0.3 Å for an sp^3-hybridized CH_3 group). This displacement from total "symmetrical linearity" explains the different Y−C bond lengths. A linear $Y-CH_3-Al$ linkage was also found in the heterobimetallic complex $[Cp^*_2Y(\mu\text{-}AlMe_4)]_2$ (176(1)°)[17] while the $Zr-CH_3-Zr$ moiety in complex $[Cp_2Zr(C,O\text{-}\eta^2\text{-}OCCHCH_2CMe_3)]_2\text{-}(\mu\text{-}AlMe_2)(\mu\text{-}Me)$[18b] has a more acute angle of 147.8(3)° and $Zr-C(CH_3)$ bond distances of 2.456(7) and 2.559(7) Å. The bridging carbon atom is, however, displaced only by 0.08 Å from the hydrogen atom plane.

The $Y-[(AlMe_3)_2(\mu_4\text{-}CH)]-Y$ moiety is certainly the most striking structural feature of **3** representing the first rare-earth metal-bonded methylidine group. The Y−C bond distances of the 4-coordinate methylidine carbon atoms are rather short (2.444(3)−2.464(3) Å). For comparison, the bridging and terminal Y−C bond distances in $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$[14] and $[Y(CH_3)(THF)_6]^{2+}\text{-}[BPh_4]^-{}_2$[19] are 2.62(2) and 2.418(3) Å, respectively. The only structurally characterized "Ln═C" complex $[Sm\{C(Ph_2P{=}N{-}SiMe_3)_2\text{-}\kappa^3C,N,N'\}(NCy_2)(THF)]$ shows a Sm−C distance of 2.467(4) Å.[20] The $Y-Me(AlMe_3)$ bond distances in **3** are 2.640(3)−2.700(3) Å, similar to those of the heterometal-bridged metallocene $[Cp^*_2Y(\mu\text{-}AlMe_4)]_2$ (2.65(2), 2.67(2) Å),[17] albeit slightly longer than those in $Y(AlMe_4)_3$ (2.505(7)−2.514(8) Å).[21] The Al−C(methylidine) bond lengths range from 1.984(3) to 1.993(3) Å, and are shorter than those found in $[(Cp^*M)_3Al_6Me_8(CH)_5(CH_2)_2]$ (M = Zr: 2.096(7)−2.168(7) Å, M = Hf: 2.126(7)−2.158(7) Å)[7a] and $[(Me_2Al)_2(\mu\text{-}CH)(AlCl_2Me)_2]^-$ (2.020(8), 2.029(5)).[9c]

Given the pronounced stability of complexes **1** and **2** in hexane, we have been intrigued by the interaction of these discrete halfyttrocene complexes. Indeed, an equimolar reaction of **1** with **2** in toluene yielded moderate yields (47%) of **3** within 5 days (Scheme 1). Although **1** exhibits a highly fluxional $\eta^2 \leftrightarrow \eta^3$ tetramethylaluminate coordination, dissociation of $AlMe_3$ in solution is not observed; **1** is even sublimable at <100 °C/10^{-3} Torr without decomposition.[12] These findings corroborate speculations about intrinsically labile $Ti-CH_3-Al$ moieties, formed via $[TiCH_3]\cdot AlMe_3$ complexation, to behave as benign species favoring hydrogen abstraction from the bridging methyl groups.[8]

In conclusion, a plausible reaction pathway for the formation of **3** might include intermolecular deprotonation of the bridging 5-coordinate aluminate methyl ligand in **1** by **2** and formation of a "Y−methylene−Y" fragment, followed by a second intramolecular deprotonation and dimerization, as well as evolution of a total of four methane molecules.

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Supporting Information Available: Crystallographic data for **2** and **3** and experimental details for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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