"Ionic Carbenes": Synthesis, Structural Characterization, and Reactivity of Rare-Earth Metal Methylidene Complexes

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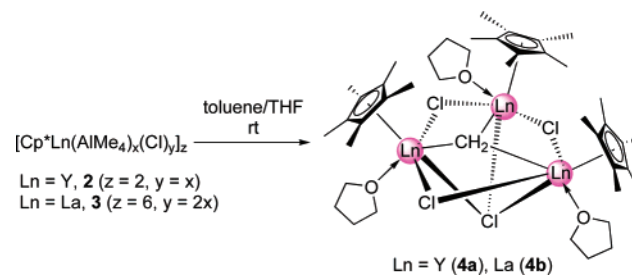*Department of Chemistry, University of Bergen, Allégaten 41, N-5007 Bergen, Norway*

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Transition metal carbene/alkylidene complexes are prominent reagents in organometallic chemistry not only due to their bonding features (Fischer- versus Schrock-type) but also due to their importance in organic synthesis and as catalytic intermediates.[1] Particularly, the Tebbe reagent $[Cp_2Ti(\mu\text{-}CH_2)(\mu\text{-}Cl)Al(CH_3)_2]$ and its variants developed by Grubbs became standard reagents in organic chemistry.[2–9] Such Schrock-type alkylidene complexes utilize the nucleophilic character of the methylidene carbon atom in Wittig-type reactions by converting (functionalized) aldehydes and ketones into terminal alkenes.[8] Moreover, olefin metathesis reactions have been proved by labeling studies.[4] For group 4 complexes, deprotonation of $AlMe_3$ and thermally induced methyl ligand degradation seem to be exclusive reaction pathways for the generation of methylidene ligands. A variety of crystallographically characterized titanium "alkylidene" complexes revealed the stabilizing role of aluminum,[2] late transition metal centers, such as Rh,[6] titanacyclobutane ring formation,[5] and cluster embedding.[10] For Zr and Hf, several complexes containing $M\text{-}CH_2\text{-}Al$ and $M\text{-}CRH\text{-}Al$ linkages, including $[Cp_2ZrCH(CH_2{}^tBu)AlCl({}^iBu)_2]$, were structurally characterized.[9,11,12] In addition, Al-free $M\text{-}CH_2\text{-}M$ moieties were found in $[\{(Cp^*)(C_2B_9H_{11})Zr\}_2(\mu\text{-}CH_2)]$,[12a] $[(Ph_2N)_2Ti(\mu\text{-}CH_2)]_2$,[12b] and $[(Cp_2ZrMe)_2(\mu\text{-}CH_2)]$.[12c] To the best of our knowledge, discrete $M{=}CH_2$ with M = Ti, Zr, and Hf have not yet been structurally identified so far, although low-temperature NMR spectroscopic and laser-ablation matrix-IR studies suggested their formation.[13]

In rare-earth metal chemistry, alkylidene complexes have been elusive.[14] Several "neutral" N-heterocyclic carbenes (NHCs) have been used as strong donor ligands in di- and trivalent complexes.[15,16] Covalently bonded "carbenes" were postulated ("$[Er(CHSiMe_3)(CH_2SiMe_3)]_n$")[17] and structurally evidenced in complexes $[Sm\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}(NCy_2)(THF)]$[18] and $[Ln\{C(Ph_2P{=}S)_2\text{-}\kappa^3C,S,S'\}(\mu\text{-}I)(THF)_2]_2$ (Ln = Sm, Tm).[19] Herein, we would like to present the first rare-earth metal methylidene complexes with a highly nucleophilic $CH_2{}^{2-}$ moiety stabilized by ionic interactions with three adjacent Ln^{3+} centers.

Reaction of $Cp^*Ln(AlMe_4)_2$ (**1**)[20] with Me_2AlCl was previously shown to yield mixed $AlMe_4$/chloride cluster species, the nuclearity of which depends on the metal ion size (Scheme 1).[21] Treatment of the in toluene sparingly soluble complex $\{Cp^*Y[(\mu\text{-}Me)_2AlMe_2](\mu\text{-}Cl)\}_2$ (**2**) with THF led to a clear solution from which colorless crystals were obtained after 3 days at ambient temperature (Scheme 1). X-ray structure analysis revealed the formation of a trinuclear cluster $[Cp^*_3Y_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}CH_2)(THF)_3]$ (**4a**) with all the aluminum metal centers displaced. The toluene insoluble cluster $\{Cp^*_6La_6[(\mu\text{-}Me)_3AlMe]_4(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_6\}$ (**3**) dissolved slowly in a toluene/THF (2/3) mixture to form a clear colorless solution (Scheme 1). Surprisingly, an X-ray crystallographic study of the crystals, which were harvested after 2 days at ambient temperature, showed $[Cp^*_3La_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}CH_2)(THF)_3]$ (**4b**) as an isostructural pendant of **4a**.

Scheme 1. Methylidene Formation by Donor(THF)-Induced Tetraalkylaluminate Cleavage

$[Cp^*Ln(AlMe_4)_x(Cl)_y]_z$ →(toluene/THF, rt)

Ln = Y, **2** (z = 2, y = x)
Ln = La, **3** (z = 6, y = 2x)

Ln = Y (**4a**), La (**4b**)

Reaction products **4** of this highly reproducible synthesis seem to be kinetically favored and are sparingly soluble in THF-d_8. The ^1H NMR spectrum of yttrium complex **4a** shows three Cp^* signals at 1.97, 1.96, and 1.95 ppm (2:1:2 integral ratio) compared to one for **4b** at 2.05 ppm. This signal splitting is also visible in the ^{13}C NMR spectrum and suggests sterically highly congested smaller yttrium metal centers, resulting in a hindered rotation of the Cp^* ligands. The two methylidene protons in **4a** are also magnetically nonequivalent, appearing as two multiplets at −0.39 and −0.85 ppm ($^2J_{YH}$ = 2.4 Hz). No such signals were observed for **4b**, probably caused by three adjacent quadrupolar lanthanum nuclei. Due to the poor solubility of complexes **4**, ^{13}C NMR signals of the methylidene ligands were not observable even after 36 h of measuring time. Complexes **4a** and **4b** are isostructural and crystallize in the monoclinic space group $P2_1/n$. Each Ln atom is surrounded by one Cp^*, three bridging chlorides, one THF, and one μ_3-bridging methylidene group, resulting in a distorted pseudo-octahedral geometry. The core of the cluster adopts a distorted hexagonal bipyramid (pseudo 3-fold rotation axis), with alternating Ln and μ_2-bridging chloride ions in the equatorial and a μ_3-chloride and the methylidene groups in the apical positions, as well as crystallographically nonequivalent THF molecules. The most striking structural feature of complexes **4** is the presence of an unprecedented unique methylidene ligand. The three $Y\text{-}CH_2$ bonds are almost equidistant (2.424(2)–2.450(2) Å), while the $La\text{-}CH_2$ distances range from 2.537(3) to 2.635(3) Å. Despite the eight-coordinate metal centers and a μ_3-bridging methylidene carbon atom, the $Ln\text{-}CH_2$ distances are comparatively short. The bridging methyl ligands in eight-coordinate $[(1,3\text{-}Me_2C_5H_3)_2Y(\mu\text{-}Me)]_2$[22] show $Y\text{-}C$ distances of av. 2.61 Å, while the terminal $Y\text{-}C$ bond length in seven-coordinate $[Y(CH_3)(THF)_6]^{2+}[BPh_4]^-{}_2$ is 2.418(3) Å.[23] The $Sm\text{-}C$ distance in $[Sm\{C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}(NCy_2)(THF)]$ was measured as 2.467(4) Å.[18] The postulation of $CH_2{}^{2-}$ units in **4** irrevocably directs the attention to other doubly negatively charged small ligands, such as O^{2-} and NH^{2-}. For example, the recently reported six-coordinate halfyttrocene clusters $[Y_4(C_5Me_4SiMe_3)_4(\mu_3\text{-}O)_2(Me_3SiCCHCHCSiMe_3)]$ and $[Y_4(C_5Me_4SiMe_3)_4(\mu\text{-}H)_2(\mu_3\text{-}O)(Me_3SiCCHCHCSiMe_3)]$ feature $Y\text{-}O(O^{2-})$ distances of 2.176(2)–2.187(2) and 2.142(3)–2.229(3) Å, respec-
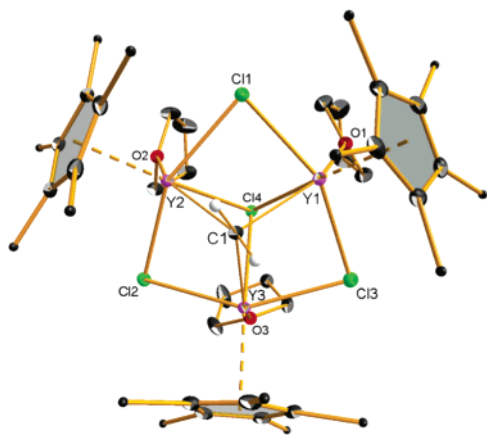
Figure 1. Molecular structure of $[Cp*_3Y_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}CH_2)(THF)_3]$, **4a**; the central part is shown with atomic displacement parameters at the 50% level and refined H atoms. Terminal C atoms in the Cp* groups are shown isotropically with an arbitrary radius and without H atoms, also hydrogens on the THF rings have been omitted for clarity. The molecular structure of $[Cp*_3La_3(\mu\text{-}Cl)_3(\mu_3\text{-}Cl)(\mu_3\text{-}CH_2)(THF)_3]$ (**4b**) is isostructural.

tively,[24] while the tetranuclear constrained geometry complex $\{[\eta^5\text{-}\mu_2\text{-}C_9H_6SiMe_2NH)Er]_2(\mu_3\text{-}Cl)(THF)\}_2(\mu_4\text{-}NH)\cdot THF$ with eight-coordinate erbium centers exhibits $Er-N(NH^{2-})$ distances of 2.386-(4) and 2.425(1) Å.[25] The $Y-Cl$ distances in **4a** vary from 2.7028(6) to 2.7287(6) Å $(\mu_2\text{-}Cl)$ and from 2.8522(5) to 2.8897(5) Å $(\mu_3\text{-}Cl)$, which is consistent with literature data, for example, 2.776(6) Å in eight-coordinate $[Cp*_2Y(\mu\text{-}Cl)YClCp*_2]$[26] and av. 2.820(5)–2.897-(6) Å in six-coordinate $[Y_3(\mu_3\text{-}OCMe_3)(\mu_3\text{-}Cl)(\mu_2\text{-}OCMe_3)_2(\mu_3\text{-}OCMe_3)_3(OCMe_3)_4(THF)_2]$.[27] The $La-Cl$ bond distances varying from 2.8614(8) to 2.8929(8) $(\mu_2\text{-}Cl)$ and 3.0014(7) to 3.0334(7) Å $(\mu_3\text{-}Cl)$ appear slightly elongated compared to those of eight-coordinate hexanuclear precursor $\{Cp*_6La_6[(\mu\text{-}Me)_3AlMe]_4(\mu_3\text{-}Cl)_2\text{-}(\mu_2\text{-}Cl)_6\}$ (av. 2.822 Å $(\mu_2\text{-}Cl)$, av. 3.040 Å $(\mu_3\text{-}Cl)$).[21]

A preliminary reactivity protocol showed that methylidene complexes **4** are capable of acting as Schrock-type nucleophilic carbenes. Aiming at a Tebbe reagent analogous methylidene transfer, we carried out NMR-scale reactions with various carbonylic substrates. Accordingly, reaction mixtures in THF turned slightly yellow (benzaldehyde, cyclohexanone, cyclohexenone) or brightly orange (fluorenone). Cyclohexanone (85%, **4b**) and fluorenone (89%, **4b**) were converted in good yields. Although the resulting Ln oxo complexes could not be obtained in single-crystalline form, CH_2^{2-}/O^{2-} group interchange under retention of the cluster entity can be rationalized on the basis of known oxo clusters.[24] The reaction of **4** with δ-valerolactone occurred via donor (THF) ligand exchange, as evidenced by ^1H NMR spectroscopy. Such ligand exchange was previously shown for $Cp*_2Y(OMe)\text{-}(THF)$[28] and verified by the X-ray structure analysis of $YCl_3\text{-}(C_6H_{10}O_2)_3$.[29] Addition of more than 3 equiv of δ-valerolactone per trinuclear cluster resulted in instantaneous ring-opening polymerization. Although polymer properties are not a subject of this paper, a living polymerization is proposed (additional δ-valerolactone was polymerized even after 3 days). Moreover, one is tempted to speculate about the dianionic methylidene moiety to act as a novel bisinitiator.

In conclusion, rare-earth metal methylidene complexes were found as kinetically favored products in proton abstraction reactions involving heteroleptic heterobimetallic $[Ln\{(\mu\text{-}Me)_2AlMe_2\}(Cl)]$ moieties.[30] The CH_2^{2-} dianionic group seems to be preferentially stabilized by Ln_3 cluster entities of both large (La) and smaller (Y) rare-earth metal cations, even in the absence of co-stabilizing

alkylated aluminum metal centers. The reactivity of the novel methylidene derivatives is hallmarked by the nucleophilic character of such "ionic carbenes" as evidenced by the Tebbe reagent analogous transfer of the methylidene group to carbonyl functionalities.

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

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