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Generation of Dimethylsilylene and Allylidene Holmium Complexes from Trimethylsilylated Allyl Ligands

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Allyl ligands containing trimethylsilyl substituents have been incorporated into thermally stable complexes with metals from across the periodic table.[1] In the case of the f-elements, both neutral species[2−4] and anionic lanthanates[3,5] have been isolated. In all these compounds, the trimethylsilylated ligands function as bulky η^3-bonded units that provide enhanced solubility and stability, but are not involved in more complex metal−ligand interactions. We have now found that the trimethylsilyl groups are potential sites of reactivity in organolanthanide allyl complexes. The resultant generation of dimethylsilylene and allylidene ligands represents previously unobserved transformations in f-element chemistry.

When lanthanide triflates are treated with 3 equiv of the potassium salt of the bis(1,3-trimethylsilyl)allyl anion, KA′ (A′ = [1,3-$(SiMe_3)_2C_3H_3$]), the neutral triallyl lanthanide products A'_3-Ln(THF) (Ln = Ce, Nd, Tb) can be isolated.[4] The use of rigorously anhydrous holmium triflate produces a THF-free A'_3Ho complex (eq 1; see Supporting Information for details).

$$Ho(OTf)_3 + 3\,KA' \xrightarrow{THF} A'_3Ho + 3\,KOTf\downarrow \qquad (1)$$

Even vacuum-dried $Ho(OTf)_3$ retains traces of coordinated water, however, and it can alter the outcome of reactions. The reaction of holmium triflate that contains ca. 3% water[6] with 3 equiv of KA′ in THF at −78 °C immediately produces an orange solution. Workup after stirring for no more than 4 h yields A'_3Ho; if the reaction time is extended up to 15 h, however, a different hydrocarbon-soluble yellow-orange complex (**1**) can be isolated in good (74%) yield. It is indefinitely stable at room temperature under inert atmosphere and tolerates brief (<10 min) exposure to air without visible decomposition. Crystals of **1** grown from hexanes solution contain the dimeric species illustrated in Figure 1. There are two independent but virtually identical molecules in the asymmetric unit, each positioned on a crystallographic inversion center. One η^3-coordinated allyl ligand is bound to each metal, but hydrogen abstraction from a trimethylsilyl group has occurred on a second allyl ligand associated with each metal center, forming dimethylsilylene units that bridge the holmium atoms. The bridging carbons are nearly symmetrically positioned between the holmium centers at 2.478(4) and 2.512(4) Å. These distances are slightly shorter than the 2.563(18) Å separation observed for the bridging methyl groups in $[Li(tmed)]_3[Ho(\mu\text{-}Me)_6]$,[7] possibly reflecting the di-negative charge of the ligands in **1**.

When the reaction that produced **1** is allowed to continue for more than 20 h before workup, a second yellow-orange dinuclear product (**2**) can be isolated. The X-ray structure of crystals grown from hexanes reveals that, in addition to two dimethylsilylene bridges, the metal centers are joined with a μ-η^1,η^3-allylidene ligand (Figure 2). A THF ligand completes the coordination sphere of each metal. In **2**, the methylene carbons of the dimethylsilylene bridges are at longer distances and are more asymmetrically bonded than those in **1**, with distances from C16 and C25 ranging from 2.517(5) to 2.629(5) Å. The bridging allylidene has Ho−C6 distances

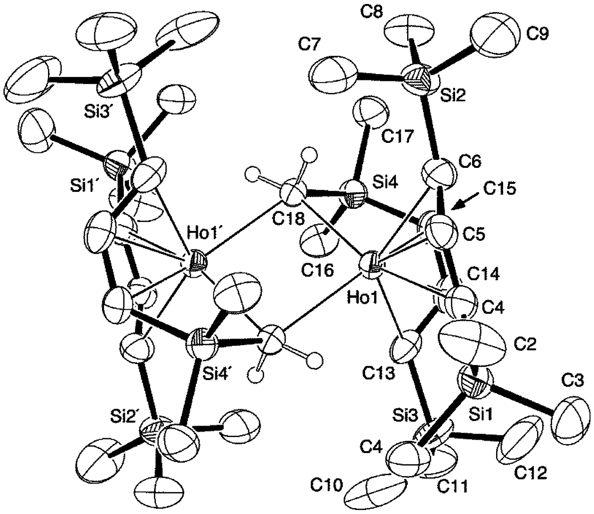

Figure 1. ORTEP of **1**, with thermal ellipsoids at the 50% level. Hydrogen atoms not part of the dimethylsilylene bridges have been omitted for clarity. Selected bond distances [Å]: Ho1−C4, 2.603(4); Ho1−C5, 2.617(4); Ho1−C6, 2.510(4); Ho1−C13, 2.528(4); Ho1−C14, 2.595(4); Ho1−C15, 2.575(4); Ho1−C18, 2.478(4); Ho1′−C18, 2.512(4).

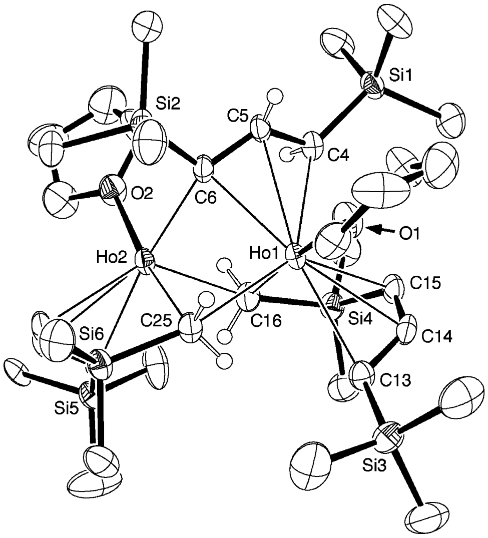

Figure 2. ORTEP of **2**, with thermal ellipsoids at the 50% level. Hydrogen atoms not part of the dimethylsilylene or allylidene bridges have been omitted for clarity. Selected bond distances [Å]: Ho1−C4, 2.564(5); Ho1−C5, 2.645(5); Ho1−C6, 2.500(5); Ho2−C6, 2.422(5); Ho1−C16, 2.570(5); Ho1−O1, 2.383(4); Ho2−C16, 2.517(5); Ho1−C25, 2.629(5); Ho2−C25, 2.519(5), Ho2−O2, 2.367(4).

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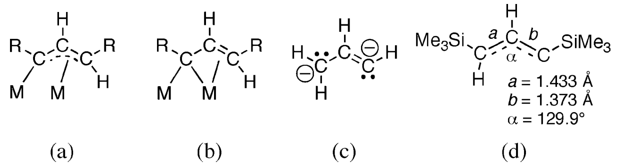


Figure 3. (a) Delocalized allylidene bonding (R = $SiMe_3$ in **2**). (b) Vinylalkylidene bonding scheme. (c) Most stable Lewis structure of the allyl dianion. (d) Geometry optimized $[1,3\text{-}(SiMe_3)_2C_3H_2]^{2-}$ ion.

of 2.422(5) and 2.500(5) Å. As a consequence of being bridged by three dianionic ligands, the Ho···Ho distance in **2** has contracted from the 3.5243(8) Å separation observed in **1** to 3.1874(4) Å. The latter is the shortest yet observed in an organoholmium compound.[8]

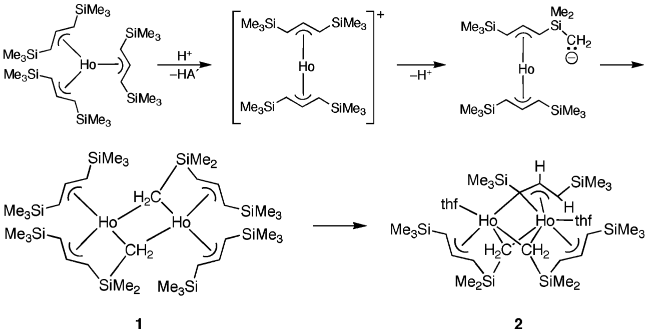
The similar carbon−carbon distances within the allylidene ligand (C4−C5 = 1.425(7) Å; C5−C6 = 1.410(7) Å; C4−C5−C6 = 126.2(5)°) are an indication that a delocalized description of the bonding (Figure 3a) is more appropriate than a localized vinylalkylidene scheme (Figure 3b). The delocalization appears to be a feature of the allyl dianion itself. Although several Lewis structures can be written for the ion, the most stable suggests that it should have distinctly different C−C bonds (Figure 3c). Nevertheless, a DFT geometry optimization of the (gas phase) $[H_2CC(H)CH]^{2-}$ ion converges to bond lengths of 1.403 and 1.402 Å (C−C−C = 127.3°).[9] When the model includes trimethylsilyl groups (i.e., $[(Me_3Si)HCC(H)C(SiMe_3)]^{2-}$), the C−C bond lengths differ by only 0.06 Å (Figure 3d).[9] Consistent with the largely ionic bonding expected in organolanthanide complexes,[10] the holmium framework appears to have preserved the major structural features of the isolated anion.

The mechanism of formation of **1** and **2** is of interest, particularly as lanthanide triflates are widely used as Lewis acids in organic transformations.[11] Although not previously observed in allyl complexes, C−H activation of trimethylsilyl groups is known in cyclopentadienyl compounds of the early transition metals. For example, when $(C_5Me_4SiMe_3)_2Ti^{IV}Cl_2$ is treated with magnesium metal, the paramagnetic species $(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2CH_2)(\eta^5\text{-}C_5Me_4SiMe_3)Ti^{III}$ is one of the products.[12] Similar C−H activation has been extensively investigated in zirconium metallocenes.[13] Analogous reductive elimination is not available for the generation of **1**, as holmium is not known in oxidation states other than zero and three (the Ho(III)/Ho(II) reduction potential is estimated at −2.9 V,[14] and no Ho(II) compounds exist).[15] Abstraction of a proton from a $SiMe_3$ group can also be initiated with a Lewis acid, such as $B(C_6F_5)_3$, with no formal change of oxidation state. In these cases, the Lewis acid serves to remove an alkyl group from the metal to form a cationic intermediate, followed by the cyclometalation of the $SiMe_3$ group.[16] Such a situation does not exist with the present compounds.

Residual water in the holmium triflate is probably responsible for the formation of **1** and **2**. A possible reaction sequence involves the initial, rapid formation of the neutral A'_3Ho complex (eq 1), but slow protonation of a single allyl ligand would produce an equivalent of the HA′ propene and the monocation $[A'_2Ho]^+$. The latter could undergo self-abstraction of a hydrogen from a trimethylsilyl group, followed by dimerization to form **1** ($[Ho(A')(A'\text{-}SiMe_2CH_2)]_2$) (Scheme 1). A second protonation step and removal of an allyl ligand in **1** would generate the cationic $[Ho_2(A'\text{-}SiMe_2CH_2)_2(A')]^+$ complex, which on loss of a C−H proton would yield the allyl dianion in complex **2**. This ligand transformation is reminiscent of the ability of air-deactivated (presumably hydrated) silica gel to convert the allyl complex $Ru(CO)(\eta^3\text{-}C_3H_5)Cp$ to the allylidene species $Ru_2(CO)(\mu\text{-}CO)(\mu\text{-}\eta^1,\eta^3\text{-}CHCHCH_2)Cp_2$.[17]

In summary, the first examples of binuclear dimethylsilylene and allylidene lanthanide compounds have been obtained from the conversion of sterically bulky allyl anions in the presence of partially hydrated holmium triflate. It is clear that trimethylsilyl groups on allyl ligands cannot always be assumed to be completely unreactive in f-element complexes. Even without an oxidation state change or d-orbital participation in the metal−ligand bonding, these transformations bear striking parallels to reactions in cyclopentadienyl transition metal chemistry.

Scheme 1. Possible Route to the Synthesis of **1** and **2**



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Supporting Information Available: Synthetic details for A'_3Ho, **1**, and **2**; crystallographic details, X-ray crystallographic files (CIF), and additional views and packing diagrams for **1** and **2**; and complete ref 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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