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Multi-Electron Redox Reactivity of A Samarium(II) Hydrido Complex

Xianghui Shi, Peng Deng, Thayalan Rajeshkumar, Laurent Maron, and Jianhua Cheng

Well-defined low-valent molecular rare-earth metal hydrides are rare, and limited to YbII and EuII centers. Here, we report the first example of divalent samarium(II) hydrido complex \( [\text{Cp}^{\text{Ad}}\text{Sm}(\mu-H)(\text{DABCO})] \). \( \text{Cp}^{\text{Ad}} \) is a 15-electron ancillary ligand (Figure 1). Complexes bearing terminal hydrido ligands were achieved by increasing the steric bulk of the surrounding coordination sphere. Mechanistic studies suggest that complex \( \text{Cp}^{\text{Ad}}\text{Sm}(\mu-H)(\text{DABCO}) \) exhibits multi-electron redox reactivity toward a variety of substrates. Exposure of complex \( \text{Cp}^{\text{Ad}}\text{Sm}(\mu-H)(\text{DABCO}) \) with CO results in trivalent samarium(III) mixed-bisformate/carbonate complex \( [\text{Cp}^{\text{Ad}}\text{Sm}(\mu-\eta^1:\eta^2-\text{CO})(\mu-\eta^1:\eta^2-\text{CO})(\mu-\eta^1:\eta^2-\text{CO})(\mu-H)(\text{DABCO})] \), which is a new type of isocarbonyl complex.

Introduction

The chemistry of molecular hydrides of rare-earth metals has been extensively studied in the past four decades.\(^{[1]}\) However, despite their significant roles in various stoichiometric and catalytic reactions, such complexes are dominated by trivalent rare-earth metal centers.\(^{[1]}\) The difficulties in isolating discrete divalent rare-earth metal hydrides are mainly attributed to the larger ionic radius and higher reactivity, compared with trivalent rare-earth metal. So far, structurally characterized divalent rare-earth metal hydrides species are scarce, consisting of a handful of ytterbium(II) hydrides\(^{[3-9]}\) and three examples of europium(II) hydrides complexes\(^{[10]}\), albeit all lanthanides (II), except the radioactive promethium, are accessible in soluble molecules.\(^{[11]}\)

The group of Takats reported the first example of divalent ytterbium hydride complex \( [[\text{Tp}^{\text{Bu},\text{Me}}\text{Yb}(\mu-H)]_2 \) (Figure 1).\(^{[11]}\) The first mononuclear divalent ytterbium hydride complex \( [[\text{Tp}^{\text{Ad},\text{Pr}}\text{Yb}(\mu-H)](\text{THF})] \) (Figure 1) bearing a terminal hydrido ligand was achieved by increasing the steric bulk of Trofimenko’s tris(pyrazolyl)borate.\(^{[12]}\) Three other
examples of cationic divalent ytterbium hydrides [(Me₂TACD)₂Yb₂(μ-H)(2n=1)](2+n) (n = 0, 1) (Me₂TACD = 1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) (Figure 1, VII).[9]

Very recently, the bulky β-diketiminate ligand frameworks [BDI(ΟCH²)₆] and [BDI(OAr₅)] (BDI = [HC(C(Me)₃)N-Dipp/Ar₅]; Dipp = 2,6-Pr₂C₆H₄, Ar = 2,6-C₆H₄-C₆H₅ (DCHP) or 2,4,6-C₆H₃-C₆H₅ (TCHP)) have been developed for the kinetic stabilization of the first europium(II) hydrides complexes (Figure 1, VIII).[10]

Divalent ytterbium hydrides have been involved in a variety of organic transformations, and the oxidation state of ytterbium center remains intact in most cases.[5,12] A more versatile chemistry can confidently be predicted for rare-earth metal hydrides with a very reducing metal center.

In the classical textbook, Sm²⁺, Yb²⁺ and Eu²⁺ are regarded as the most common three Ln²⁺ in molecular lanthanide complexes in solution.[13] The Ln³⁺/Ln²⁺ redox potentials for Sm²⁺, Yb²⁺ and Eu²⁺ are -1.55, -1.15 and -0.35 V versus NHE, respectively.[14] Divalent samarium complexes, such as Sm²⁺(THF),[15] and (Cp²⁺)₂Sm²⁺(THF), (Cp²⁺ = C₅Me₅)[16] have been widely used as powerful electron-transfer reagents in various organic transformations. Compared with divalent ytterbium hydrides, the synthesis and structural characterization of divalent samarium hydrides are more challenging, because of the larger ionic radius (Yb²⁺: 1.02 Å, Sm²⁺: 1.17 Å; CN = 6),[17] more reducing metal center and paramagnetic nature (Yb²⁺: diamagnet; Sm²⁺: 3.5~3.8 μB).[18] Molecular divalent samarium hydride complexes [SmH₂(THF)]₂[19] and [(Cp)²Sm(H)(THF)]₂[20] have been surmised for decades, but without crystal structures. Gambarotta et al. described an anionic divalent samarium hydride species, tetraneuclear [([Ph₃C(2H₄)N]Sm)₂(H)(THF)₂]⁺, obtained serendipitously from the reduction of trivalent samarium precursor ([Ph₃C(2H₄)N]Sm[Cl] with sodium in THF. However, the hydride position in the crystal structure is elusive.[21] No further reactivity studies were presented, as far as we know.

As the ionic radii for Sr²⁺ and Sm²⁺ are very similar (Sr²⁺: 1.18 Å, Sm²⁺: 1.17 Å; CN = 6),[17] there are strikingly similar interatomic parameters in their crystal structures.[22] More recently, our group found that the sterically demanding penta-arylcyclopentadienyl ligand Cp²⁺ (Cp²⁺ = C₅Ar₅, Ar = 3,5-Pr₂-C₆H₄)²[23] can serve as an excellent ligand for supporting all the heavy alkaline-earth metal hydrides [(Cp²⁺)AE(μ-H)(S)]₂ (AE = Ca, Sr, Ba; S = THF; AE = Sr, Ba, S = DABCO = 1,4-diazabicyclooctane) as the same dimer.[23a] Encouraged by this success, we turn attention to the synthesis of divalent samarium hydrides. Herein, we report the first example of structurally characterized neutral divalent samarium(II) hydrido complex [(Cp²⁺)²Sm²⁺(μ-H)(THF)]₂ (1),[24] generating from moderate pressure (20 atm) hydrogenolysis of the corresponding samarium(II) alkyl precursor. The preliminary reactivities of divalent samarium(II) hydrides with Se, azobenzene (PhN=NPh), CO₂, and CS₂ are presented as well.

Results and discussion

As the strontium hydrides precursor, strontium alkyl complex [(Cp²⁺)Sr(CH(SiMe₃)₂)](THF)]₂[25a] was generated from the reaction of (Cp²⁺)H with [Sr(CH(SiMe₃)₂)](THF)]₂.[24] However, the samarium analogue “[Sm²⁺(CH(SiMe₃)₂)](THF)]₂” is inaccessible. Protonolysis reactions of (Cp²⁺)H with samarium benzyl complexes, such as [Sm²⁺(CH₃)₂P(THF)]₃[25] and [(DMAT)₂Sm²⁺(THF)]₂ (DMAT = 2-MeO-C₆H₄) failed. Thus, our approach to alkyl precursor [(Cp²⁺)Sm²⁺(THF)]₂[25a] in tetrahydrofuran (THF), followed by the exchange of coordinated THF with DABCO, afforded heteroleptic divalent samarium(II) iodide complex [(Cp²⁺)Sm²⁺(μ-I)(DABCO)]₂ (2) as dark-green crystals in 92% isolated yield. Reaction of complex 2 with KCH(SiMe₃)₂[26] in benzene gave half-sandwich samarium(II) alkyl complex [(Cp²⁺)Sm²⁺(CH(SiMe₃)₂)](DABCO)](3) as dark-brown solid in 86% isolated yield. Since complex 3 is highly soluble in hydrocarbon solvents, such as hexane, no crystallographically definable product could be isolated.

Hydrogenolysis of complex 3 in hexane under 20 atm H₂ successfully afforded the corresponding hydride complex [(Cp²⁺)Sm²⁺(μ-I)(DABCO)]₂ (4) as dark-brown crystals in 78% isolated yield (Scheme 1), concomitant with CH₃(SiMe₃)₂.
Complex 4 is slightly soluble in hexane, and well soluble in benzene. Complex 4 decomposed completely in C6D6 within two days and converted quickly to samarocene [(CpAr5)SmII] (S) in THF through ligand redistribution at room temperature. The molecular structure of complex 5 (ESI, Figure S32) is similar to other deca-arylarsamocenes [(C5R4−R−C6H4)3SmIII] (R = Et, n-Bu).[22,29] Due to the paramagnetic nature of the SmIII ion, the signals of complex 4 in 1H NMR spectrum are very broad and cannot be full assignment. However, the bridging hydrides signal can be located at 1.63 ppm, corroborated by 1H NMR spectrum for the deuteron analogue [(CpAr5)SmIII(μ-D)(DABCO)]2 (4-D). Magnetic measurements demonstrate that the magnetic moments of complexes 2 and 4 at 300K are 3.2 μB and 3.9 μB, respectively, consistent with divalent samarium derivatives.[18]

The dimeric nature of complex 4 in solid state is revealed by X-ray crystallographic studies, and isostructural to [(CpAr5)Sr(μ-H)(DABCO)].[23a,30] Each SmII center is coordinated with one CpAr5 ligand, one DABCO ligand and two bridging hydrido ligands. The bridging hydrido ligand (H1) can be located by difference Fourier syntheses and refined isotopically (Figure 2). The bond distances of Sm1–N1 (2.652(4) Å), Sm1–Cent1 (2.594 Å) and Sm1–Sm1 (3.796(5) Å), are almost identical to those in [(CpAr5)Sr(μ-H)(DABCO)].[23a] The Sm–H distances of 2.26(6) Å and 2.48(5) Å fall in the range of 2.26(5)–2.86(6) Å found in the molecular strontium hydride complexes.[23a,30] Thus, complex 4 represents the first example of a structurally characterized Sm(II) hydride complex, in comparison with a dozen examples of trivalent samarium(III) hydrides.[31]

As shown in scheme 2, complex 4 can readily reduce two equivalents of elemental Se in a four-electron reduction to afford the corresponding trivalent samarium complex [(CpAr5)SmII(μ-Se)(DABCO)]2 (6) in 77% isolated yield. The four-electron reduction formally involves two one-electron hydride reductions and two one-electron SmIII/SmII reductions. In this case, the distinct color change of benzene solution from dark brown to pale brown was observed instantly, in company with the release of H2.

The molecular framework of complex 6 is similar to complex 2, except the bridging atoms and the oxidation state of Sm centers (ESI, Figure S30 and S33). The bond lengths of Sm–Se (2.7349(7)–2.7524(6) Å) in complex 6 are comparable to those in samarium complex [(CpAr5)SmII(THF)]2(μ-Se) (2.782(1) and 2.779(1) Å).[32]

Complex 4 can also act as a four-electron reductant in the reduction of 2 equivalents of PhN-NPh to give [(CpAr5)SmII(μ-PhN-NPh)]2 (7) as red-brown solid in 89% isolated yield. As shown in Figure S34, the bond distance of N1–N2 (1.462(3) Å) in the [PhN-NPh]2+ unit is comparable to the previously reported samarium(III) complex [(CpAr5)SmII(μ-PhN-NPh)(THF)]2 (1.44(1) Å),[33a] in contrast to reductive cleavage of azobenzene into uranium(VI) bis(imido) complex (CpAr5)U(=NPh)2.[33b]

Rare-earth metal complexes have revealed plentiful chemistry with carbon dioxide (CO2) and carbon disulfide (CS2).[34]

**Scheme 2. Reactions of complex 4 with Se and azobenzene.**

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**Figure 3.** Molecular structure of complex 8. All the hydrogen atoms, except H2 and H3, are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sm1–O2 2.354(2), Sm1–O3 2.397(3), Sm1–O5 2.338(2), Sm1–O7 2.426(2), Sm1–N1 2.605(3), Sm2–O1 2.373(3), Sm2–O3 2.398(3), Sm2–O4 2.346(2), Sm2–O6 2.406(3), Sm2–O7 2.644(2), C1–O1 1.251 (6), C1–O2 1.204(6), C1–O3 1.349(8), C2–O4 1.248(7), C2–O5 1.206(7), C3–O6 1.249(5), C3–O7 1.271(4), Sm1–Cent1 2.523, Sm2–Cent2 2.453, O2–C1–
Computed enthalpy profile for the reaction of 4 with four equivalents of CO₂ at room temperature. The energies are given in kcal/mol.
reaction coordinate, it yields a very stable formiate-hydride di-
smarium(II) intermediate (Int2). In this complex, the formiate
ligand is ($\mu_2$-bonded to the two Sm centers. This intermediate
readily insertion a second CO$_2$ molecule with a very low barrier
(5.1 kcal/mol) to form the bisformiate di-samarium(II)
intermediate (Int3), which is thermodynamically highly stable (-
113.4 kcal/mol). Int3 then reacts with a third molecule of CO$_2$
in an expected redox-fashion. Indeed, the two Sm(II) undergo a
single electron transfer (SET) to CO$_2$, which is doubly reduced, and
each Sm center is oxidized to +III. This intermediate (Int4), that is
usually called the “key intermediate” in SET reactions, adopts a
dioxocarbene form as already reported by Paparo et al. in
titanium chemistry. This step is slightly endothermic by 5.7
kcal/mol so that Int4 is expected to be quite reactive. Thus, Int4
readily reacts with a fourth molecule of CO$_2$. This reaction implies
the release of one DABCO molecule to allow CO$_2$ to bind to one
Sm(III) center (Int5). This ligand exchange is endothermic by 9.9
kcal/mol from Int4, that is 15.6 kcal/mol from Int3. Then from
Int5, a C-O bond formation occurs between the doubly reduced
CO$_2$ and the other CO$_2$ molecule (bonded to Sm) via TS3. The
associated barrier is 12.1 kcal/mol from Int5, that is 27.7 kcal/mol
from Int3, in line with a kinetically accessible reaction. The
formation of the C-O bond allows the formation of the carbonate
ligand and the release of a CO molecule, as observed in complex
8. The formation of this complex is highly exothermic (-131.6
kcal/mol).

Conclusions

In summary, we have demonstrated the synthesis, isolation and
structurally characterization of dimeric divalent samarium
hydrido complex 4 bearing a super-bulky penta-
arylcyclopentadienyl ligand. Complex 4 showed four-electron
reduction toward various substrates, such as Se$_2$, PhN=NPh and
CO$_2$, to afford the corresponding double Se$^2$-[PhN-NPh]$^3$, and
[CS$_2$]$^2$ bridged trivalent samarium complexes, respectively,
without suffering from ligand loss or ligand scrambling. For
comparison, Hydride insertion and two-electron reductive
disproportionation of CO$_2$ were observed in the formation
of mixed bis-formate/carbonate complex 8, corroborated by DFT
calculations. These preliminary reactivities indicate that
complex 4 can provide an entry into an exciting new area
involving the cooperation of highly reactive hydride and a
strong reducing metal center.

Author Contributions

X. S. carried out the synthesis and characterization of complexes
1-9. P. D. assisted in the NMR spectroscopy experiment and
crystal structure analysis. T. R. and L. M. performed the
theoretical calculation. J. C. conceived this project and provided
guidance. The manuscript was written through contributions of
all authors.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

This work was supported by the National Natural Science
Foundation of China (No. 21901238 and 22271272). L.M. is a
senior member of the Institut Universitaire de France. Chinese
Academy of Science is acknowledged for financial support (LM)
and CalMip for a generous grant of computing time.

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