

Bridging silyl groups in σ -bond metathesis and [1, 2] shifts. An experimental and computational study of the reaction between cerium metallocenes and MeOSiMe₃.

(This article is dedicated to Dietmar Seyferth on the occasion of his retirement as founding editor of Organometallics)

Evan L. Werkema,^a Ahmed Yahia,^{b,c} Laurent Maron,^b Odile Eisenstein^d and Richard A. Andersen^a.

a) Department of Chemistry and Chemical Sciences Division of Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720-1460. b) LPCNO, Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, F-31077 Toulouse, France, and CNRS, LPCNO, F-31077 Toulouse, France, c) ICSM UM5257, CEA-CNRS-UM2, Site de Marcoule, BP17171, 30207 Bagnols-sur-Cèze, France, d) Institut Charles Gerhardt, Université Montpellier 2, CNRS 5253, cc 1501, Place E. Bataillon, F-34095 Montpellier France.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, State, and Community Programs, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California.

Abstract

The reaction of $\text{Cp}'_2\text{CeH}$ ($\text{Cp}' = 1,2,4\text{-(Me}_3\text{C)}_3\text{C}_5\text{H}_2$) with MeOSiMe_3 gives $\text{Cp}'_2\text{CeOMe}$ and HSiMe_3 and the reaction of the metallacycle, $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$, with MeOSiMe_3 yields $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$, formed from hypothetical $\text{Cp}'_2\text{CeCH}_2\text{OSiMe}_3$ by a [1, 2] shift also known as a silyl-Wittig rearrangement. Although both cerium products are alkoxides, they are formed by different pathways. DFT calculations on the reaction of the model metallocene, Cp_2CeH , and MeOSiMe_3 show that the lowest energy pathway is a H for OMe exchange at Ce that occurs by way of a σ -bond metathesis transition state as SiMe_3 exchanges partners. The formation of $\text{Cp}_2\text{CeOCH}_2\text{SiMe}_3$ occurs by way of a low activation barrier [1, 2] shift of the SiMe_3 group in $\text{Cp}_2\text{CeCH}_2\text{OSiMe}_3$. Calculations on a model metallacycle, $\text{Cp}[\text{C}_5\text{H}_4\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$, show that the metallacycle favors

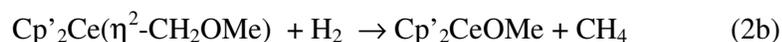
CH bond activation over σ -bond metathesis involving the transfer of the SiMe₃ group in good agreement with experiment. The σ -bond metathesis involving the transfer of SiMe₃ and the [1, 2] shift of SiMe₃ reactions have in common a pentacoordinate silicon at the transition states. A molecular orbital analysis illustrates the connection between these two Si-O bond cleavage reactions and traces the reason why they occur for a silyl but not for an alkyl group to the difference in energy required to form a pentacoordinate silicon or carbon atom in the transition state. This difference clearly distinguishes a silyl from an alkyl group as shown in the study of “ pyrolysis of tetramethylsilane yielding free d-orbitals by Seyferth and Pudvin in *ChemTech* **1981**, 11, 230-233”.

Introduction

[1, 2]-SiR₃ group shifts are common in silyl containing compounds.¹ These dyotropic rearrangements are known either as a Brook, retro-Wittig or a retro-Brook, silyl-Wittig, rearrangement depending on the direction of the silyl group shift.²⁻⁴ The silyl-Wittig rearrangement involves cleavage of an O-Si bond in a silyl ether and formation of a C-Si bond as symbolized in eq. 1. The retro-Wittig involves the reverse transformation and has been shown to occur in neutral molecules. Suprafacial-suprafacial [1, 2] shifts are Woodward-Hoffmann disallowed in carbon chemistry but the activation barriers are much lower when the migrating group can readily get to a pentacoordinate condition, such as when the migrating group is SiR₃.



In the silyl-Wittig rearrangement, the anions are usually associated with solvent separated lithium cations, and the organometallic compounds are seldom isolated. This article shows that related chemistry occurs in the reaction of lanthanide complexes with silyl ethers. The C-O bond in Me₂O was shown recently to be cleaved by [1,2,4-(Me₃C)₃C₅H₂]₂CeH, abbreviated as Cp'₂CeH, in a two-step reaction.⁵ The first step is an α-CH activation, eq. 2a, followed by a slow step in which the CH₂ fragment is trapped by H₂, eq. 2b. The methoxymethyl compound was isolated and characterized by X-ray crystallography. The reactivity pattern, illustrated in eq. 2, is general since methylhalides follow a similar two-step mechanism.^{5,6}



The ether cleavage reaction is also general since the net reaction between Cp'₂CeH and (RCH₂)₂O, R = Me, Et, Pr, forms Cp'₂CeOCH₂R and RCH₃, but the reaction mechanism is different when the ethers contain β-CH bonds.⁷

Understanding the thermodynamic similarity but kinetic dissimilarity between Cp'₂Ce(η²-CH₂OMe) and the postulated precursor compound in the silyl-Wittig rearrangement, where OMe is replaced by OSiMe₃, is the justification for undertaking the experimental and computational studies described below. The computational studies provide quantitative mechanistic information about the O-Si bond cleavage process and the role five-coordinate silicon plays in lowering the activation free energy of the transition state.

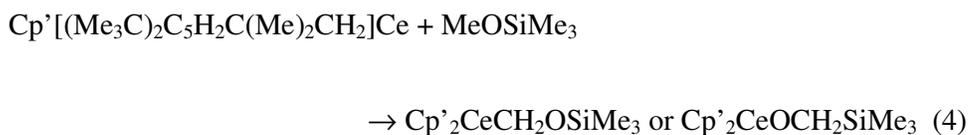
Results

Experimental Studies

Addition of an excess of MeOSiMe₃ to Cp'₂CeH in C₆D₁₂ in an NMR tube at 20°C results in an instantaneous color change from purple to red. Examination of the ¹H NMR spectrum shows only resonances due to Cp'₂CeOMe,⁸ HSiMe₃, and unreacted MeOSiMe₃. The net reaction shown in eq. 3 is a H for OMe exchange, in which the Si-O bond, rather than the C-O bond is cleaved.



Previously reported studies on the reaction chemistry of Cp'₂CeH with common organic compounds are often complemented by reactions with the metallacycle, Cp'[(Me₃C)₂C₅H₂C(Me)₂CH₂]Ce, since dihydrogen is not present in the latter reactions and therefore cannot act as a trapping reagent. In the present case, however, the reaction between MeOSiMe₃ and the metallacycle does not yield the cerium methoxide complex but the substituted methoxide Cp'₂CeOCH₂SiMe₃, isolated as a red solid that is purified by vacuum sublimation at 190°C. The thermal stability of Cp'₂CeOCH₂SiMe₃ is in stark contrast to that of, for example, Cp'₂CeCH₂Ph, which slowly eliminates toluene, forming the metallacycle in solution at 20°C and on attempted sublimation.⁹ The ¹H NMR spectrum of the sublimed material has chemical shift patterns similar to those observed for Cp'₂CeCH₂Ph⁹ or Cp'₂Ce(η²-CH₂OMe),⁵ but does not allow a distinction to be made between the C-bound or O-bound isomer, eq. 4.



The X-ray crystal structure, Figure 1, clearly shows that the isolated compound is the O-bound isomer.

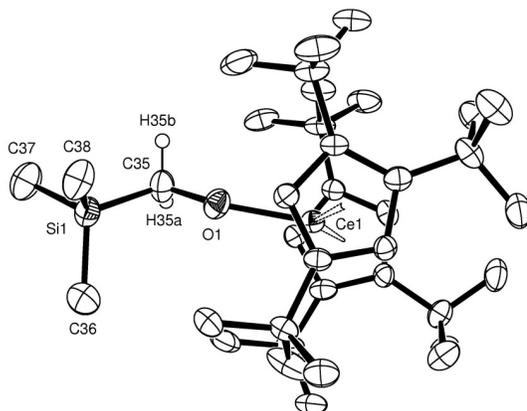


Figure 1. ORTEP of [1,2,4-(Me₃C)₃C₅H₂]₂CeOCH₂SiMe₃, 50% probability ellipsoids. The non-hydrogen atoms are refined anisotropically and the hydrogen atoms (not shown) are placed in calculated positions and not refined, except the two hydrogens on C(35) that are located and refined isotropically: Ce-C(ave) = 2.85 ± 0.06 Å, range 2.766(4) Å to 2.948(5) Å, Ce-C(ring centroid) 2.58 Å. Ce-O = 2.113(3) Å, Ce-O-C(35) = 158.7(4)°, O-C(35)-Si = 114.0 (3)°, Cp'(ring centroid)-Ce-Cp'(ring centroid) = 149°, Cp'(ring centroid)-Ce-O = 105°(ave).

The important stereochemical feature revealed in the ORTEP in Figure 1 is that the compound is an alkoxide, not a trimethylsilyloxymethyl derivative, which is consistent with its thermal stability. The bond distances and angles in the Cp'₂Ce fragment are in the range found in all of the other solid state structures containing this fragment.⁵⁻¹⁰ The key datum is the Ce-O distance of 2.113(3) Å, which is identical to the Ce-O distance in Cp'₂Ce(*trans*-OCH=CHO)Cp'₂ of 2.118(3) Å and close to the two independent Ce-O distances in the *cis*-isomer of 2.173(4) Å and 2.170(5) Å.⁸ The Ce-

O distance in $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ is substantially shorter than the expected value for a Ce-C distance in an η^1 -alkyl derivative; the Ce-C distance in $\text{Cp}'_2\text{Ce}(\eta^2\text{-CH}_2\text{OMe})$, $\text{Cp}'_2\text{Ce}(\eta^1\text{-CH}_2\text{Ph})$, and $\text{Cp}'_2\text{Ce}(\eta^1\text{-4-methylbenzyl})$ are 2.488(4) Å, 2.577(4) Å, and 2.576(7) Å, respectively.^{5,9} Further, the two hydrogen atoms on C(35) are located and refined isotropically, which provides the final proof that the isomer is O-bound.

Monitoring the reaction between the metallacycle and MeOSiMe_3 by ^1H NMR spectroscopy shows that the reaction is quantitative at 20°C and the chemical shifts of the isolated compound are identical to those generated upon mixing these reagents. No intermediate is detected. Further, since BPh_3 is an efficient trap for the conversion of $\text{Cp}'_2\text{Ce}(\eta^2\text{-CH}_2\text{OMe})$ to $\text{Cp}'_2\text{CeOMe}$ and $\text{PhCH}_2\text{BPh}_2$,⁵ monitoring the reaction between the metallacycle and MeOSiMe_3 in presence of BPh_3 shows that the Lewis acid does not affect the net reaction. The latter experiment suggests that, if $\text{Cp}'_2\text{CeCH}_2\text{OSiMe}_3$ is formed, the lifetime of the C-bound isomer is short, implying that the rearrangement barrier is low. Further, mixing the metallacycle- d_{53} with MeOSiMe_3 in C_6D_{12} at 20°C does not incorporate deuteria in MeOSiMe_3 , implying that the rearrangement of the postulated intermediate is not reversible.

Computational studies

Models and Generalities

The Cp' ligand is modeled by C_5H_5 , Cp , and Cp_2CeH is abbreviated as $[\text{Ce}]\text{H}$. The metallacycle is modeled by $\text{Cp}[\text{C}_5\text{H}_4\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ and is abbreviated as $[\text{Ce}]\text{Met}$. The substrate, MeOSiMe_3 , is represented in full. The DFT(B3PW91) method described in the Experimental Section has been used as in related studies.^{5,6} The Gibbs free energy, G , of all extrema are given relative to the separated reactants $[\text{Ce}]\text{H}$ and MeOSiMe_3 . The activation barrier is defined as the difference in Gibbs

free energy between a transition state and its associated reactant. The α - and β -CH terminology refers to the bonds that are α and β relative to the oxygen atom; therefore the α -CH activation refers to the OCH₃ group while β -CH activation refers to the OSi(CH₃)₃ group.

The computational results are divided into several sections since the reaction of MeOSiMe₃ with Cp'₂CeH and the metallacycle give different products. In the first part, all of the pathways that could result from the reaction between [1,2,4-(Me₃C)₃C₅H₂]₂CeH, modeled by Cp₂CeH, and MeOSiMe₃ are analyzed. In the second part, the reactions that are initiated with the α -CH activation product, Cp₂CeCH₂OSiMe₃, are presented, along with reactions of the model metallacycle Cp[C₅H₄C(Me)₂CH₂]Ce.

Calculations with Cp₂CeH as a model.

The Gibbs free energy profiles for all of the reactions studied are shown in Figure 2.

All reactions start by the formation of an ether adduct with a free energy of about -5 kcal mol^{-1} indicating that adduct formation more than compensates the loss of entropy. The ether adducts that start the reactions differ by the conformation of the ether ligand but the energy difference between these conformational isomers is less than 1 kcal mol^{-1} . This difference is not discussed further and the starting structure for all reactions is called the ether adduct.

a) Sigma bond metathesis

The term σ -bond metathesis describes a reaction in which σ -bonds are cleaved and formed in a concerted manner without change of the oxidation number of the metal center. The kite-shape transition state is composed of four atoms or groups of atoms that exchange their partners, as indicated in Figure 2. Following Goddard and Rappé, this reaction is a $[2s + 2s]$ reaction in Woodward–Hoffmann nomenclature and is prevalent in organometallic chemistry while forbidden in organic chemistry.^{11,12}

From the ether adduct, two σ -bond metathesis pathways are possible, one in which the O-C bond is cleaved and CH_4 is formed and one in which the O-Si bond is cleaved and HSiMe_3 is formed (Figure 2). Cleavage of the O-C bond requires that the CH_3 group is located at the β -position of the four-member ring transition state, while the cleavage of O-Si requires that the SiMe_3 group occupies that site. The Gibbs free energies of these two transition states are strikingly different, $43.3 \text{ kcal mol}^{-1}$ for the σ -bond metathesis involving the CH_3 group and only $5.2 \text{ kcal mol}^{-1}$ for that involving the SiMe_3 group. The high energy of the σ -bond metathesis involving the CH_3 group is a recurring theme as shown in previous studies. In the case of the H for H exchange reaction between $[\text{Ce}]\text{H}$ and CH_4 , it is 70 kcal mol^{-1} ,¹³ but introduction of electron withdrawing groups lowers the energy of the transition state by about half. For

example, the free energy of the transition state is about 30 kcal mol⁻¹ for the H for halide exchange in the reaction of [Ce]H and CH₃X when X is F or I.⁵ When X = OMe,⁵ the value is 43.5 kcal mol⁻¹ and it varies little when the alkyl group is Et, n-Pr or n-Bu.⁷ It was originally proposed that the high energy associated with carbon achieving this transition state is related to the high energy CH₅⁻, in which the carbon is five-coordinate. Electron withdrawing groups stabilize CH₄X⁻ but the energy is still on the order of 30 kcal mol⁻¹. The role of the SiMe₃ group is therefore exceedingly important in this elementary step. It is well known that silicon readily increases its coordination number as the hypothetical anion SiH₅⁻ is more stable than CH₅⁻ relative to SiH₄ or CH₄ and H.¹⁴ Previous computational studies of the reactions of silyl derivatives with lanthanide metallocenes show that the silyl group favors σ -bond metathesis pathways. For example, the H for H exchange between Cp₂LnH and SiH₄ has a very low lying σ -bond metathesis transition state.¹⁵ Likewise the σ -bond metathesis transition state for transferring SiH₃ is a very low energy pathway in the reactions of Cp₂LnH and CH₃SiH₃,¹⁶ or Cp₂SmH and PhSiH₃.¹⁷

The geometry of the transition states for the methyl and the trimethylsilyl transfer is shown in Figure 3. The geometry around carbon and silicon is rather similar; in both cases, the atom at the β position of the four-member ring is pentacoordinate. In the case of the methyl group, the geometry at carbon is intermediate between a trigonal bipyramid and a square pyramid. In the case of trimethylsilyl, the geometry at silicon is a square pyramid in which the OMe and the H groups are *cis* to each other in the basal plane.

Therefore the σ -bond metathesis reaction between [Ce]H and MeOSiMe₃ is an energetically accessible reaction if it involves cleavage of the Si-O bond. The low

activation barrier of this reaction is clearly due to the ability of the silicon atom to become pentacoordinate at the transition state.

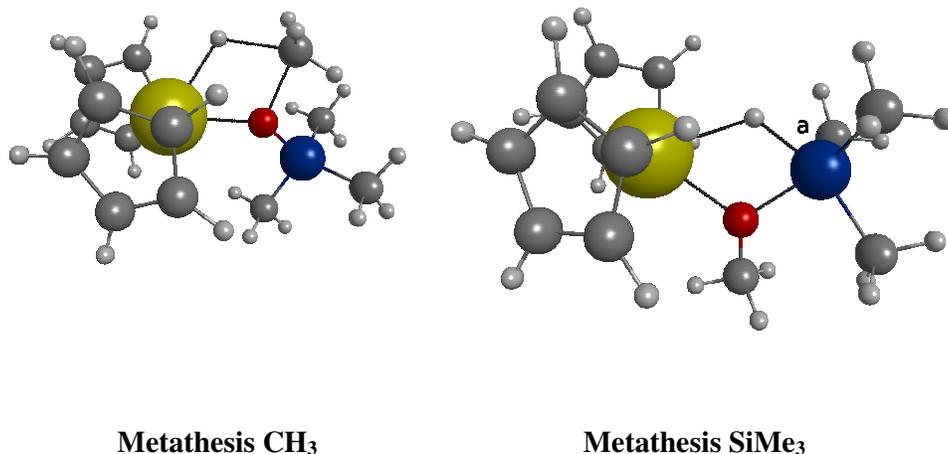


Figure 3. Optimized geometries of the transition states for the σ -bond metathesis reactions between Cp_2CeH and MeOSiMe_3 ; on the left-hand side, transfer of the methyl group and on the right-hand side, transfer of the trimethylsilyl group are shown (“a” marks the apical ligand of the square base pyramid, see Figure 2. The color code is Ce, yellow; Si, blue; O, red; C, gray.

b) Reactions initiated by CH activation

Activation of the α -CH bond of the methyl group in MeOSiMe_3 has a transition state with a Gibbs free energy of 12 kcal mol^{-1} , slightly lower than that of $13.8 \text{ kcal mol}^{-1}$ obtained for Me_2O . The resulting three-member ring in $[\text{Ce}](\eta^2\text{-CH}_2\text{OSiMe}_3)$ has a Gibbs free energy of $-2.9 \text{ kcal mol}^{-1}$, also slightly lower than that of $-0.9 \text{ kcal mol}^{-1}$ for $[\text{Ce}](\eta^2\text{-CH}_2\text{OMe})$. The Gibbs free energy of the transition state for elimination of CH_2 and trapping by H_2 is $32.3 \text{ kcal mol}^{-1}$, again lower than that of $37.9 \text{ kcal mol}^{-1}$ calculated for $[\text{Ce}](\eta^2\text{-CH}_2\text{OMe})$. Therefore the SiMe_3 group has a

stabilizing influence on the transition state energies. Despite the stabilizing effect of SiMe_3 , the transition state for extrusion of CH_2 and capture by H_2 is high in energy compared to those calculated for methylhalides, which range between 15 and 18 kcal mol^{-1} , rendering the elimination of CH_2 and trapping by H_2 unlikely. The α -CH activation pathway has a higher activation barrier than the σ -bond metathesis with SiMe_3 transfer. This is consistent with fact that $\text{Cp}'_2\text{CeOSiMe}_3$ is not observed experimentally in the reaction between $\text{Cp}'_2\text{CeH}$ and MeOSiMe_3 .

The β -CH activation on the methyl group of SiMe_3 begins from the ether adduct. The transition state for β -CH activation has a Gibbs free energy of 8.8 kcal mol^{-1} , which is lower than that for the α -CH activation. From this transition state, the four-member CeOSiC ring forms with an energy of -10.5 kcal mol^{-1} . However, no transition state for elimination of $\text{CH}_2=\text{SiMe}_2$ could be located and the four-member ring cannot evolve further. This is in agreement with the low stability of compounds with a Si-C double bond.¹⁸ The β -CH activation has a transition state that is higher in energy than that of the σ -bond metathesis with trimethylsilyl transfer and the four-member ring does not form even though it is moderately exoergic relative to separated $[\text{Ce}]\text{H}$ and MeOSiMe_3 .

c) Reactions of $\text{Cp}_2\text{Ce}(\eta^2\text{-CH}_2\text{OSiMe}_3)$

When the reactant is $[\text{Ce}]\text{H}$, the calculations indicate that the preferred reaction is σ -bond metathesis with trimethylsilyl transfer. All other reactions have higher energy transition states, and therefore access to the three-member ring $[\text{Ce}](\eta^2\text{-CH}_2\text{OSiMe}_3)$ is not possible. However, $\text{Cp}'_2\text{Ce}(\eta^2\text{-CH}_2\text{OSiMe}_3)$ is presumably generated when $\text{CH}_3\text{OSiMe}_3$ is added to the metallacycle, $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$, by

analogy with the reaction of CH₃OMe with the metallacycle that yields Cp'₂Ce(η²-CH₂OMe).⁵ In this section, the reactions pathways that originate from Cp₂Ce(η²-CH₂OSiMe₃), formed by CH activation of the methyl group of MeOSiMe₃, are presented.

From [Ce](η²-CH₂OSiMe₃), a transition state for the [1, 2] migration of the trimethylsilyl group is located with a Gibbs free energy of 13.2 kcal mol⁻¹ above [Ce](η²-CH₂OSiMe₃) and the formation of [Ce]OCH₂SiMe₃ is exoergic by -16.8 kcal mol⁻¹ relative to this intermediate, see Figure 2. The more thermodynamically favored product, [Ce]OSiMe₃, which is exoergic by -67 kcal mol⁻¹ relative to separated [Ce]H and CH₃OSiMe₃, is not formed because the transition state for elimination of CH₂ and trapping by H₂ is much higher in energy. The formation of [Ce]OCH₂SiMe₃ is under kinetic control. The calculated geometry of [Ce]OCH₂SiMe₃ is close to that of Cp'₂CeOCH₂SiMe₃, since the Ce-O distances are 2.161 Å and 2.113(3) Å, respectively, and the Ce-O-C angle is significantly more open in the calculated structure (172° vs. 158.7(4)°). The bending at oxygen is known to occur on a flat potential energy surface and the difference between calculated and experimental values is not surprising.

The calculated structure of the three-member ring in [Ce](η²-CH₂OSiMe₃), shown in Figure 4, differs from [Ce](η²-CH₂OMe) essentially by lengthening the C...O bond by 0.024 Å, in accord with the ability of SiMe₃ to stabilize a negatively charged oxygen. In addition, the four atoms in the CeCH₂ fragment are essentially coplanar since the angles at carbon sum to 357.4°. The same value is found in [Ce](η²-CH₂OMe). Therefore, in [Ce](η²-CH₂OSiMe₃) as in [Ce](η²-CH₂OMe), the σ lone

pair of CH₂ points towards Ce while the carbon 2p orbital points to oxygen, in accord with Bent's rules.⁵

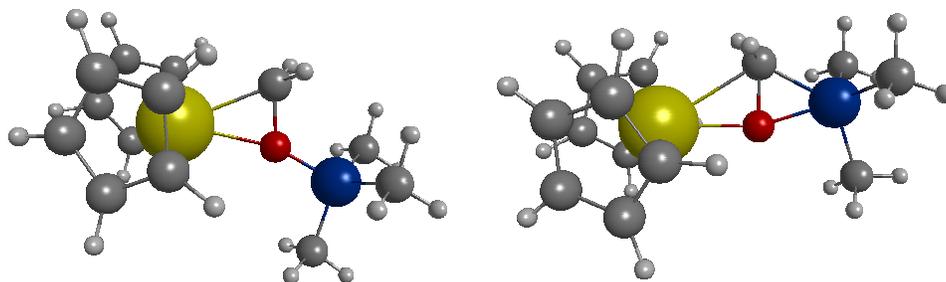


Figure 4. Optimized structures for the Cp₂Ce(η²-CH₂OSiMe₃) intermediate on the left-hand side, and the transition state for the [1, 2] shift of SiMe₃ on the right-hand side. The color code is Ce, yellow; Si, blue; O, red; C, gray.

The structure of the transition state for the [1, 2] shift of the silyl group is shown in Figure 4. The four atoms Ce, O, C, and Si are co-planar. On going from [Ce](η²-CH₂OSiMe₃) to the transition state, the Ce-O bond is shortened from 2.44 Å to 2.31 Å, the C-O is marginally shortened from 1.485 to 1.480 Å and the Ce-C bond is significantly lengthened from 2.50 to 2.71 Å. The trimethylsilyl group bridges the C-O bond with a Si-O distance of 1.89 Å and a Si-C distance of 2.04 Å, and the resulting Ce-O-Si angle is 162° and the Ce-C-Si angle is 121°. The CH₂ effectively inverts its orientation in the rearrangement. In the transition state, the hydrogens on the CH₂ group are oriented away from the trimethylsilyl group, and the four atoms in the SiCH₂ fragment are not strictly coplanar since the sum of the angles at C is 354°, and the hybridization of carbon is between sp³ and sp². The overall geometry of the transition state therefore resembles the bridging formaldehyde dianion in Cp'₂Ce(OCH₂)CeCp'₂ with the SiMe₃ replacing one of the Cp'₂Ce fragments.⁸ Ab-initio calculations comparing silyl to methyl migrations show that the barriers for [1,

2] shifts are much lower for silyl relative to methyl for gas phase anions and lithium stabilized molecules.¹⁹

Reactions of Cp[C₅H₄C(Me)₂CH₂]Ce.

The CH activation of the methyl group and the σ -metathesis with SiMe₃ and CH₃ were studied with a model of the metallacycle in which the cyclopentadienyl groups do not have additional CMe₃ groups, for better comparison with Cp₂CeH. The goal of this section is to obtain insight as to why the reactivity of the metallacycle differs from that of the hydride.

The free energy profiles for the CH activation of the methyl and SiMe₃ groups of MeOSiMe₃ as well as the σ -bond metathesis involving migration of SiMe₃ and Me are shown in Figure 5.

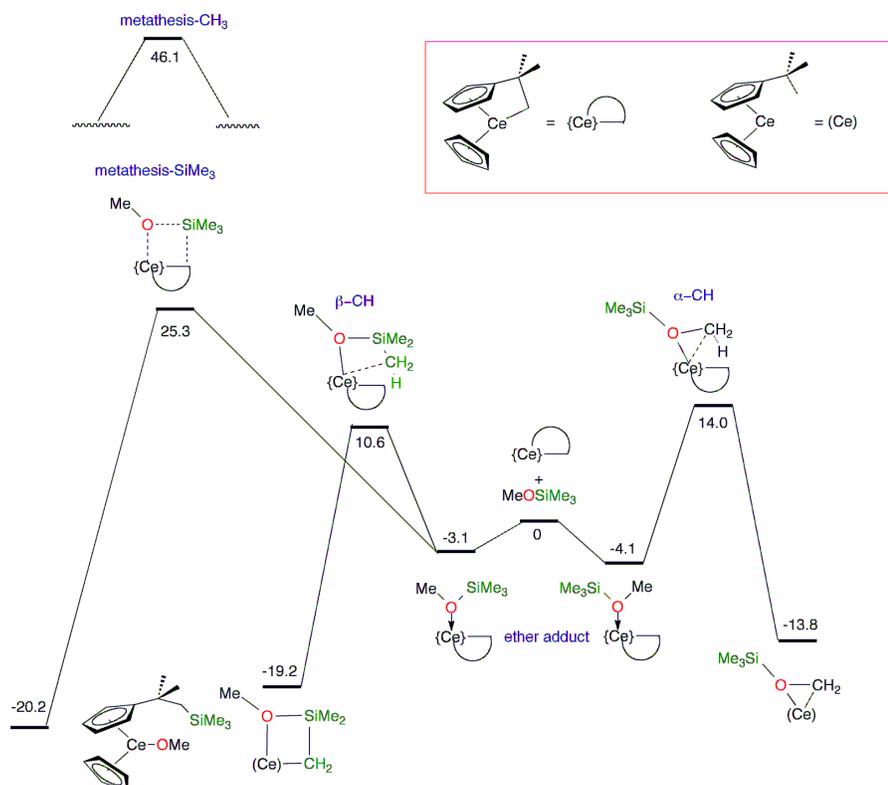


Figure 5. Free energy profiles (kcal mol⁻¹) for the reaction of MeOSiMe₃ and Cp[C₅H₄C(Me)₂CH₂]Ce.

The α -CH activation in the methyl group starts with the formation of an adduct whose free energy is 4.1 kcal mol⁻¹ lower than the separated reactants, Cp[C₅H₄C(Me)₂CH₂]Ce and MeOSiMe₃. The free energy of the transition state for the α -CH activation in the Me group is 14.0 kcal mol⁻¹ above separated reactants. Starting from a slightly different MeOSiMe₃ adduct whose energy is 3.1 kcal mol⁻¹ below separated reactants, the free energy of the transition state for σ -bond metathesis with SiMe₃ transfer is 25.3 kcal mol⁻¹ above separated reactants. This transition state yields Cp[C₅H₄(C(Me)₂CH₂SiMe₃)]Ce(OMe) in which one of the cyclopentadienyl ring has a CMe₂CH₂SiMe₃ substituent. The reaction is exergonic by -20.2 kcal mol⁻¹ but its transition state is higher by 11.3 kcal mol⁻¹ than the α -CH activation. The σ -bond metathesis involving the migration of the methyl group has a high activation barrier of 46.1 kcal mol⁻¹. The activation of the β -CH bond in the SiMe₃ group has a transition state with a slightly lower free energy than the activation at the methyl group, and leads to a four-member ring that is only slightly more stable than the three-member ring. As discussed previously this four-member ring cannot evolve further and this path is not productive. The barrier for the reverse reaction is not very high and this metallacycle does not accumulate. Overall, the preferred first step for the reaction of the metallacycle is the α -CH bond activation on the methyl group. This reaction yields the selective formation of the three-member ring [Ce](η^2 -CH₂OSiMe₃).

The σ -bond metathesis is significantly disfavored for the metallacycle, even for SiMe₃. In contrast, the CH bond activation either at the Me or the SiMe₃ groups has similar activation barriers for the metallacycle and the hydride. Thus, using the

metallacycle in place of the hydride disfavors the σ -bond metathesis but does not modify the energy profiles of the proton transfer reaction, which becomes the preferred pathway.

Discussion

The reaction mechanism previously developed for the net H for X exchange in the reaction of $\text{Cp}'_2\text{CeH}$ and CH_3X , when X is a halide or methoxide, is a two-step process: the first step involves an α -CH activation followed by a second higher energy step that involves trapping of the methylene fragment by dihydrogen. The postulated intermediate, $\text{Cp}'_2\text{Ce}(\eta^2\text{-CH}_2\text{X})$, in the α -CH activation step is isolated when $\text{X} = \text{OMe}$.⁵ As outlined above, when $\text{X} = \text{OSiMe}_3$, the H for OMe exchange in eq. 3 is rapid and no intermediate is observed by ^1H NMR spectroscopy, which is consistent with a reaction that proceeds through a concerted transition state in which the SiMe_3 group bridges the H and OMe groups as they exchange partners. This type of transition state is referred to as a σ -bond metathesis transition state.²⁰ This inference is supported by the computational studies presented above and discussed below.

In the reactions mentioned above, when $\text{Cp}'_2\text{CeH}$ is replaced by the metallacycle, intermediates are observed in the ^1H NMR spectra when $\text{X} = \text{Cl}$, Br , I and OMe . Isolation of the intermediate when $\text{X} = \text{OMe}$ in both reactions strengthens our contention that the two-step pathway is followed in both reactions. Given that the reaction of $\text{Cp}'_2\text{CeH}$ with MeOSiMe_3 does not follow a two-step mechanism, it is not obvious that $\text{Cp}'_2\text{CeCH}_2\text{OSiMe}_3$ will form when MeOSiMe_3 and the metallacycle are mixed. Indeed, the C-bound isomer is not observed and the isolated product is $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$, presumably resulting from a [1, 2] shift in $\text{Cp}'_2\text{CeCH}_2\text{OSiMe}_3$,

eq. 4. No intermediates are observed by ^1H NMR spectroscopy nor detected when the methylene trapping reagent, BPh_3 , is present. The mechanism of the related intramolecular rearrangement of $\text{Cp}_2\text{Zr}(\text{Cl})(\eta^2\text{-CH}_2\text{OSiMe}_3)$ to $\text{Cp}_2\text{Zr}(\text{Cl})(\text{OCH}_2\text{SiMe}_3)$ has been studied.²¹

The [1, 2] shift of a SiR_3 group is classified as a silyl-Wittig rearrangement^{1,3} since the Wittig rearrangement involves a [1, 2] shift of a saturated carbon.^{1a,22,23} West showed that the deprotonation of $(\text{Ph})(\text{D})(\text{H})\text{COSiMe}_3$ by Me_3CLi (-78°C) followed by hydrolysis yields $(\text{Ph})(\text{Me}_3\text{Si})(\text{D})\text{COH}$. The reaction proceeds by inversion of stereochemistry at the saturated carbon center and is proposed to go through a five-coordinate silicon, in which the Me_3Si group bridges the C and O atoms in the transition state. West also noted the similarity of the silyl-Wittig rearrangement to the Brook or retro-Wittig rearrangement in which $(\text{Ph})(\text{Me}_3\text{Si})(\text{H})\text{C}(\text{OD})$ in presence of a catalytic amount of base gives $(\text{Ph})(\text{D})(\text{H})\text{C}(\text{OSiMe}_3)$.^{2b,3c,4} The Brook rearrangement is intramolecular and proceeds with inversion of stereochemistry at the saturated carbon but with retention of configuration at silicon.

As shown in the computational section, the preferred σ -bond metathesis exchanging H and OMe exchange, and the postulated O to C shift of SiMe_3 both involve five coordinate silicon. Thus, the two apparently dissimilar reactions are connected by a common thread, that is, the ease with which silicon becomes five coordinate. In both reactions, four electrons are involved in the transformation. As shown in Figure 6, the transition state for the σ -bond metathesis can be viewed schematically as formed from SiMe_3^+ interacting with $\text{Cp}_2\text{Ce}(\text{H})(\text{OMe})^-$, where the four electrons are localized in the Ce-H and Ce-OMe bonds of the anion. In Figure 6,

the cerium fragment is qualitatively represented by $\text{Cp}_2\text{Ce}(\text{H})_2^-$ where the density is localized on the two hydrogen atoms with some cerium character to form the two polarized σ -bonds.²⁴ The occupied orbitals describing the Ce-H bonds form the symmetric and antisymmetric combination shown. The trimethylsilyl cation is pyramidal with empty orbitals of *a* and *e* symmetry (in C_{3v} symmetry) that are Si-C antibonding. The lower energy orbital of *a* symmetry is made mostly of a Si $3p_z$ orbital combined with some 3s character, the extent of which depends on the degree of pyramidalization of the SiMe_3 fragment at the transition state. This orbital interacts with the in-phase combination of the Ce-H orbitals in $[\text{Ce}](\text{H})_2^-$. The higher lying orbitals of *e* symmetry are the out-of-phase combination of the Si $3p_x$ and $3p_y$ orbitals with the Me groups. One of these *e* orbitals has the appropriate symmetry to interact with the out-of-phase combination of the Ce-H orbitals in $[\text{Ce}](\text{H})_2^-$. The orientation of SiMe_3 is not important since any linear combination of the two empty orbitals of *e* symmetry is appropriate to provide the same interaction with the out-of-phase combination of the Ce-H orbitals in $[\text{Ce}](\text{H})_2^-$. When a SiMe_3 group is replaced by a CH_3 group, the interaction between the orbital of *a* symmetry remains but the orbital of *e* symmetry is much higher in energy and therefore unable to stabilize the out-of-phase combination.¹⁴ An electronegative group such as halide or alkoxide lowers the energy of all empty orbitals but the silyl group stabilization is greater.

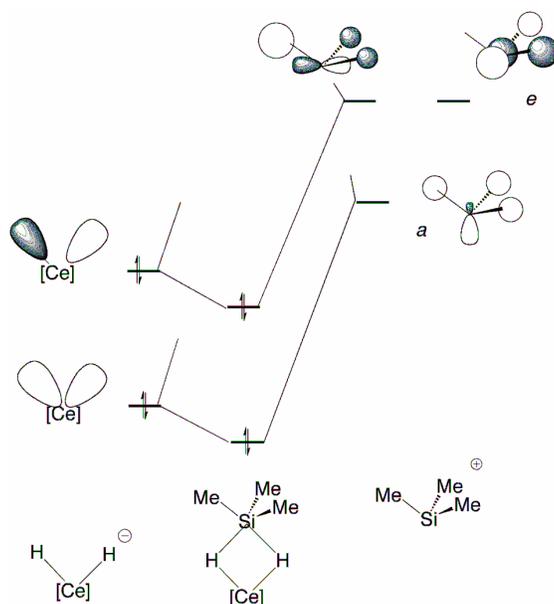


Figure 6. Schematic interaction diagram showing the Ce-H bonding orbitals in $[\text{Ce}](\text{H}_2)^-$ and SiMe_3^+ in the σ -bond metathesis transition state for trimethylsilyl transfer.

The [1, 2] migration of a silyl group, the silyl-Wittig rearrangement, can be treated similarly, since this rearrangement involves the migration of a SiMe_3 group. The transition state can be created from two fragments, one of which is the dinegative formaldehyde group, CH_2O^{2-} , that interacts with the two cationic fragments, Cp_2Ce^+ and SiMe_3^+ . The four electrons in the π and π^* orbitals of CH_2O^{2-} are shown in Figure 7, which are the occupied in-phase and out-of-phase combinations of carbon and oxygen p_π orbitals. The cerium fragment acts to stabilize the dianion by electrostatic interaction. The migration of the SiMe_3^+ cation is energetically accessible because it has two low-lying empty orbitals of appropriate symmetry to interact at the transition state with the filled π and π^* orbitals of the dinegative formaldehyde. The *a* and *e*

parentage orbitals on the trimethylsilyl fragment are the same ones used to stabilize the metathesis transition state.

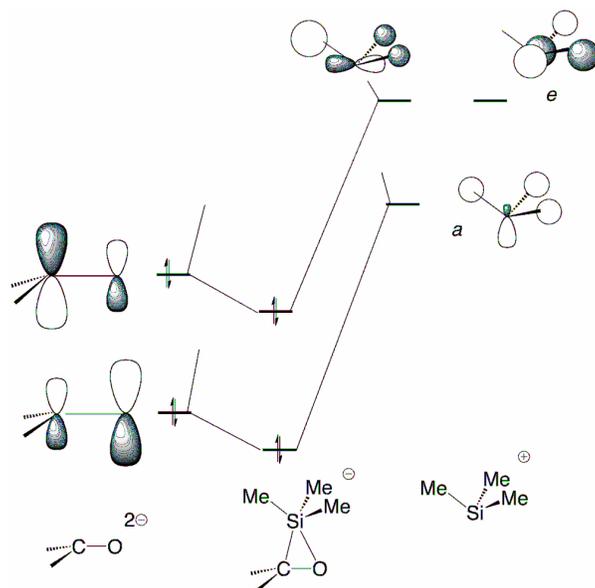


Figure 7. Schematic interaction diagram between the formaldehyde dianion and SiMe_3^+ at the transition state for the [1, 2] shift.

The unifying principle that connects the transition states in these two reactions is the symmetry of the frontier orbitals involved and the total number of electrons implicated in the two transformations. Thus, the notion of isolobality, used to describe the bonding properties of fragments in molecules, can be extrapolated to the σ -bond metathesis and the silyl-Wittig rearrangement that are isolobal when the migrating group is silyl.

Conclusion

The experimental reaction between $\text{Cp}'_2\text{CeH}$ and MeOSiMe_3 gives $\text{Cp}'_2\text{CeOMe}$ and HSiMe_3 and the calculated potential energy surfaces show that the

pathway of H for OMe exchange proceeds by a low free energy transition state in which the SiMe₃ group migrates as a cation in a σ -bond metathesis transition state. The reaction of the metallacycle with MeOSiMe₃ yields Cp'₂CeOCH₂SiMe₃, which is postulated to form by a [1, 2] shift from the initially formed Cp'₂CeCH₂OSiMe₃. The calculations show that the metallacycle favors the CH bond activation over the SiMe₃ migration while the opposite result is obtained for the hydride. The calculated activation barrier for the [1, 2] shift, in which the SiMe₃ group migrates from the oxygen to the carbon, is low. Both of these reactions proceed through transition states in which silicon is five coordinate. Construction of interaction diagrams for each reaction shows the σ -bond metathesis and the silyl-Wittig rearrangement are isolobal processes when the migrating group is silyl.

Experimental Details

General

All manipulations were performed under an inert atmosphere using standard Schlenk and dry box techniques. All solvents were dried and distilled from sodium or sodium benzophenone ketyl. Methoxytrimethylsilane was obtained commercially and purified by distillation followed by vacuum transfer. NMR spectra were recorded on Bruker AV-300 or AV-400 spectrometers at 20°C in the solvent specified. J-Young NMR tubes were used for all NMR tube experiments. Electron impact mass spectrometry and elemental analyses were performed by the microanalytical facility at the University of California, Berkeley. The abbreviation Cp' is used for the 1,2,4-*tert*-butylcyclopentadienyl ligand.

Cp'₂CeOCH₂SiMe₃

$\text{Cp}'_2\text{CeCH}_2\text{C}_6\text{H}_5$ ^{9,25} (0.63g, 0.90 mmol) was dissolved in pentane (20 mL) and methoxytrimethylsilane (0.2 mL, 1.4 mmol) was added via syringe. The red solution was stirred for 4 days, and then taken to dryness. The resulting red powder was put into a glass ampoule, which was sealed under vacuum, and heated at 190°C. Over a period of 7 days, red crystals formed on the walls of the ampoule. The crystals were placed in a clean ampoule, sealed under vacuum, and resublimed. Yield: 120 mg (0.17 mmol, 19%). ¹H NMR (C_6D_6): δ 25.42 (2H, $\nu_{1/2}$ = 250 Hz), 3.45 (9H, $\nu_{1/2}$ = 4 Hz), -0.90 (36H, $\nu_{1/2}$ = 1500 Hz), -13.27 (18H, $\nu_{1/2}$ = 30 Hz); the ring CH resonance was not observed. MS (M^+) m/z (calc, found) 709 (100, 100) 710 (47, 61) 711 (27, 41) 712 (9, 18) 713 (2, 5). Anal. Calcd. for $\text{C}_{38}\text{H}_{69}\text{CeSiO}$: C, 64.27; H, 9.79. Found C, 64.48; H, 9.68. Full crystallographic details are included as Supporting Information. Triclinic cell space group $\text{P}2_1/\text{n}$: $a = 10.269(2)$ Å, $b = 20.104(5)$ Å, $c = 18.983(4)$ Å, $\beta = 97.329(3)$ °, $V = 3886.7(16)$ Å³.

NMR tube reaction: $\text{Cp}'_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_5)$ was dissolved in cyclohexane- d_{12} in an NMR tube. A drop of $\text{CH}_3\text{OSiMe}_3$ was added, the sample was shaken and allowed to stand. After 4 hours, resonances due to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ had appeared in the ¹H NMR spectrum; the ratio of $\text{Cp}'_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_5)$ to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ was 3:1. After 1 day at 19°C, the ratio was 1:2. After 4 days, resonances due to $\text{Cp}'_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_5)$ were absent from the ¹H NMR spectrum. Integration relative to the solvent residual proton resonance indicated the conversion of $\text{Cp}'_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_5)$ to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ was quantitative.

NMR tube reaction of $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ and $\text{CH}_3\text{OSiMe}_3$ in cyclohexane- d_{12} .

$\text{Cp}'_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_5)$ was dissolved in cyclohexane- d_{12} and heated at 60°C for 12 hours, yielding a deep purple solution of $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$. A drop of $\text{CH}_3\text{OSiMe}_3$ was added, the sample was shaken, and allowed to stand. After 15 minutes, resonances due to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ had appeared in the ^1H NMR spectrum; the ratio of $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ was 1:2. After 1 day at 19°C , resonances due to $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ were absent from the ^1H NMR spectrum. Integration relative to the solvent residual proton resonance indicated the conversion of $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ was quantitative.

NMR tube reaction of $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$, BPh_3 , and $\text{CH}_3\text{OSiMe}_3$ in cyclohexane- d_{12} .

$\text{Cp}'_2\text{Ce}(\text{CH}_2\text{C}_6\text{H}_5)$ and slightly greater than one equivalent of BPh_3 were dissolved in cyclohexane- d_{12} and heated at 60°C for 12 hours, yielding a solution of $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ and BPh_3 . A drop of $\text{CH}_3\text{OSiMe}_3$ was added, the sample was shaken and allowed to stand. After 30 minutes, the purple solution had turned red, and resonances due to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ had appeared in the ^1H NMR spectrum; the ratio of $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ was 1:9. After 1 day at 19°C , resonances due to $\text{Cp}'[(\text{Me}_3\text{C})_2\text{C}_5\text{H}_2\text{C}(\text{Me})_2\text{CH}_2]\text{Ce}$ were absent from the ^1H NMR spectrum and only those due to $\text{Cp}'_2\text{CeOCH}_2\text{SiMe}_3$ remained.

NMR tube reaction of $\text{Cp}'_2\text{CeH}$ and $\text{CH}_3\text{OSiMe}_3$ in cyclohexane- d_{12} .

$\text{Cp}'_2\text{CeH}$ was dissolved in cyclohexane- d_{12} in an NMR tube. A drop of $\text{CH}_3\text{OSiMe}_3$ was added, the sample was shaken. The purple solution instantly turned red. Within 5

minutes, the only paramagnetic resonances in the ^1H NMR spectrum were those of $\text{Cp}'_2\text{CeOCH}_3$.⁸ Diamagnetic resonances due to HSiMe_3 ²⁶ were also present.

Integration relative to the solvent residual proton resonance indicated the conversion of $\text{Cp}'_2\text{CeH}$ to $\text{Cp}'_2\text{CeOCH}_3$ was quantitative.

Computational details

The Stuttgart-Dresden-Bonn Relativistic large Effective Core Potential (RECP) was used to represent the inner shells of Ce.²⁷ The associated basis set²⁷ augmented by an f-polarization function ($\alpha = 1.000$) was used to represent the valence orbitals.²⁸ Si has also been represented by an RECP,²⁹ with the associated basis set augmented by a d polarization Gaussian function ($\alpha = 0.284$). The atoms C, O, and H were represented by an all-electron 6-31G(d, p) basis set.³⁰ Calculations were carried out at the DFT(B3PW91) level³¹ with Gaussian 03.³² The nature of the extrema (minimum or transition state) was established with analytical frequencies calculations and the intrinsic reaction coordinate (IRC) was followed to confirm that the transition states connect to reactants and products. The zero point energy (ZPE) and entropic contribution have been estimated within the harmonic potential approximation. The Gibbs free energy, G, was calculated at $T = 298.15\text{K}$ and 1 atm.

Acknowledgment

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences (OBES), of the U.S. Department of Energy (DOE) under Contract No. DE-AC02-05CH11231. We thank F. J. Hollander and A. G. DiPasquale at CHEXRAY, the U.C. Berkeley X-ray diffraction facility, for help with the crystallography. A.Y. thanks the Computer Center, CCRT of the CEA, the CINES and the CALMIP for a generous donation of computation time. L.M. is also a junior member of the Institut

Universitaire de France, L.M. and O.E thank the CNRS and Minister of High Education and Research for funding, and A.Y. thanks the CEA for PhD fellowship.

Supporting information (SI) available: X-ray crystallographic data (CIF), optimized structures, E and G (in a. u.) for all stationary points. Crystallographic data for the structure in this paper has also been deposited with the Cambridge Crystallographic Data Center. Copies of the data CCDC 771392 for [1,2,4-(Me₃C)₃C₅H₂]₂CeOCH₂SiMe₃ can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

References

- 1 (a) Tomooka, K. in *The Chemistry of Organolithium Compounds*. Part 2, Patai Series, The Chemistry of Functional Groups, Rappoport, Z. and Marek, I. Eds. Wiley 2004 pp 749-828. (b) Kira, M.; Iwamoto, T. in *The Chemistry of Organic Silicon Compounds* Patai Series, Rappoport, Z. and Apeloig, Y. Eds. Wiley, 2001, Vol 3, pp 853-948.
- (2) (a) Brook, A. G.; Bassindale, A. R. in *Rearrangements in Ground and Excited States* vol. 2 de Mayo, P. Ed. Academic press, 1980, pp 149-227. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, 7, 77.
- (3) (a) West, R.; Lowe, R.; Stewart, H. F.; Wright, A. *J. Am. Chem. Soc.* **1971**, 93, 282. (b) Wright, A.; West R. *J. Am. Chem. Soc.* **1974**, 96, 3222. (c) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, 96, 3227. (d) West R. *Adv. Organomet. Chem.* **1977**, 16, 1.

- (4) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33.
- (5) Werkema, E. L.; Andersen, R. A.; Yahia, A.; Maron, L.; Eisenstein, O. *Organometallics* **2009**, *28*, 3173.
- 6 Werkema, E. L.; Messines, E.; Perrin, L.; Maron, L.; Eisenstein, O.; Andersen, R. *J. Am. Chem. Soc.* **2005**, *127*, 7781.
- 7 Werkema, E. L.; Andersen, R. A.; Yahia, A.; Maron, L.; Eisenstein, O. *New J. Chem.* 2010 Advance publication, **DOI**: 10.1039/C0NJ00261E.
- 8 Werkema, E. L.; Maron, L.; Eisenstein, O.; Andersen, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 2529. Correction *J. Am. Chem. Soc.* **2007**, *129*, 6662.
- 9 Werkema, E. L.; Andersen, R. A.; Maron, L.; Eisenstein, O. *Dalton Trans.* **2010**, *39*, 6648.
- 10 Werkema, E. L.; Andersen, R. A. *J. Am. Chem. Soc.* **2008**, *131*, 7153.
- 11 (a) Steigerwald, M. L.; Goddard, W. A. *J. Am. Chem. Soc.* **1984**, *106*, 308. (b) Rappé, A. K.; Upton, T. H. *J. Am. Chem. Soc.* **1992**, *114*, 7507.
- 12 Balcells, D.; Clot, E.; Eisenstein, O. *Chem. Rev.* **2010**, *110*, 749.
- 13 (a) Folga, E.; Ziegler, T. *Can. J. Chem.* **1992**, *70*, 333. (b) Perrin, L.; Maron, L.; Eisenstein, O. *J. Chem. Soc. Dalton Trans.* **2002**, 534. (c) Perrin, L.; Maron, L.; Eisenstein, O. ACS Book Series 885 *Organometallic C-H Bond Activation* A. Goldman and K. Goldberg Eds. **2004** pp116-135.
- 14 (a) Sini, G.; Hiberty, P. C.; Shaik, S. S. *J. Chem. Soc. Chem. Commun.* **1989**, 772. (b) Sini, G.; Ohanessian, G.; Hiberty, P. C.; Shaik, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 1407.
- 15 Perrin, L.; Maron, L.; Eisenstein, O. *Inorg. Chem.* **2002**, *41*, 4355.
- 16 Perrin, L.; Eisenstein, O.; Maron, L. *New J. Chem.* **2007**, *31*, 549.

- 17 Perrin, L.; Maron, L.; Eisenstein, O.; Tilley, T. D. *Organometallics*, **2009**, *28*, 3767.
- 18 (a) Ahlrich, R.; Heinszmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7452. (b) Gutowsky, H. S.; Chen, J.; Hajduck, P. J.; Chuang, C.; Emilsson, T. *J. Am. Chem. Soc.* **1991**, *113*, 4747.
- 19 (a) Antoniotti, P.; Tonachini, G. *J. Org. Chem.* **1993**, *58*, 3622. (b) Antoniotti, P.; Canepa, C.; Tonachini, G. *J. Org. Chem.* **1994**, *59*, 3952.
- 20 Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.
- 21 Erker, G.; Bendix, M.; Petrenz, R. *Organometallics* **1994**, *13*, 456.
- 22 Wittig, G.; Löhmann, L. *Liebigs Ann. Chem.* **1942**, *550*, 260.
- 23 Schöllkopf, U. *Angew. Chem. Int. Ed. Ed.* **1970**, *9*, 763.
- 24) The Cp₂Ce fragment stabilizes the ligands mainly by electrostatic interaction with a small covalent contribution, Perrin, L.; Maron, L.; Eisenstein, O. *Faraday Discuss.*, **2003**, *124*, 25 and references therein.
- 25 Maron, L.; Werkema, E. L.; Perrin, L.; Eisenstein, O.; Andersen, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 279.
- 26 Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Letters* **1997**, *26*, 437.
- 27) (a) Dolg, M.; Stoll, H.; Savin, A.; Preuß, H. *Theor. Chim. Acta* **1989**, *75*, 173.
Dolg, M.; Stoll, H.; Preuß, H. *Theor. Chim. Acta* **1993**, *85*, 441.
- 28) Maron, L. Eisenstein, O. *J. Phys. Chem. A*, **2000**, *104*, 7140.
- 29) Bergner, A. Dolg, M. Küchle, W. Stoll, H. Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.
- 30) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
- 31) Perdew, J. J. P.; Wang, Y. *Phys. Rev. B*, 1992, **82**, 13244. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Burke, K.; Perdew, J. P.; Yang, W. in “*Electronic Density*

Functional Theory: Recent Progress and New Directions” Dobson, J. F.; Vignale, G.,
Das, M. P. Eds. **1998**, Plenum.

32) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.;
Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.;
Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.;
Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota,
K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai,
H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo,
C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi,
R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador,
P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.;
Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J.
V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.;
Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-
Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.;
Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc.,
Wallingford Gaussian 03, Revision E.01, CT, 2004.

TOC

The SiMe₃ groups in the σ -bond metathesis and [1, 2] shift reactions have isolobal transition states.

