



HAL
open science

α -C-C Agostic interactions and C-H bond activation in scandium cyclopropyl complexes

Cheng Xu, Guangyu Li, Michel Etienne, Xuebing Leng, Yaofeng Chen

► **To cite this version:**

Cheng Xu, Guangyu Li, Michel Etienne, Xuebing Leng, Yaofeng Chen. α -C-C Agostic interactions and C-H bond activation in scandium cyclopropyl complexes. *Inorganic Chemistry Frontiers*, 2020, 7, pp.4822-4831. 10.1039/D0QI01163K . hal-03128995

HAL Id: hal-03128995

<https://hal.science/hal-03128995v1>

Submitted on 2 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

α -C-C Agostic interactions and C-H bond activation in scandium cyclopropyl complexes

Cheng Xu,^a Guangyu Li,^a Michel Etienne,^{*b} Xuebing Leng^a and Yaofeng Chen^{*a}

This paper addresses the problem of the observation of so-called C-C agostic interactions in cyclopropyl complexes of scandium. Three new cyclopropyl complexes of scandium based on β -diketiminato ligand were synthesized including by an intramolecular C-H bond activation reaction in one case. X-ray diffraction analysis revealed distorted cyclopropyl groups in the complexes, and the distortion could be observed in solution as well for one of the complexes thanks to the natural abundance INADEQUATE NMR spectroscopy which showed the markedly reduced J_{C-C} coupling constant. This signature of the C-C agostic interaction was further examined using DFT modelling which, together with NBO calculations, indicated that C-H and C-C agostic interactions are not exclusive but can complement each other accounting for the distortions. The intramolecular C-H bond activation in scandium biscyclopropyl complex was investigated by isotopic labeling experiments, which indicated a direct proton abstraction of the isopropyl group in β -diketiminato ligand by cyclopropyl group.

Introduction

The poor overlap of carbon based orbitals within a strained cyclopropyl ring raises their energy and make them spatially exposed, imparting them unique chemical properties.¹⁻⁴ One consequence in organometallic complexes $[M]-(c-C_3H_5)$ is that so-called α -C-C agostic distortions or interactions – formally three center-two electron bonds – are preferred to the much more common C-H agostic interactions whether they be with the α - or β -C-H bonds.^{5,6} This has been observed in unsaturated early transition⁷⁻⁹ and alkaline^{10,11} metal complexes especially. For rare-earth metals, the bimetallic complex $[(C_5Me_5)_2Y(\mu-c-C_3H_5)_2Li(thf)]$ exhibits C-C agostic interactions with both lithium and yttrium centers, and the interaction with lithium being more electrostatic in nature when that with yttrium being more covalent.¹² This represented a single example of a C-C agostic rare-earth metal complex since C-C agostic interactions between rare-earth metals and remote cyclopropyl rings have only been computed so far.¹³

In this paper, we present our efforts to synthesize monometallic scandium cyclopropyl complexes. Their characterization in the solid state and in solution indicate that C-C agostic interactions are present. DFT is used to better define the nature of the interactions.

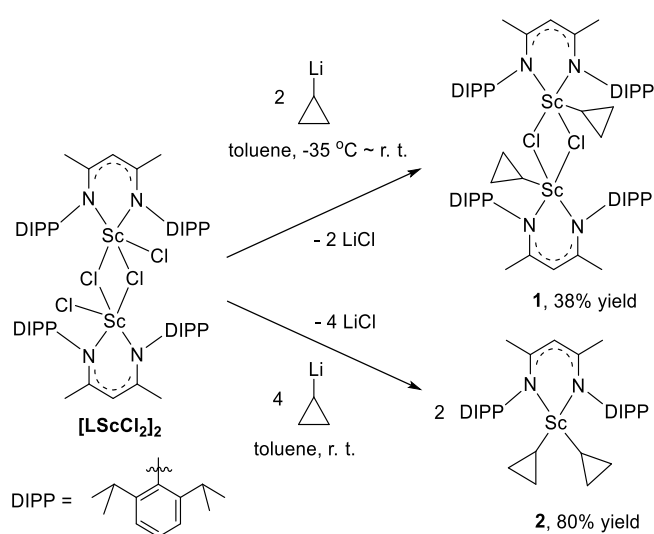
An intramolecular C-H bond activation reaction degrades an ancillary ligand allowing the comparison between different types of alkyl ligands intramolecularly confirming that cyclopropyl groups are privilege structures to observe C-C agostic interactions.

Results and discussion

Synthetic and structural aspects

Scandium dichloride $[LSc(\mu-Cl)Cl]_2$ ($L = [MeC(NDIPP)CHC(Me)(NDIPP)]^-$, $DIPP = 2,6-(iPr)_2C_6H_3$) and cyclopropyl lithium were prepared as reported.^{14,15} Reactions of $[LSc(\mu-Cl)Cl]_2$ with cyclopropyl lithium in a 1 : 2 or 1 : 4 molar ratio in toluene provided scandium cyclopropyl chloride complex $[LSc(\mu-Cl)(c-C_3H_5)]_2$ (**1**) and biscyclopropyl complex $[LSc(c-C_3H_5)_2]$ (**2**) in 38% and 80% yields, respectively (Scheme 1). Both complexes were characterized by NMR spectroscopy (1H and $^{13}C\{^1H\}$), elemental analysis, and single-crystal X-ray crystallography. The 1H NMR spectra in C_6D_6 indicated a time-averaged C_{2v} symmetry of cyclopropyl group in **1** and **2** at room temperature. The $C_{\alpha}H$ of cyclopropyl group in **1** resonates as a triplet of triplet at $\delta = -0.45$ ppm ($^3J_{H-H} = 10.5, 8.1$ Hz), the corresponding $C_{\alpha}H$ in **2** appears shifted slightly downfield ($\delta = -0.06$ ppm, $^3J_{H-H} = 10.3, 8.2$ Hz). The chemical shifts of $ScCH_3$ in the scandium methyl chloride complex $[LSc(\mu-$

Cl)Me]₂ and dimethyl complex [LScMe₂(THF)] are 0.29 and -0.15 ppm, respectively.^{14,16} All the C_βH signals of the cyclopropyl groups in **1** and **2** appear as doublets, and their chemical shift values range from 0.38 to 0.61 ppm. The ¹³C{¹H} NMR spectra confirm the C_{2v} symmetry of cyclopropyl group in the complexes, with only one C_βH signal at δ = 9.4 ppm for **1** and δ = 7.4 ppm for **2**. Due to the quadrupolar relaxation, the C_α signals appear as broad singlets at δ = 33.2 and 30.8 ppm for **1** and **2**, respectively; the assignment of these two signals was assisted with the HSQC spectra of the complexes.



Scheme 1 Synthesis of **1** and **2**.

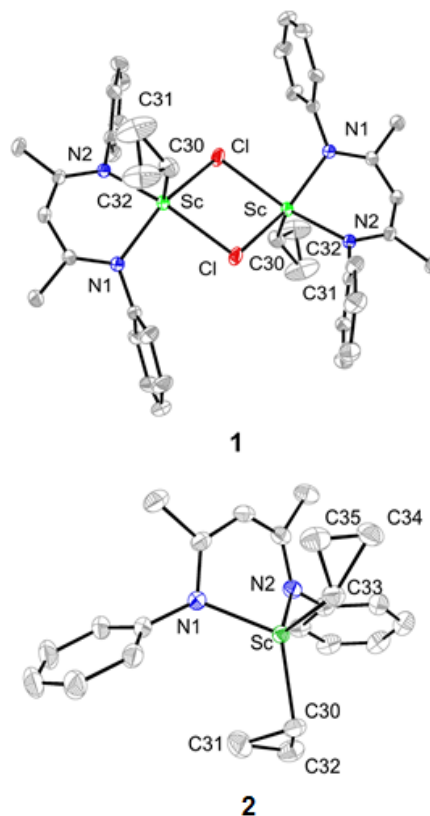
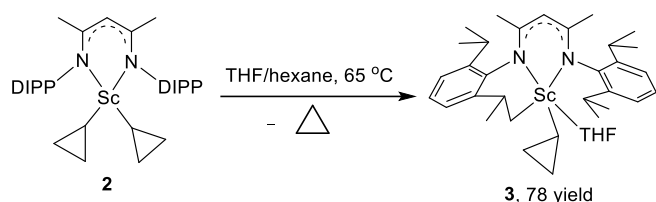


Fig. 1 ORTEP drawings of **1** and **2** with thermal ellipsoids set at 30% probability level. Isopropyl groups of DIPP and hydrogen atoms have been omitted for clarity.

The single-crystal X-ray diffraction analysis showed that complex **1** exists as a dimer in the solid state, in which each pentacoordinated scandium ion is coordinated by two nitrogen atoms of L, two bridging chlorides and one carbon atom of cyclopropyl ligand (Fig. 1). Two Sc-Cl bond lengths are 2.558(1) and 2.540(1) Å. The Sc-C30 bond length is 2.195(2) Å, which is close to the Sc-C(methyl) bond length in [LScMe₂(THF)] (2.210(9) and 2.245(9) Å).¹⁴ The distances from the scandium ion to two C_β atoms of the cyclopropyl ligand, 3.354 and 3.364 Å, are long, indicating no interaction between the scandium ion and the C_β atoms. The two Sc-C_α-C_β bond angles are close (132.3(2)° and 132.0(2)°). Complex **2** is monomeric, with the scandium ion being coordinated by two nitrogen atoms of L and two cyclopropyl carbon atoms (Fig. 1) in a pseudotetrahedral environment. The two Sc-C_α bonds, Sc-C30 and Sc-C33, are 2.180(2) and 2.195(2) Å, respectively, similar to that in **1** (2.195(2)

Å). There is an inconspicuous unsymmetrical coordination of one cyclopropyl ring in **2**, which can be described by the difference between the Sc...C31 distance (Sc...C31: 2.904 Å) and other Sc...C β distances (Sc...C32: 3.248 Å, Sc...C34: 3.389 Å and Sc...C35: 3.335 Å). Such distortion is also exhibited by the different Sc-C α -C β angles, the Sc-C30-C31 (101.7(1)°) angle is smaller than other Sc-C α -C β angles [Sc-C30-C32: 122.3(1)°, Sc-C33-C34: 131.0(1)°, Sc-C33-C35: 126.6(1)°]. C30-C31 (1.526(3) Å) is barely longer than C30-C2 (1.510(3) Å) which remains similar to the C β -C β in the other cyclopropyl group [C33-C34 = 1.516(2), C33-C35 = 1.522(2) Å].



Scheme 2 Thermolysis of **2** into **3**.

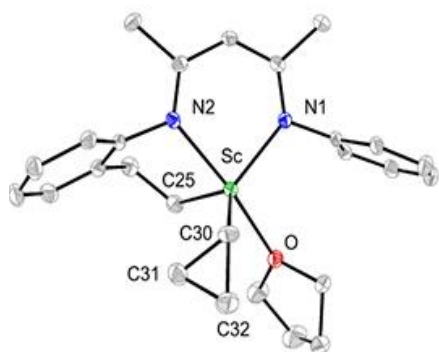


Fig. 2 ORTEP drawing of **3** with thermal ellipsoids set at 30% probability level. Isopropyl groups of DIPP and hydrogen atoms have been omitted for clarity.

As observed with other dialkyl complexes of scandium,¹⁴ complex **2** slowly eliminates cyclopropane at room temperature ($\delta = 0.14$ ppm in the ^1H NMR

spectrum) to give a complicated mixture in C_6D_6 at room temperature. Interestingly, in the presence of THF, complex **2** nearly quantitatively converts into a new complex **3** in 24 h at 65 °C with elimination of cyclopropane. A scaled-up reaction in hexane/THF provided **3** in 78% isolated yield as a yellow solid, in which a C-H bond of an isopropyl group in **2** has been activated to form a new dianionic ligand (L-H) as shown in Scheme 2. Complex **3** was characterized by NMR spectroscopy (^1H and $^{13}\text{C}\{^1\text{H}\}$), elemental analysis and single-crystal X-ray crystallography. The latter revealed there are two crystallographically independent molecules in the unit cell of **3**; these two molecules have very close structural parameters and one molecule was taken as the example to analyze the structural parameters (Fig. 2). In **3**, the scandium ion is coordinated by two nitrogen atoms and one carbon atom of the newly formed ligand (L-H), one carbon atom of the cyclopropyl ligand and one oxygen atom of THF. The scandium atom is in a trigonal bipyramidal environment with O and N2 forming the apical sites [$\text{N2-Sc-O} = 169.94(11)^\circ$]. The distances from the scandium ion to the isopropyl carbon atom and cyclopropyl carbon atom are 2.273(4) and 2.184(4) Å, respectively. The cyclopropyl ring and its coordination to the scandium atom are significantly distorted. The Sc-C30-C31 angle (95.9(3)°) is much smaller than the Sc-C30-C32 angle (132.7(3)°). In addition, the Sc...C31 distance (2.793 Å) is 0.60 Å shorter than the Sc...C32 distance (3.391 Å). Within 3σ , C30-C31 (1.531(6) Å) is not statistically stretched as compared to C30-C32 (1.505(5) Å).

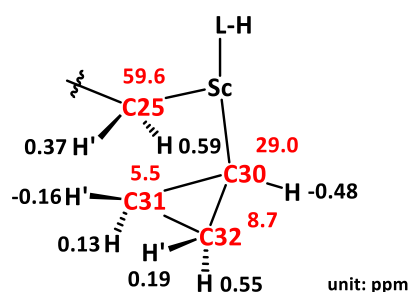


Fig. 3 ^1H and ^{13}C NMR data for key protons and carbons in **3**. Data color code: black, ^1H NMR data; red, ^{13}C NMR data.

The unusual distortion of the cyclopropyl ring prompted a detailed NMR investigation on the underlying agostic interaction in complex **3**. First of all, a comprehensive assignment of all protons and carbons of the cyclopropyl ring in **3** was realized through ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR with the aid of HSQC, COSY and NOESY sequences, as shown in Fig. 3. The assignments indicated that, in solution, complex **3** adopts a conformation fully consistent with that in the solid state revealed by X-ray crystallography. The ^1H NMR spectrum showed five signals for the five protons of the cyclopropyl ring, [C30H: -0.48 (m, 1H), C31H: 0.13, -0.16 (m, 2H), C32H: 0.55, 0.19 (m, 2H)]. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed two signals for the two C_β atoms of the cyclopropyl ring, C31 at 5.5 ppm and C32 at 8.7 ppm when C_α (C30) was observed as a broad signal due to quadrupolar relaxation at 29.0 ppm. The NOESY spectrum played a vital role in uncovering the spatial arrangement of above protons with the guidance of characteristic proton (C25H) of the L-H ligand. Apart from the detailed assignment of the protons in the cyclopropyl ring, the NOESY spectrum also depicted the greater intensity of coherent signal for the C25H'-C31H' than the C25H'-C32H' (Fig. 4), indicating that the cyclopropyl ring in **3** presents a distorted configuration with the C30-C31 bond approaching to the scandium ion in the solution phase. Subsequently, the ^1H - ^1H EXSY and variable temperature ^1H NMR spectra (303 - 343 K) were recorded, no proton exchange or rotation of the cyclopropyl ring in **3** was observed even at 343 K in C_6D_6 , illustrating the relative stable geometry conformation of the cyclopropyl ring in **3**.

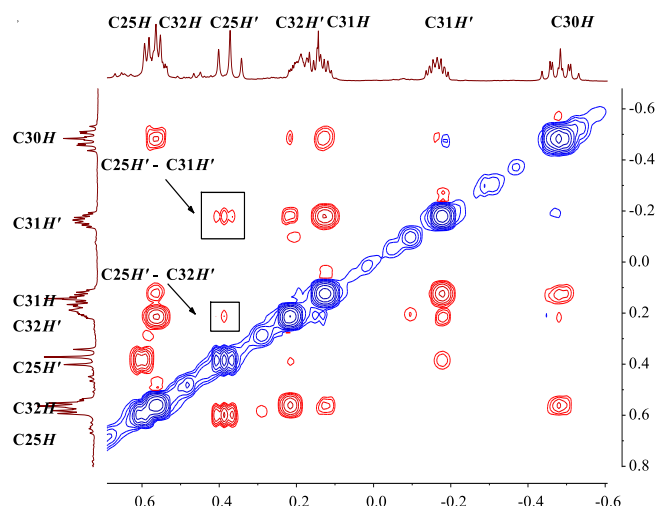
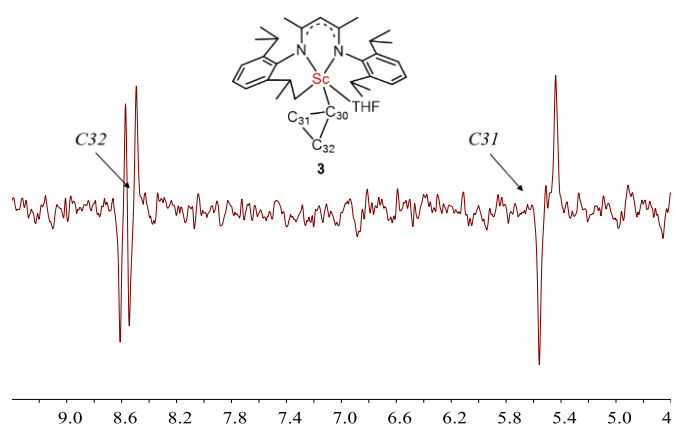


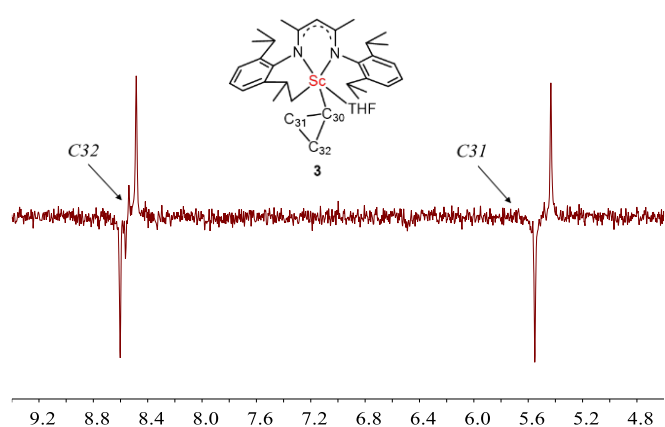
Fig. 4 Expansion plot of the NOESY spectrum of **3** (400 MHz, C_6D_6).

The $^1J_{\text{C-H}}$ values were then obtained from a gated ^{13}C NMR spectrum. The C31 and C32 atoms resonate as triplets with the $^1J_{\text{C-H}}$ values of 158 and 155 Hz, respectively, which are similar to the $^1J_{\text{C-H}}$ value of cyclopropane (161 Hz) and indicate the absence of agostic interaction between the scandium ion and the corresponding β -C-H bonds of the cyclopropyl ring. Due to quadrupolar relaxation, $^1J_{\text{C}(\beta)\text{H}}$ could not be measured. The agostic interaction between the scandium ion and the C-C bond of the cyclopropyl ring was then investigated. A remarkable decrease of $^1J_{\text{C-C}}$ value is the key evidence for the presence of such agostic interaction.^{9,12,17} Fortunately, owing to well resolved resonance of C_β signals, good solubility of **3** (ca. 0.4 M in C_6D_6), and the utility of sensitivity boosted cryogenetic probe, inherently challenging 1D INADEQUATE spectra of high quality were successfully acquired and the $^1J_{\text{C-C}}$ values of C_β signals were obtained. The C32 signal displays two doublets with $^1J_{\text{C-C}}$ values of 14.8 and 3.2 Hz; while the C31 signal appears as a doublet with $^1J_{\text{C-C}}$ values of 14.8 Hz (Fig. 5a). Therefore, the $^1J_{\text{C31-C32}}$ value is 14.8 Hz and the $^1J_{\text{C30-C32}}$ value is 3.2 Hz. This small value is linked to the low electronegativity of the scandium. The observation of C31 signal as a single doublet instead of two can be rationalized in two ways: (a) the $^1J_{\text{C31-C30}}$ value is the

same or very close to the $^1J_{C31-C32}$ value, so the peaks overlap; (b) the $^1J_{C31-C30}$ value is very small and indeed less than the line width of the experiment (< 2.0 Hz) hence not detectable. Therefore, we recorded the ^{13}C - ^{13}C INADEQUATE spectrum of **3** optimized for $J = 15$ Hz (Fig. 5b), which showed that the intensity of the C31 doublet is not twice but equal to that of the C32 doublet. This result clearly indicated that the $^1J_{C31-C30}$ value is too small to be detected, and such small $^1J_{C31-C30}$ value revealed an agostic interaction between the scandium ion and the C30-C31 bond of the cyclopropyl ring. Unfortunately, this could not be confirmed in the absence of the C30 signal (however, see Computational Study below).

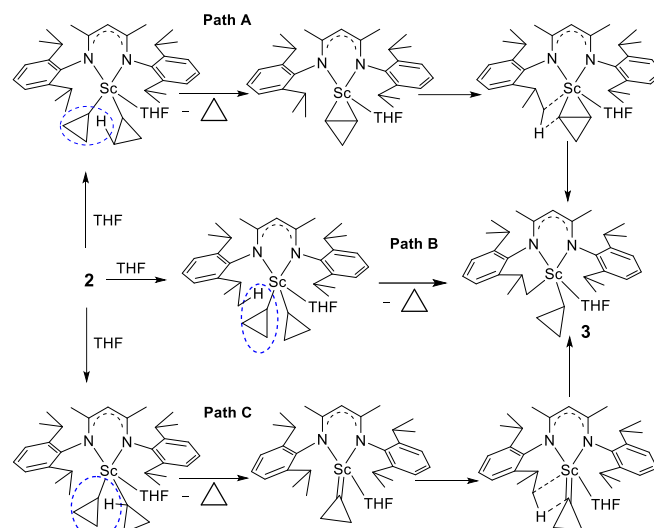


(a)



(b)

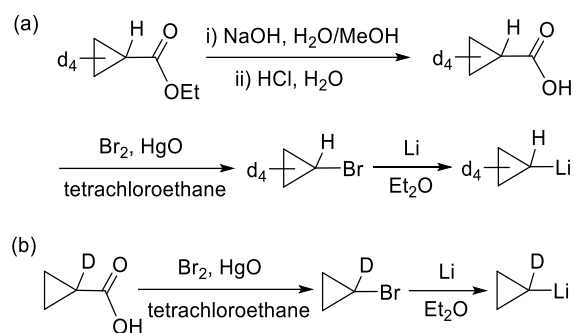
Fig. 5 ^{13}C - ^{13}C INADEQUATE spectra of **3**, optimized for $J = 3$ Hz (a) and $J = 15$ Hz (b), respectively.



Scheme 3 Three possible pathways for the thermolysis of **2** into **3**.

There are three plausible pathways by which complex **2** eliminates cyclopropane to give complex **3** (Scheme 3): (1) Path A, one of the cyclopropyl ligands abstracts a proton from the other cyclopropyl ligand first to form a scandium η^2 -cyclopropene intermediate, which is unstable and subsequently undergoes a σ -bond metathesis between the Sc-C bond and the C-H bond of the isopropyl group; (2) Path B, one of the cyclopropyl ligands abstracts a proton from the isopropyl group of L; (3) Path C, an α -H abstraction to form a cyclopropylidene intermediate, followed by a deprotonation of the isopropyl group of L. To investigate the reaction pathway, we decided to synthesize complex **2-d₈** which contains two 2,2,3,3-tetradeuteriocyclopropyl ligands and study its thermolysis. It can be reasonably envisioned that, if complex **3** is formed via Path A, the cyclopropenyl

ligand in the η^2 -cyclopropene intermediate would abstract a proton from the isopropyl group to generate the complex **3-d₃**, which would display the cyclopropyl C $_{\beta}$ H signal in the 1 H NMR spectrum; on the contrary, if complex **3** is formed via Path B or C, the thermolysis of **2-d₈** would give the complex **3-d₄**, in which no signal of the C $_{\beta}$ H of the cyclopropyl would be observed in the 1 H NMR spectrum.

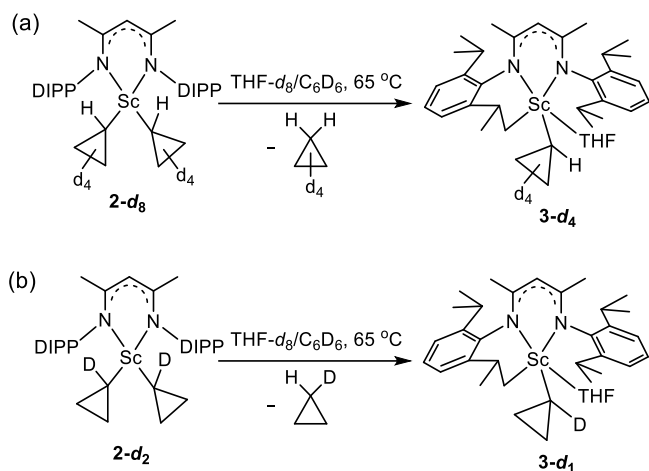


Scheme 4 Synthesis of 2,2,3,3-tetradeuteriocyclopropyl lithium and 1-monodeuteriocyclopropyl lithium.

Tetradeuteriocyclopropyl lithium was firstly synthesized, as shown in Scheme 4a. Ethyl 2,2,3,3-tetradeuteriocyclopropanecarboxylate was prepared using THF-*d*₈ as a starting material in three steps according to the procedures reported by Meijere and co-workers.¹⁸ Ethyl 2,2,3,3-tetradeuteriocyclopropanecarboxylate was hydrolyzed in a H₂O/MeOH solution of NaOH, and then treated with HCl aqueous solution to give 2,2,3,3-tetradeuteriocyclopropanecarboxylic acid (66% yield). With tetradeuteriocyclopropanecarboxylic acid in hand, 2,2,3,3-tetradeuteriocyclopropyl bromide was synthesized using a Cristol-Firth reaction.¹⁹ After the completion of the reaction, excess bromine was removed by treatment with sodium thiosulfate, and benzene was added. The addition of benzene helps the distillation of 2,2,3,3-tetradeuteriocyclopropyl bromide in a small scale. The distilled tetradeuteriocyclopropyl bromide/benzene mixture was reacted with a suspension of finely divided lithium in diethylether to

provide the desired 2,2,3,3-tetradeuteriocyclopropyl lithium as a white solid; the total yield of the above two steps is 13%. Following the procedure for complex **2**, the salt metathesis of [LSc(μ -Cl)Cl]₂ with 2,2,3,3-tetradeuteriocyclopropyl lithium in a 1:4 molar ratio in toluene provided the deuterated complex **2-d₈** as a yellow solid in a 77% isolated yield. The 1 H NMR spectrum of **2-d₈** in C₆D₆ resembles that of **2**, except the absence of resonances at 0.61 and 0.41 ppm, indicating the deuteration on C $_{\beta}$ atoms. In the 2 H NMR spectrum of **2-d₈** in C₆H₆, two resonances were observed at 0.52 and 0.31 ppm for the C $_{\beta}$ D of the tetradeuteriocyclopropyl ligands. The thermolysis of **2-d₈** in THF-*d*₈/C₆D₆ at 65 °C was investigated, which clearly indicated the formation of **3-d₄** (Scheme 5a). The 1 H NMR spectral monitoring showed the appearance of the C $_{\alpha}$ H signal at -0.61 ppm and the absence of the C $_{\beta}$ H signal (Fig. S20 in the ESI). In the 2 H NMR spectrum of the product in C₆H₆, the deuterium resonances were observed in the region of -0.3 ~ 0.5 ppm (Fig. S21 in the ESI). Therefore, the complex **3** is not formed via the Path A, which is different from the reported cyclopropane elimination mechanism for zirconium²⁰ and niobium^{21–23} cyclopropyl complexes. For example, in biscyclopropyl complex [Cp₂Zr(*c*-C₃H₅)₂], one of the cyclopropyl ligands abstracts a β -proton from the other cyclopropyl ligand to release cyclopropane and generate the zirconium η^2 -cyclopropenyl species [Cp₂Zr(η^2 -*c*-C₃H₄)].²⁰

To discriminate between Path B and Path C, we need to synthesize complex **2-d₂** which contains two 1-monodeuteriocyclopropyl ligands and study its thermolysis. If complex **3** is formed via Path B, the thermolysis of **2-d₂** would give the complex **3-d₁**, in which no signal of the C $_{\alpha}$ H of the cyclopropyl would be observed in the 1 H NMR spectrum, and the 2 H NMR spectrum of the complex would displays a C $_{\alpha}$ D signal; if complex **3** is formed via Path C, the thermolysis of **2-d₂** would give the complex **3-d₀**, in which no signal of the C $_{\alpha}$ D of the cyclopropyl would be observed in the 2 H NMR spectrum, and the 1 H NMR spectrum of the complex would shows a C $_{\alpha}$ H



Scheme 5 Thermolysis of **2-d₈** into **3-d₄**, and **2-d₂** into **3-d₁**.

signal. Methyl cyclopropyl ketone- $\alpha, \alpha, \alpha, \alpha'$ - d_4 with deuterium isotopic content to 90% was prepared by protons exchange of methyl cyclopropyl ketone with 40 wt% NaOD in D_2O ,²⁴ and this ketone undergoes a haloform reaction²⁵ with NaOBr to provide 1-monodeuteriocyclopropanecarboxylic acid (90 atom % D). From 1-monodeuteriocyclopropanecarboxylic acid, 1-monodeuteriocyclopropyl lithium (90 atom % D) was synthesized in a total yield of 31% using the similar approach as that of 2,2,3,3-tetradeuteriocyclopropyl lithium (Scheme 4b), and was then subjected to the salt metathesis with 0.25 equiv. $[LSc(\mu-Cl)Cl]_2$. The reaction produced complex **2-d₂** as a yellow solid in 84% yield. The 1H NMR spectrum of **2-d₂** in C_6D_6 shows ~90%

deuteration on the α -C, and no $^3J_{H-H}$ spin-spin splitting was observed for the $C_\beta H$ (0.61 and 0.41 ppm). In the 2H NMR spectrum of **2-d₂** in C_6H_6 , one resonance was observed at -0.10 ppm for the $C_\alpha D$ of the 1-monodeuteriocyclopropyl ligands. The 1H and 2H NMR spectral monitoring on the thermolysis of **2-d₂** in $THF-d_8/C_6D_6$ or THF/C_6H_6 showed the transformation of **2-d₂** into **3-d₁** (Scheme 5b). In the 1H spectrum (Fig. S26 in the ESI), four $C_\beta H$ signals were clearly observed at 0.41, 0.10, -0.04 and -0.33 ppm, while the $C_\alpha H$ signal is very weak in line with a deuterium isotopic content of 90%. The 2H NMR showed two signals, one for the $C_\alpha D$ ($\delta = -0.74$ ppm) in **3-d₁** and the other for the CHD ($\delta = 0.06$ ppm) in eliminated monodeuteriocyclopropane (Fig. S27 in the ESI). Therefore, the complex **3** is formed via a direct proton abstraction of the isopropyl group in **L** by cyclopropyl group (Path B).

Computational study

We have used a computational approach to better define the C-C agostic interactions in complex **3** and possibly in complex **2**. We first used the experimental data for complex **3** to benchmark our study and then considered the distorted solid state molecular structure of complex **2** whose solution structure is time averaged. Optimizations were carried out in the framework of DFT with the PBE0 functional coupled to empirical dispersion corrections. Details of basis sets can be

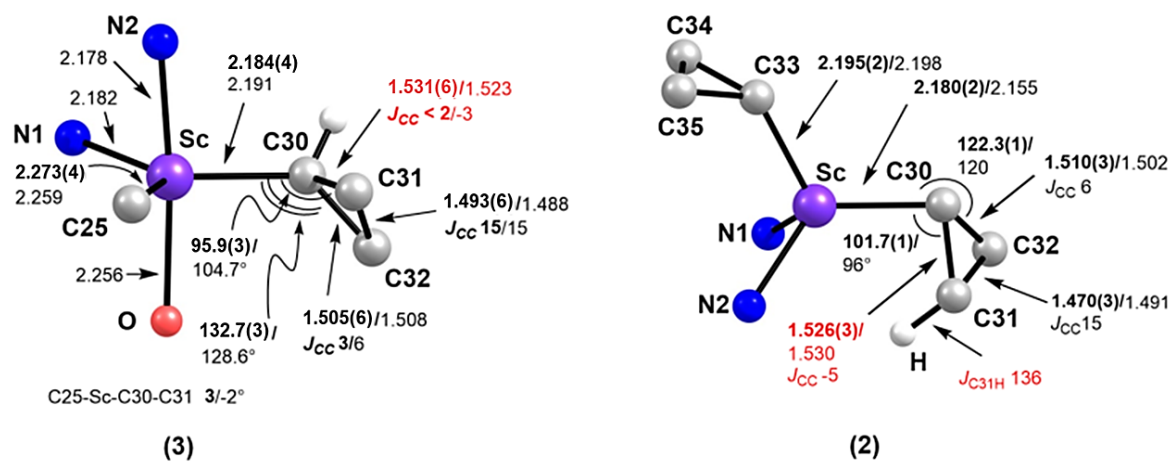


Fig. 6 Computed structures and coupling constants J for complexes **3** and **2** and comparison with experimental values when available. Only the core coordination sphere and the cyclopropyl groups are drawn for clarity. Experimental values (distance in Å, coupling constants in Hz) are boldface. Key data for agostic interactions are highlighted in red. Element color code: violet, Sc; blue, N; red, O; grey, C; off white, H.

found in the experimental section and in the Electronic Supporting Information. The results for complex **3** are summarized in Fig. 6 where it is seen that a remarkable agreement with the structural and spectroscopic data is reached, the Sc-C $_{\alpha}$ -C $_{\beta}$ angles as well as the dihedral angle C25-Sc-C30-C31, *ie* the conformation of the cyclopropyl ring, are correctly modelled. Considering the C-C bond lengths within the cyclopropyl ring, a small but clear elongation of C30-C31 bond is seen which was not statistically meaningful experimentally. As to the coupling constants, not only the trend but also the absolute values are faithfully computed (IGLOOII basis set) including J_{C-H} as references and J_{C-C} . This approach has been validated in similar studies.⁹⁻¹² For the latter, the computed values of 6 and 15 Hz are in very good agreement with the experimental values of 3 and 15 Hz found for the coupling constants involving C30-C32 and C31-C32, respectively. Therefore, the computed value of -3 Hz is consistent with our assignment of $J_{C30-C31} < 2$ Hz. The computational results together with the experimental data are consistent with the presence of an α -C-C agostic interaction in complex **3**.^{5,6,9} The results of similar calculations for complex **2** are summarized in Fig. 6 as well. The geometrical parameters are again very well reproduced. The C30

based cyclopropyl group is clearly distorted as compared to the one based on C33 which remains regular. The C30-C31 bond (1.53 Å) is indeed longer than the other C $_{\alpha}$ -C $_{\beta}$ bond (C30-C32 (1.50 Å)). The associated J_{C-C} , unavailable experimentally, are -5 and 6 Hz, respectively. The elongated C30-C31 bond associated with the reduced J_{C-C} are consistent with the presence of an Q-C-C agostic interaction in complex **2**. Examination of $J_{\beta C-H}$ values indicates that for the β -C-H pointing towards the scandium atom, a value of 136 Hz is computed. This value is somewhat reduced with respect to the other $J_{\beta C-H}$ which are in the narrow, normal range of 147-151 Hz. In complex **2**, an α -C-C agostic interaction is accompanied by a β -C-H agostic interaction. In order to probe the nature of these distortions, we carried out a Natural Bond Orbital (NBO)²⁶ study of the electronic structure of complex **2**. The NBO analysis shows two significant interactions at the second order perturbation theory involving (i) the σ -orbital of a β -C-H bond on C31 with the empty antibonding Sc-C33 with strong d character of 17 kJ/mol, and (ii) the σ -C30-C31 with d-orbitals of the scandium atom of 33 kJ/mol.[‡] These interactions are also nicely pictured in NLMOs which reveal participation of scandium d-orbitals in the C-H (*ca* 1.0 %) and C-C (*ca* 1,3 %) based NLMO, respectively (Fig. 7).

Although the absolute values might be questioned, interactions of similar magnitude have been observed in zirconium²⁰ and yttrium¹² cyclopropyl complexes. The involvement of both C-C and C-H bonds in the interaction with the rare-earth metal has been observed previously in the bimetallic complex $[(C_5Me_5)_2Y(\eta^2-C-C_3H_5)_2Li(thf)]$ albeit with different weights.¹² It reinforces the view that there is a continuum between pure β -C-H and α -C-C agostic structures with both types of interactions complementing each other depending on the metals,²⁷ the type of ligands, electron count, coordination number and geometry. The significant involvement of the C-C orbital is a distinctive property of the cyclopropyl group.

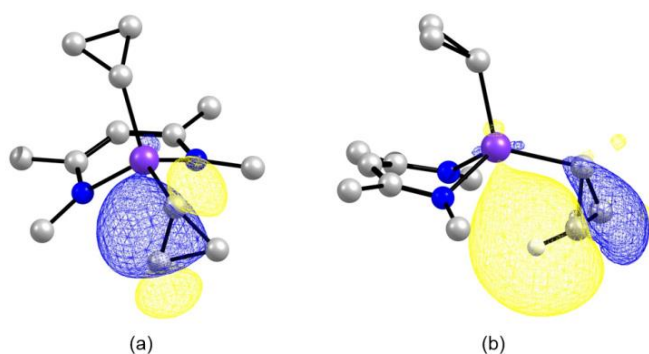


Fig. 7 NLMOs describing (a) the α -C-C interaction, (b) the α -C-H interaction in complex **2**.

Conclusions

Discrete electron deficient scandium cyclopropyl complexes have been synthesized and fully characterized for the first time. They show distortions of their coordination sphere in the solid state. In one case, solution NMR studies allow the direct measurement of the reduced J_{C-C} coupling constant. Together with DFT modelling, α -C-C agostic interactions possibly accompanied by β -C-H agostic interactions have been established. They reinforce the view that a continuum of stabilizing secondary interactions exists in the strongly electron deficient species. For the thermolysis of scandium biscyclopropyl complex, the cyclopropyl ligand prefers to abstract a

proton from the isopropyl group of β -diketiminato ligand rather than from the other cyclopropyl ligand in the complex.

Experimental

General methods

All operations were carried out under an atmosphere of argon using Schlenk techniques or in nitrogen or argon filled gloveboxes. Toluene, THF, hexane, THF- d_8 and C_6D_6 were dried over Na/K alloy, transferred under vacuum, and stored in the gloveboxes. Scandium dichloride $[LSc(\mu-Cl)Cl]_2$ (L = $[MeC(NDIPP)CHC(Me)(NDIPP)]^-$, DIPP = 2,6- $(iPr)_2C_6H_3$),¹⁴ cyclopropyl lithium,¹⁵ ethyl 2,2,3,3-tetradeuteriocyclopropanecarboxylate¹⁸ and 1-monodeuteriocyclopropanecarboxylic acid²⁵ were prepared as reported. 1H , 2H and ^{13}C NMR spectra were recorded on a Bruker AV III 400 spectrometer, a Varian MR400 spectrometer or an Agilent MR400 spectrometer. Variable-temperature NMR spectra, 1H - 1H EXSY and NOESY spectra were acquired on a Bruker NEO 600 spectrometer. INADEQUATE experiments were performed on a Bruker NEO 500 spectrometer equipped with a BBO cryoprobe. All chemical shifts were reported in δ units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and 2H NMR was referred to $CDCl_3$ in chloroform, C_6D_6 in benzene and THF- d_8 in THF, respectively. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry.

Synthesis

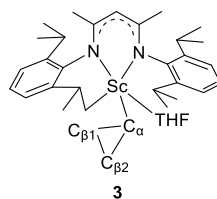
1: A solution of $[LSc(\mu-Cl)Cl]_2$ (100 mg, 0.094 mmol) in 8 mL toluene was added by a slurry of 28.4 mg cyclopropyl lithium · lithium bromide (cyclopropyl lithium: 28.5% by weight, 0.17 mmol) in 3 mL toluene at -35 °C under stirring, and then the reaction mixture was gradually warmed to room temperature. After stirring at room temperature for 4 h, the precipitate was removed by centrifugation. The volatiles of the solution were removed under vacuum to give a yellow solid. The solid was washed with hexane (2 mL \times 3) and

toluene (2 mL), and dried under vacuum to give **1** as a pale yellow solid (35 mg, 38% yield). Due to the poor solubility of **1** in C₆D₆, its ¹H and ¹³C{¹H} NMR spectra were recorded in THF-*d*₈. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ (ppm) 7.20 (m, 6H, ArH), 5.39 (s, 1H, MeC(N)CH), 3.39 (sept, 4H, ArCHMe₂), 1.82 (s, 6H, MeC(N)), 1.30 (d, ³J_{H-H} = 6.8 Hz, 12H, ArCHMe₂), 1.19 (d, ³J_{H-H} = 6.6 Hz, 12H, ArCHMe₂), 0.48 (d, ³J_{H-H} = 8.1 Hz, 2H, C_βH₂), 0.38 (d, ³J_{H-H} = 10.5 Hz, 2H, C_βH'₂), -0.45 (tt, ³J_{H-H} = 10.5, 8.1 Hz, 1H, C_αH). ¹³C{¹H} NMR (100 MHz, THF-*d*₈, 25 °C): δ (ppm) 169.1 (MeC(N)CH), 147.5, 144.4 (*i*-ArC and *o*-ArC), 127.2, 125.3 (*p*-ArC and *m*-ArC), 99.1 (MeC(N)CH), 33.2 (br, C_αH), 29.5 (ArCHMe₂), 26.0, 25.7 (MeC(N) and ArCHMe₂), 9.4 (C_βH₂). Anal. Calcd (%) for C₃₂H₄₆ClN₂Sc: C, 71.29; H, 8.60; N, 5.20. Found: C, 70.53; H, 8.12; N, 5.03.

2: A solution of [LSc(μ-Cl)Cl]₂ (500 mg, 0.47 mmol) in 10 mL toluene was added by a slurry of 284 mg cyclopropyl lithium · lithium bromide (cyclopropyl lithium: 28.5% by weight, 1.69 mmol) in 5 mL toluene at room temperature under stirring. After stirring at room temperature for 1.5 h, the precipitate was removed by centrifugation. The volatiles of the solution were removed under vacuum to give a yellow solid. This solid was extracted with 2 mL hexane, the extract was stored at -35 °C to give **2** as yellow needle crystals (365 mg, 80% yield). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) 7.15 (m, 6H, ArH), 4.91 (s, 1H, MeC(N)CH), 3.43 (sept, 4H, ArCHMe₂), 1.56 (s, 6H, MeC(N)), 1.44 (d, ³J_{H-H} = 6.8 Hz, 12H, ArCHMe₂), 1.19 (d, ³J_{H-H} = 6.8 Hz, 12H, ArCHMe₂), 0.61 (d, ³J_{H-H} = 10.7 Hz, 2H, C_βH₂), 0.41 (d, ³J_{H-H} = 8.2 Hz, 2H, C_βH'₂), -0.06 (tt, ³J_{H-H} = 10.3, 8.2 Hz, 1H, C_αH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 168.0 (MeC(N)CH), 143.6, 143.0 (*i*-ArC and *o*-ArC), 127.3, 124.9 (*p*-ArC and *m*-ArC), 94.9 (MeC(N)CH), 30.8 (br, C_αH), 29.5 (ArCHMe₂), 26.1, 25.1, 24.6 (ArCHMe₂ and MeC(N)), 7.4 (C_βH₂). ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 30.8 (br, C_αH, ¹J_{C-H} was not observed due to the quadrupolar relaxation), 7.4 (¹J_{C-H} = 159 Hz, C_βH₂). Anal. Calcd (%) for C₃₅H₅₁N₂Sc: C, 77.17; H, 9.44; N, 5.14. Found: C, 76.75; H, 9.01; N, 5.09.

3: Complex **2** (500 mg, 0.92 mmol) in a mixed solvent of hexane (10 mL) and THF (200 mg) was heated at 65 °C

for 24 h. After cooled to room temperature, the volatiles of the reaction solution were removed under vacuum. The residue was washed with hexane (1 mL × 3), and dried under vacuum to give **3** as a yellow solid (360 mg, 78% yield).



¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) 7.42, 7.31 and 7.03 (m, 6H, ArH), 5.20 (s, 1H, MeC(N)CH), 3.58, 3.43 and 3.11 (m, 3H, ArCHMe₂, overlapped with THF-H signals), 3.25 (m, 1H, Sc-CH₂CH), 1.87 and 1.68 (s, 6H, MeC(N)), 1.62 (d, 3H, Sc-CH₂CHCMe) 1.48, 1.39, 1.30, 1.10 and 1.00 (d, 18H, ArCHMe₂, overlapped with THF-H signals), 0.59 and 0.37 (m, 2H, Sc-CH₂CHAr), 0.55 and 0.19 (m, 2H, C_{β2}H₂), 0.13 and -0.16 (m, 2H, C_{β1}H₂), -0.48 (m, 1H, C_αH). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 165.9, 165.8 (MeC(N)CH), 147.6, 145.8, 145.5, 144.4, 144.3, 143.0 (*i*-ArC and *o*-ArC), 126.7, 126.3, 124.9, 124.7, 124.2, 122.4 (*p*-ArC and *m*-ArC), 98.3 (MeC(N)CH), 71.0 (THF-C), 59.6 (br, Sc-CH₂CH), 39.9, 29.3, 28.9, 28.8 (ArCHMe₂ and Sc-CH₂CH), 29.0 (br, C_αH), 26.7~23.9 (ArCHMe₂ and Sc-CH₂CHCMe), 8.7 (C_{β2}H₂), 5.5 (C_{β1}H₂). ¹³C NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) 29.0 (br, C_αH, ¹J_{C-H} was not observed due to quadrupole relaxation), 8.7 (¹J_{C-H} = 155 Hz, C_{β2}H₂), 5.5 (¹J_{C-H} = 158 Hz, C_{β1}H₂). Anal. Calcd (%) for C₃₆H₅₄N₂Osc: C, 75.10; H, 9.45; N, 4.87. Found: C, 75.08; H, 9.38; N, 5.03.

2,2,3,3-Tetradeuteriocyclopropanecarboxylic acid:

Ethyl 2,2,3,3-tetradeuteriocyclopropanecarboxylate (2.60 g, 22 mmol) in 10 mL MeOH was added to a NaOH aqueous solution (3.52 g NaOH (88 mmol) in 10 mL H₂O) at room temperature under stirring. After stirring under reflux for 4 h, the reaction mixture was cooled to room temperature and MeOH was removed under vacuum. The reaction mixture was cooled to 0 °C, and was carefully brought to pH ≈ 6 by adding a 1.0 M HCl solution. The mixture was extracted with ethyl acetate 50 mL × 3, the combined organic extracts were washed with 50 mL brine, dried over anhydrous sodium

sulfate and distilled under reduced pressure to give 2,2,3,3-tetradeuteriocyclopropanecarboxylic acid (b.p. 76 °C, 15 mmHg) as a colorless liquid (1.31 g, 66% yield). ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ (ppm) 11.96 (br, 1H, COOH), 1.58 (s, 1H, C_αH). ^2H NMR (60 MHz, CHCl_3 , 25 °C): δ (ppm) 1.03, 0.90 (s, C_βD_2).

2,2,3,3-Tetradeuteriocyclopropyl lithium: To a vigorously stirring suspension of HgO (1.56 g, 7.20 mmol) in 1,1,2,2-tetrachloroethane (10 mL) was added dropwise a mixture of 2,2,3,3-tetradeuteriocyclopropanecarboxylic acid (1.30 g, 14.4 mmol) and bromine (2.31 g, 14.4 mmol) in 1,1,2,2-tetrachloroethane (10 mL) over a period of 0.5 h. The reaction mixture was stirred at 35 ~ 40 °C until the evolution of carbon dioxide ceased. Stirring in the sealed flask was maintained at room temperature for another 12 h. After the precipitate was removed by centrifugation, the mixture was washed with sat. aq. $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL), and the residual aqueous phase was extracted with 5 mL benzene. The organic extracts in tetrachloroethane and benzene were combined, and washed with 10 mL brine, dried over anhydrous sodium sulfate and distilled under ambient pressure (b.p. 65 ~ 80 °C) to provide 2,2,3,3-tetradeuteriocyclopropyl bromide/benzene mixture as a colorless liquid. This mixture was added dropwise to a suspension of finely divided lithium (200 mg, 28.8 mmol) in 10 mL Et_2O at room temperature. After stirring for 12 h, the precipitate was removed by centrifugation. The volatiles of the solution were removed under vacuum, the residue was washed with toluene (3 mL \times 3) and hexane (1 mL), and dried under vacuum to provide 2,2,3,3-tetradeuteriocyclopropyllithium \cdot lithium bromide as a white solid 320 mg (2,2,3,3-tetradeuteriocyclopropyllithium: 31% by weight). The total yield of the above two steps is 13%. ^1H NMR (400 MHz, $\text{THF}-d_8$, 25 °C): δ (ppm) -2.54 (s, 1H, C_αH). ^2H NMR (60 MHz, THF, 25 °C): δ (ppm) 0.35, -0.17 (s, C_βD_2).

2-d₈: Following the procedure described for complex **2**, reaction of $[\text{LSc}(\mu\text{-Cl})\text{Cl}]_2$ (200 mg, 0.19 mmol) with 115 mg 2,2,3,3-tetradeuteriocyclopropyllithium \cdot lithium bromide (2,2,3,3-tetradeuteriocyclopropyllithium: 31% by weight, 0.68 mmol) gives **2-d₈** as a yellow solid (160

mg, 77% yield). ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ (ppm) δ 7.16 (m, 6H, ArH), 4.92 (s, 1H, MeC(N)CH), 3.45 (sept, 4H, ArCHMe₂), 1.57 (s, 6H, MeC(N)), 1.45 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, ArCHMe₂), 1.20 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, ArCHMe₂), -0.08 (s, 1H, C_αH). ^2H NMR (60 MHz, C_6H_6 , 25 °C): δ (ppm) 0.52, 0.33 (s, C_βD_2).

1-Monodeuteriocyclopropyl lithium: Following the procedure described for 2,2,3,3-tetradeuteriocyclopropyl lithium, from 1-monodeuteriocyclopropanecarboxylic acid (4.50 g, 51.7 mmol), 1.91 g 1-monodeuteriocyclopropyl lithium \cdot lithium bromide was obtained as a white solid (1-monodeuteriocyclopropyllithium: 30% by weight) in 31% yield. ^1H NMR (400 MHz, $\text{THF}-d_8$, 25 °C): δ (ppm) 0.36 (s, 2H, C_βH_2), -0.16 (s, 2H, $\text{C}_\beta\text{H}'_2$). ^2H NMR (60 MHz, THF, 25 °C): δ (ppm) -2.52 (s, C_αD).

2-d₂: Following the procedure described for complex **2**, reaction of $[\text{LSc}(\mu\text{-Cl})\text{Cl}]_2$ (500 mg, 0.470 mmol) with 290 mg 1-monodeuteriocyclopropyl lithium \cdot lithium bromide (1-monodeuteriocyclopropyllithium: 30% by weight, 1.78 mmol) gives **2-d₂** as a yellow solid (410 mg, 84% yield). ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ (ppm) δ 7.16 (m, 6H, ArH), 4.93 (s, 1H, MeC(N)CH), 3.45 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 4H, ArCHMe₂), 1.58 (s, 6H, MeC(N)), 1.45 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, ArCHMe₂), 1.20 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 12H, ArCHMe₂), 0.61 (s, 2H, C_βH_2), 0.41 (s, 2H, $\text{C}_\beta\text{H}'_2$). ^2H NMR (60 MHz, C_6H_6 , 25 °C): δ (ppm) -0.10 (s, C_αD).

X-ray Crystallography

Single crystals of **1** were grown from a toluene solution; single crystals of **2** and **3** were grown from hexane solutions. The suitable single crystals were mounted under a nitrogen atmosphere on a glass fiber, and data collection was performed at 170(2) K on a Bruker D8 Venture diffractometer with graphite-monochromated Ga K α radiation ($\lambda = 1.34139$ Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using SADABS program.²⁸ The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were included

in the structure calculation. Calculations were carried out using the SHELXL-2015 and Olex2 program.²⁹ Crystallographic data and refinement parameters are listed in Table S1 of ESI.

Computational details

Calculations were performed at the DFT level with the software Gaussian09, revision D.01.³⁰ Geometry optimizations were carried out without symmetry constraints in the gas phase using the PBE0 functional³¹ and including dispersion corrections (GD3-BJ).³² The scandium atom was described using the Stuttgart/Dresden ECP (SDD) pseudo-potential and its associated basis set³³ to which was added an f polarization function.³⁴ All other atoms were described with the def2-SVP basis set except those directly bonded to the scandium atom (N, O) and the carbon atoms of the cyclopropyl groups for which the def2-TZVP basis set was used.³⁵ The nature of the stationary points was ascertained by a vibrational analysis within the harmonic approximation (1 atm and 298 K). Minima were identified by a full set of real frequencies. Computation of the NMR coupling constants was realized with the IGLOII basis set for carbon and hydrogen atoms.³⁶ NBO calculations were carried out with NBO6 as implemented in Gaussian09.³⁷ Drawings were produced with the software Chemcraft.³⁸

Conflicts of interest

There are no conflicts to declare

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 21732007, 21890721, 21821002), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000), and the Program of Shanghai Academic Research Leader.

Notes and references

‡ As a reference, we used the NBO delocalizations of the σ -C-C orbitals in the σ^* -C-C within a cyclopropyl ring which describes the bonding in any cyclopropane

derivative. These interactions are in the range 17 – 21 kJ/mol for the present study (see ESI).

- 1 A. de Meijere, Bonding Properties of Cyclopropane and Their Chemical Consequences, *Angew. Chem. Int. Ed. Engl.*, 1979, **18**, 809–826.
- 2 K. B. Wiberg, Bent bonds in organic compounds, *Acc. Chem. Res.*, 1996, **29**, 229–234.
- 3 P. Rademacher, Photoelectron spectra of cyclopropane and cyclopropene compounds, *Chem. Rev.*, 2003, **103**, 933–976.
- 4 A. de Meijere, Introduction: Cyclopropanes and Related Rings, *Chem. Rev.*, 2003, **103**, 931–932.
- 5 M. Etienne and A. S. Weller, Intramolecular C–C agostic complexes: C–C sigma interactions by another name, *Chem. Soc. Rev.*, 2014, **43**, 242–259.
- 6 B. G. Harvey and R. D. Ernst, Transition-Metal Complexes with (C–C)→M Agostic Interactions, *Eur. J. Inorg. Chem.*, 2017, **2017**, 1205–1226.
- 7 J. Jaffart, M. Etienne, M. Reinhold, J. E. McGrady and F. Maseras, An unprecedented α -C–C agostic interaction in a cyclopropyl tris(pyrazolyl)boratoniobium complex, *Chem. Commun.*, 2003, 876–877.
- 8 J. Jaffart, M. L. Cole, M. Etienne, M. Reinhold, J. E. McGrady and F. Maseras, C–H and C–C agostic interactions in cycloalkyl tris(pyrazolyl)boratoniobium complexes, *Dalton Trans.*, 2003, 4057–4064.
- 9 C. Boulho, T. Keys, Y. Coppel, L. Vendier, M. Etienne, A. Locati, F. Bessac, F. Maseras, D. A. Pantazis and J. E. McGrady, C–C Coupling Constants, J_{CC} , Are Reliable Probes for α -C–C Agostic Structures, *Organometallics*, 2009, **28**, 940–943.
- 10 Q. Dufrois, J.-C. Daran, L. Vendier, C. Dinoi and M. Etienne, Triangles and Squares for a Unique Molecular Crystal Structure: Unsupported Two-Coordinate Lithium Cations and CC Agostic Interactions

- in Cyclopropyllithium Derivatives, *Angew. Chem. Int. Ed.*, 2018, **57**, 1786–1791.
- 11 Q. Dufrois, L. Vendier and M. Etienne, α -CC agostic structures and aggregation diversity in cyclopropyllithium derivatives, *Chem. Commun.*, 2016, **52**, 6781–6784.
- 12 Y. Escudie, C. Dinoi, O. Allen, L. Vendier and M. Etienne, An Unsymmetrical bis C–C Agostic Heterobimetallic Lithium Yttrium Complex, *Angew. Chem. Int. Ed.*, 2012, **51**, 2461–2464.
- 13 S. Tobisch, Organolanthanide-Mediated Ring-Opening Ziegler Polymerization (ROZP) of Methylene-cycloalkanes: A Theoretical Mechanistic Investigation of Alternative Mechanisms for Chain Initiation of the Samarocene-Promoted ROZP of 2-Phenyl-1-methylene-cyclopropane, *Chem. Eur. J.*, 2005, **11**, 3113–3126.
- 14 P. G. Hayes, W. E. Piers, L. W. M. Lee, L. K. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, Dialkylscandium Complexes Supported by β -Diketiminato Ligands: Synthesis, Characterization, and Thermal Stability of a New Family of Organoscandium Complexes, *Organometallics*, 2001, **20**, 2533–2544.
- 15 D. B. Denney and F. J. Gross, Preparation and some chemistry of tricyclopropylphosphine, *J. Org. Chem.*, 1967, **32**, 2445–2447.
- 16 L. K. Knight, W. E. Piers, P. Fleurat-Lessard, M. Parvez and R. McDonald, β -Diketiminato Scandium Chemistry: Synthesis, Characterization, and Thermal Behavior of Primary Amido Alkyl Derivatives, *Organometallics*, 2004, **23**, 2087–2094.
- 17 T. N. Valadez, J. R. Norton and M. C. Neary, Reaction of $Cp^*(Cl)M(Diene)$ ($M = Ti, Hf$) with Isonitriles, *J. Am. Chem. Soc.*, 2015, **137**, 10152–10155.
- 18 M. von Seebach, S. I. Kozhushkov, H. Schill, D. Frank, R. Boese, J. Benet-Buchholz, D. S. Yufit and A. de Meijere, Stereoselective Preparation of Six Diastereomeric Quatercyclopropanes from Bicyclopropylidene and Some Derivatives, *Chem. Eur. J.*, 2007, **13**, 167–177.
- 19 J. S. Meek and D. T. Osuda, BROMOCYCLOPROPANE, *Organic Synthesis*, 1963, **43**, 9.
- 20 Y. Hu, N. Romero, C. Dinoi, L. Vendier, S. Mallet-Ladeira, J. E. McGrady, A. Locati, F. Maseras and M. Etienne, β -H Abstraction/1,3-CH Bond Addition as a Mechanism for the Activation of CH Bonds at Early Transition Metal Centers, *Organometallics*, 2014, **33**, 7270–7278.
- 21 P. Oulié, C. Dinoi, C. Li, A. Sournia-Saquet, K. Jacob, L. Vendier and M. Etienne, CH Bond Activation of Unsaturated Hydrocarbons by a Niobium Methyl Cyclopropyl Precursor. Cyclopropyl Ring Opening and Alkyne Coupling Reaction, *Organometallics*, 2017, **36**, 53–63.
- 22 C. Boulho, P. Oulié, L. Vendier, M. Etienne, V. Pimienta, A. Locati, F. Bessac, F. Maseras, D. A. Pantazis and J. E. McGrady, C–H Bond Activation of Benzene by Unsaturated η^2 -Cyclopropene and η^2 -Benzynes Complexes of Niobium, *J. Am. Chem. Soc.*, 2010, **132**, 14239–14250.
- 23 C. Li, C. Dinoi, Y. Coppel and M. Etienne, CH Bond Activation of Methane by a Transient η^2 -Cyclopropene/Metallabicyclobutane Complex of Niobium, *J. Am. Chem. Soc.*, 2015, **137**, 12450–12453.
- 24 R. A. Wolf, M. J. Migliore, P. H. Fuery, P. R. Gagnier, I. C. Sabeta and R. J. Trocino, Properties of small-ring free radicals. 2. Thermal decomposition of alicyclic percarboxylates, *J. Am. Chem. Soc.*, 1978, **100**, 7967–7976.
- 25 A. I. Vogel, *A Textbook of Practical Organic Chemistry*, 5th edn, 1989, p. 859.
- 26 A. E. Reed, L. A. Curtiss and F. Weinhold, Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint, *Chem. Rev.*, 1988, **88**, 899–926.

- 27 M. Montag, I. Efremenko, Y. Diskin-Posner, Y. Ben-David, J. M. L. Martin and D. Milstein, Exclusive C–C Oxidative Addition in a Rhodium Thiophosphoryl Pincer Complex and Computational Evidence for an η^3 -C–C–H Agostic Intermediate, *Organometallics*, 2012, **31**, 505–512.
- 28 G. M. Sheldrick, *SADABS: An Empirical Absorption Correction Program for Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.
- 29 (a) G. M. Sheldrick, *SHELXS-97 and SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997 and 2008. (b) G. M. Sheldrick, *SHELXS-2014*; University of Göttingen: Göttingen, Germany, 2014. (c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.*, 2009, **42**, 339–341. (d) *SMART*, Version 5.628; Bruker AXS Inc.: Madison, WI, 2002. (e) *SAINT+*, Version 6.22a; Bruker AXS Inc.: Madison, WI, 2002. (f) *SAINT+*, Version v7.68A; Bruker AXS Inc.: Madison, WI, 2009. (g) *SHELXTL NT/2000*, Version 6.1; Bruker AXS Inc.: Madison, WI, 2002. (h) G. M. Sheldrick, Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, **71**, 3–8..
- 30 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.
- 31 C. Adamo and V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
- 32 S. Grimme, S. Ehrlich and L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
- 33 M. Dolg, U. Wedig, H. Stoll and H. Preuss, Energy-adjusted ab initio pseudopotentials for the first row transition elements, *J. Chem. Phys.*, 1987, **86**, 866–872.
- 34 A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, A set of f-polarization functions for pseudo-potential basis sets of the transition metals Sc–Cu, Y–Ag and La–Au, *Chem. Phys. Lett.*, 1993, **208**, 111–114.
- 35 F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
- 36 M. Schindler and W. Kutzelnigg, Theory of magnetic susceptibilities and NMR chemical shifts in terms of localized quantities. II. Application to some simple molecules, *J. Chem. Phys.*, 1982, **76**, 1919–1933.
- 37 NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.
- 38 Chemcraft - graphical software for visualization of quantum chemistry computations. <https://www.chemcraftprog.com>.