α-C–C agostic interactions and C–H bond activation in scandium cyclopropyl complexes†

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This paper addresses the problem of the observation of the so-called C–C agostic interactions in cyclopropyl complexes of scandium. Three new cyclopropyl complexes of scandium based on the 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 a markedly reduced $J_{\text{C-C}}$ 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 the scandium bicyclopropyl complex was investigated by isotopic labelling experiments, which indicated a direct proton abstraction of the isopropyl group in the β-diketiminato ligand by a cyclopropyl group.

Introduction

The poor overlap of carbon-based orbitals within a strained cyclopropyl ring increases their energy and makes them spatially exposed, imparting them with unique chemical properties.1–4 One consequence in organometallic complexes [M]–[c-C₃H₅] is that the so-called α-C–C agostic distortions or interactions – formally three center-two electron bonds – are preferred to the much more common C–H and C–C interactions, whether they be with the α- or β-C–H bonds.5,6 This has been observed especially in unsaturated early transition5,7 and alkaline10,11 metal complexes. For rare-earth metals, the bimetallic complex [[C₃Me₂]₂Y[μ-c-C₃H₅]₂Li(thf)] exhibits C–C agostic interactions with both lithium and yttrium centers, and the interaction with lithium is more electrostatic in nature while that with yttrium is more covalent.12 This represents 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 indicates 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 privileged structures to observe C–C agostic interactions.

Results and discussion

Synthesis and structural aspects

Scandium dichloride [LSc(μ-Cl)]₂ (L = [MeC(NDIPP)CHC(Me)₂NDIPP]²⁻, DIPP = 2,6-(iPr)₂C₆H₃) and cyclopropyl lithium were prepared as reported.14,15 The reactions of [LSc(μ-Cl)]₂ with cyclopropyl lithium in a 1 : 2 or 1 : 4 molar ratio in toluene provided the scandium cyclopropyl chloride complex [LSc(μ-Cl)[c-C₃H₅]₂] (1) and the bicyclopropyl complex [LSc(c-C₃H₅)₂] (2) in 38% and 80% yields, respectively (Scheme 1). Both complexes were characterized by NMR spectroscopy (¹H and ¹³C[¹H]), elemental analysis, and single-crystal X-ray crystallography. The ¹H NMR spectra in C₆D₆ indicated a time-averaged Cᵥ symmetry of the cyclopropyl group in 1 and 2 at room temperature. The CᵥH of the cyclopropyl group in 1 resonates as a triplet of triplet at δ = −0.45 ppm (¹JH-H = 10.5, 8.1 Hz), and
the corresponding CαH in 2 appears to be shifted slightly downfield (δ = −0.06 ppm, JH–H = 10.3, 8.2 Hz). The chemical shifts of ScCH3 in the scandium methyl chloride complex [LSc(μ-Cl)Me2] and the dimethyl complex [LScMe2(THF)] are 0.29 and −0.15 ppm, respectively.14,16 All the CβH 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 C2v symmetry of the cyclopropyl group in the complexes, with only one CβH signal at δ = 9.4 ppm for 1 and δ = 7.4 ppm for 2. Due to quadrupolar relaxation, the Cα 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.

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 the cyclopropyl ligand (Fig. 1). The 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 lengths in [LScMe2(THF)] (2.210(9) and 2.245(9) Å).14 The distances from the scandium ion to the two Cβ atoms of the cyclopropyl ligand, 3.354 and 3.364 Å, are long, indicating no interaction between the scandium ion and the Cβ atoms. The two Sc–Cα–Cβ 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–Cα 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⋯Cβ 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–Cα–Cβ angles, with the Sc–C30–C31 (101.7(1)°) angle being smaller than other Sc–Cα–Cβ 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 C30–32 (1.510(3) Å) which is similar to Cα–Cβ in other cyclopropyl groups [C33–C34 = 1.516(2) Å and C33–C35 = 1.522(2) Å].

As observed with other dialkyl complexes of scandium,14 complex 2 slowly eliminates cyclopropane at room temperature (δ = 0.14 ppm in the 1H NMR spectrum) to give a complicated mixture in C6D6 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 the 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 di-anionic ligand (L–H) as shown in Scheme 2. Complex 3 was characterized by NMR spectroscopy (1H and 13C{1H}), elemental analysis and single-crystal X-ray crystallography. The latter

Scheme 1 Synthesis of 1 and 2.

Scheme 2 Thermolysis of 2 into 3.
revealed that 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 [N2-Sc-O = 169.94 (11)°]. The distances from the scandium ion to the isopropyl carbon atom and the 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⋯Sc distance (3.391 Å) is not statistically stretched as compared to C30–C32 (1.531(6) Å).

The unusual distortion of the cyclopropyl ring prompted a detailed NMR investigation of 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 13C NMR spectra (303 K) and the use of a sensitivity boosted cryogenic probe, the inherently challenging 1D INADEQUATE genetic probe, the well-resolved resonance of 1H NMR data; red, 13C NMR data. The 1H NMR spectrum showed two 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 13C{1H} NMR spectrum showed two signals for the two Cβ atoms of the cyclopropyl ring, C31 at 5.5 ppm and C32 at 8.7 ppm when C6D6 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 the above protons with the guidance of the 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 the coherent signal of C25H–C31H than that of C25H′–C32H′ (Fig. 4), indicating that the cyclopropyl ring in 3 presents a distorted configuration with the C30–C31 bond approaching the scandium ion in the solution phase. Subsequently, 1H–1H EXSY and variable temperature 1H NMR spectra (303–343 K) were recorded, and no proton exchange or rotation of the cyclopropyl ring in 3 was observed even at 343 K in C6D6, illustrating the relatively stable geometry conformation of the cyclopropyl ring in 3.

The JCC-H values were then obtained from a gated 13C NMR spectrum. The C31 and C32 atoms resonate as triplets with JCC-H values of 158 and 155 Hz, respectively, which are similar to the JCC-H value of cyclopropane (161 Hz) and indicate the absence of an agostic interaction between the scandium ion and the corresponding β-C–H bonds of the cyclopropyl ring. Due to quadrupolar relaxation, JCC-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 the JCC-C value is the key evidence for the presence of such agostic interaction.9,12,17 Fortunately, owing to the well-resolved resonance of Cβ signals, the good solubility of 3 (ca. 0.4 M in C6D6), and the use of a sensitivity boosted cryogenic probe, the inherently challenging 1D INADEQUATE spectra of high quality were successfully acquired and the JCC-C values of Cβ signals were obtained. The C32 signal displays two doublets with JCC-C values of 14.8 and 3.2 Hz, while the C31 signal appears as a doublet with a JCC-C value of 14.8 Hz.
Therefore, the $^1J_{C31-C32}$ value is 14.8 Hz and the $^1J_{C30-C32}$ value is 3.2 Hz. This small value is linked to the low electronegativity of scandium. The observation of the C31 signal as a single doublet instead of two can be rationalized in two ways: (a) the $^1J_{C31-C30}$ value is the same or very close to the $^1J_{C31-C32}$ value, so the peaks overlap; and (b) the $^1J_{C31-C30}$ value is very small and indeed less than the line width of the experiment (<2.0 Hz) and 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 a 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 (see the Computational studies section below).

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 isopropyl group of L; and (3) path C: an $\alpha$-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 2-4d8 which contains two 2,2,3,3-tetradeutero-cyclopropanecarboxylate ligands and study its thermolysis. It can be reasonably envisioned that if complex 3 is formed via path A, the cyclopropenyl ligand in the $\eta^2$-cyclopropene intermediate would abstract a proton from the isopropyl group to generate complex 3-4d3, which would display the cyclopropyl $\beta$-H signal in the $^1$H NMR spectrum; in contrast, if complex 3 is formed via path B or C, the thermolysis of 2-4d8 would give complex 3-4d4, in which no signal of the $\beta$-H of the cyclopropyl would be observed in the $^1$H NMR spectrum.

Tetradeuteriocyclopropyl lithium was firstly synthesized, as shown in Scheme 4a. Ethyl 2,2,3,3-tetradeuteriocyclopropanecarboxylate was prepared using THF-4d8 as a starting material in three steps according to the procedures reported by de Meijere and co-workers. 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-tetradeca-tioctropropylcarboxylic acid (66% yield). With tetradeuteroiyclopropanecarboxylic acid in hand, 2,2,3,3-tetradeca-tioctropropyl bromide was synthesized using the Cristol–Firth reaction. After the completion of the reaction, excess bromine was removed by treatment with sodium thiosulfate, and benzene was added. The addition of benzene helps in the distillation of 2,2,3,3-tetradeca-tioctropropyl bromide on a small scale. The distilled tetradeca-tioctropropyl bromide/benzene mixture was reacted with a suspension of finely divided lithium in diethylether to provide the desired 2,2,3,3-tetradeca-tioctropropyl 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-tetradeca-tioctropropyl lithium in a 1:4 molar ratio in toluene provided deuterated complex 2-d_8 as a yellow solid in 77% isolated yield. The 1H NMR spectrum of 2-d_8 in C_6D_6 resembles that of 2, except the absence of resonances at 0.61 and 0.41 ppm, indicating the deuteration on C_β atoms. In the 2H NMR spectrum of 2-d_8 in C_6D_6, two resonances were observed at 0.52 and 0.31 ppm for the C_dD of the tetradeca-tioctropropyl ligands. The thermolysis of 2-d_8 in THF-d_8/C_6D_6 at 65 °C was investigated, which clearly indicated the formation of 3-d_4 (Scheme 5a). The 1H NMR spectral monitoring showed the appearance of the C_dH signal at ~0.61 ppm and the absence of the C_dD signal (Fig. S20 in the ESL†). In the 2H NMR spectrum of the product in C_6D_6, the deuterium resonances were observed in the region of ~0.3–0.5 ppm (Fig. S21 in the ESL†). Therefore, complex 3 is not formed via path A, which is different from the reported cyclopropane elimination mechanism for zirconium and niobium cyclopropyl complexes. For example, in the bis cyclopropyl complex [CpZr(c-C_3H_4)]_2, one of the cyclopropyl ligands abstracts a β-proton from other cyclopropyl ligands to release cyclopropane and generate the zirconium η^3-cyclopropyl species [Cp,Zr(η^3-C_3H_4)].

To discriminate between path B and path C, we need to synthesize complex 2-d_2 which contains two 1-monodeuteriocyclopropyl ligands and study its thermolysis. If complex 3 is formed via path B, the thermolysis of 2-d_2 would give complex 3-d_4, in which no signal of the C_dH of the cyclopropyl would be observed in the 1H NMR spectrum, and the 2H NMR spectrum of the complex would display a C_dD signal; if complex 3 is formed via path C, the thermolysis of 2-d_2 would give complex 3-d_2, in which no C_dD signal of the cyclopropyl would be observed in the 2H NMR spectrum, and the 1H NMR spectrum of the complex would show a C_dH signal. Methyl cyclopropyl ketone-α,α,α,α',α',α'-d_4 with a deuterium isotopic content of 90% was prepared by proton exchange of methyl cyclopropyl ketone with 40 wt% NaOD in D_2O; and this ketone undergoes a halofor reaction 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 a similar approach to that of 2,2,3,3-tetradeca-tioctropropyl lithium (Scheme 4b), and was then subjected to salt metathesis with 0.25 equiv. of [LSc(μ-Cl)Cl]_2. The reaction produced complex 2-d_2 as a yellow solid in 84% yield. The 1H NMR spectrum of 2-d_2 in C_6D_6 shows ~90% deuteration on α-C, and no 3J_H-H spin–spin splitting was observed for C_dH (0.61 and 0.41 ppm). In the 2H NMR spectrum of 2-d_2 in C_6D_6, one resonance was observed at ~0.10 ppm for the C_dD of the 1-monodeuteriocyclopropyl ligands. The 1H and 2H NMR spectral monitoring of the thermolysis of 2-d_2 in THF-d_8/C_6D_6 showed the transformation of 2-d_2 into 3-d_4 (Scheme 5b). In the 1H spectrum (Fig. S26 in the ESL†), four C_dH signals were clearly observed at 0.41, 0.10, ~0.04 and ~0.33 ppm, while the C_dH signal is very weak in line with a deuterium isotopic content of 90%. The 2H NMR spectra showed two signals, one for the C_dD (δ = ~0.74 ppm) in 3-d_4, and the other for CHD (δ = 0.06 ppm) in eliminated monodeuteriocyclopropane (Fig. S27 in the ESL†). Therefore, complex 3 is formed via direct proton abstraction of the isopropyl group in L by a cyclopropyl group (path B).

Computational studies

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. The details of basis sets can be found in the Experimental section and in the ESL†. The results for complex 3 are shown in Fig. 6, where it is seen that a remarkable agreement with the structural and spectroscopic data is reached, the Sc–C_α–C_β angles and the dihedral angle C_25–Sc–C_30–C_31, i.e. 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 the C_30–C_31 bond relative to the C_30–C_32 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 refer-
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

Fig. 6 Computed structures and coupling constants $J$ of complexes 3 and 2 and their 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; and off white, H.

Fig. 7 NLMOs describing the (a) $\alpha$-C–C interaction and the (b) $\alpha$-C–H interaction in complex 2.

\[ J_{CC} < 2/3 \]

As a reference, we used the NBO delocalizations of the $\sigma$-C–C orbitals in the $\sigma^*\text{-C-C}$ orbitals within a cyclopropyl ring which describes the bonding in any cyclopropane derivative. These interactions are in the range of 17–21 kJ mol$^{-1}$ for the present study (see the ESI$^\dagger$).

\[ J_{CC} < 2/3 \]

These interactions are also nicely pictured in NLMOs which reveal the participation of scandium d-orbitals in the C–H (ca. 1.0%) and C–C (ca. 1.3%) based NLMOs, respectively (Fig. 7). Although the absolute values might be questioned, interactions of similar magnitude have been observed in zirconium$^{20}$ and yttrium$^{12}$ 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 $[[\text{C}_5\text{Me}_5\text{Y}][\text{C}_3\text{H}_3\text{Li}(\text{thf})]]$ albeit with different weights.$^{12}$ This reinforces the view that there is a continuum between pure $\beta$-C–H and $\alpha$-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.

\[ J_{CC} < 2/3 \]

\[ J_{CC} < 2/3 \]

\[ J_{CC} < 2/3 \]

\[ J_{CC} < 2/3 \]
measured. The reduced J\textsubscript{C-C} coupling constant. Together with DFT modelling, α-C-C agostic interactions possibly accompanied by β-C-H agostic interactions have been established. These reinforce the view that a continuum of stabilizing secondary interactions exists in the strongly electron deficient species. For the thermolysis of the scandium biscyclopropyl complex, the cyclopropyl ligand prefers to abstract a proton from the isopropyl group of the β-diketiminato ligand rather than from other cyclopropyl ligands 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-\textit{d}_8 and C\textsubscript{6}D\textsubscript{6} were dried over Na/K alloy, transferred under vacuum, and stored in the gloveboxes. Scandium dichloride [L\textsubscript{Sc}(Cl)]\textsubscript{2} (L = [MeC(NDIPP)\textsubscript{2}]Cl\textsubscript{2}) was prepared as reported. \textit{H}, \textit{2H} and \textit{13C} NMR spectra were recorded in C\textsubscript{6}D\textsubscript{6}, its \textit{1H} and \textit{13C}{\textit{1H}} NMR spectra were recorded in THF with DFT modelling, α and β-C-C coupling constant. Together with DFT modelling, α-C-C agostic interactions possibly accompanied by β-C-H agostic interactions have been established. These reinforce the view that a continuum of stabilizing secondary interactions exists in the strongly electron deficient species. For the thermolysis of the scandium biscyclopropyl complex, the cyclopropyl ligand prefers to abstract a proton from the isopropyl group of the β-diketiminato ligand rather than from other cyclopropyl ligands in the complex.

#### Synthesis

1. A solution of [L\textsubscript{Sc}(μ-Cl)]\textsubscript{2} (100 mg, 0.094 mmol) in 8 mL of toluene was added by a slurry of 28.4 mg of cyclopropyl lithium-lithium bromide (cyclopropyl lithium: 28.5% by weight, 1.69 mmol) into 5 mL of toluene at room temperature under stirring. After stirring at room temperature for 1.5 h, the precipitate was removed by centrifugation. The volatile of the solution were removed under vacuum. The residue was washed with hexane (1 mL x 3), and dried under vacuum to 365 mg, 80% yield. \textit{1H} NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C): \textit{δ} (ppm) 7.15 (m, 6H, Ar\textsubscript{H}), 4.91 (s, 1H, MeC(N)CH\textsubscript{2}), 3.43 (sept, 4H, ArCHMe\textsubscript{2}), 1.56 (s, 6H, Me(CN)), 1.44 (d, \textit{J}_{\textit{H-H}} = 6.8 Hz, 12H, ArCHMe\textsubscript{2}), 1.19 (d, \textit{J}_{\textit{H-H}} = 6.8 Hz, 12H, ArCHMe\textsubscript{2}), 0.61 (d, \textit{J}_{\textit{H-H}} = 10.7 Hz, 2H, C\textsubscript{6}H\textsubscript{2}), 0.41 (d, \textit{J}\textsubscript{\textit{H-H}} = 8.2 Hz, 2H, C\textsubscript{6}H\textsubscript{2}), −0.06 (tt, \textit{J}_{\textit{H-H}} = 10.3, 8.2 Hz, 1H, C\textsubscript{6}H), \textit{13C{\textit{1H}}} NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C): \textit{δ} (ppm) 168.0 (MeC(N)CH\textsubscript{2}), 143.6, 143.0 (i-ArC and o-ArC), 127.3, 124.9 (p-ArC and m-ArC), 94.9 (Me(CN)CH\textsubscript{2}), 30.8 (br, C\textsubscript{6}H), 29.5 (ArCHMe\textsubscript{2}), 26.1, 25.1, 24.6 (ArCHMe\textsubscript{2} and Me(CN)), 7.4 (C\textsubscript{6}H\textsubscript{2}). \textit{13C NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C): \textit{δ} (ppm) 30.8 (br, C\textsubscript{6}H), \textit{J}_{\textit{C-H}} was not observed due to quadrupolar relaxation), 7.4 (\textit{J}_{\textit{C-H}} = 159 Hz, C\textsubscript{6}H\textsubscript{2}). Anal. calcd (%) for C\textsubscript{35}H\textsubscript{51}N\textsubscript{2}Sc: C, 77.17; H, 9.44; N, 5.14. Found: C, 76.75; H, 9.01; N, 5.09.

2. A solution of [L\textsubscript{Sc}(μ-Cl)]\textsubscript{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 of toluene at room temperature under stirring. After stirring at room temperature for 1.5 h, the precipitate was removed by centrifugation. The volatile of the solution were removed under vacuum to give a yellow solid. This solid was extracted with 2 mL of hexane, and the extract was stored at −35 °C to give 2 as yellow needle crystals (365 mg, 80% yield). \textit{1H} NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C): \textit{δ} (ppm) 7.15 (m, 6H, Ar\textsubscript{H}), 4.91 (s, 1H, MeC(N)CH\textsubscript{2}), 1.67 (s, 6H, MeC(N)), 1.48 (d, \textit{J}_{\textit{H-H}} = 39.1 Hz, 12H, ArCHMe\textsubscript{2}), 1.11 (d, \textit{J}_{\textit{H-H}} = 39.1 Hz, 12H, ArCHMe\textsubscript{2}), 0.51 (d, \textit{J}_{\textit{H-H}} = 8.2 Hz, 2H, C\textsubscript{6}H\textsubscript{2}), −0.06 (tt, \textit{J}_{\textit{H-H}} = 10.3, 8.2 Hz, 1H, C\textsubscript{6}H), \textit{13C{\textit{1H}}} NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C): \textit{δ} (ppm) 166.0 (MeC(N)CH\textsubscript{2}), 143.6, 143.0 (i-ArC and o-ArC), 127.3, 124.9 (p-ArC and m-ArC), 94.9 (Me(CN)CH\textsubscript{2}), 30.8 (br, C\textsubscript{6}H), 29.5 (ArCHMe\textsubscript{2}), 26.1, 25.1, 24.6 (ArCHMe\textsubscript{2} and Me(CN)), 7.4 (C\textsubscript{6}H\textsubscript{2}). \textit{13C NMR (100 MHz, C\textsubscript{6}D\textsubscript{6}, 25 °C): \textit{δ} (ppm) 30.8 (br, C\textsubscript{6}H), \textit{J}_{\textit{C-H}} was not observed due to quadrupolar relaxation), 7.4 (\textit{J}_{\textit{C-H}} = 159 Hz, C\textsubscript{6}H\textsubscript{2}). Anal. calcd (%) for C\textsubscript{35}H\textsubscript{51}N\textsubscript{2}Sc: 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 being cooled to room temperature, the volatiles of the reaction solution were removed under vacuum. The residue was washed with hexane (1 mL x 3), and dried under vacuum to give 3 as a yellow solid (360 mg, 78% yield).
due to quadrupole relaxation), 8.7 (J_C-H = 155 Hz, C_β2H_3); 5.5 (J_C-H = 158 Hz, C_βH). Anal. calcd (%) for C_{36}H_{54}N_2OSc: C, 75.10; H, 9.45; N, 4.87. Found. C, 75.08; H, 9.38; N, 5.03.

2,2,3,3-Tetradecuteroicyclopropanocarbonylic acid. Ethyl 2,2,3,3-tetradecuteroicyclopropanocarbonylate (2.60 g, 22 mmol) in 10 mL of MeOH was added to a NaOH aqueous solution (3.52 g of NaOH (88 mmol) in 10 mL of H_2O) 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 its pH was carefully adjusted to 8 by adding a 1.0 M HCl solution. The mixture was extracted with ethyl acetate (50 mL × 3), and the combined organic extracts were washed with 50 mL of brine, dried over anhydrous sodium sulfate and distilled under reduced pressure to give 2,2,3,3-tetradecuteroicyclopropanocarbonylic 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, COO-D), 8.7 (1H, C_H), 3.45 (sept, 4H, ArC_H), 1.58 (s, 1H, C_H). 2H NMR (60 MHz, CHCl_3, 25 °C): δ (ppm) 1.03, 0.90 (s, C_H). 2H NMR (400 MHz, C_6D_6, 25 °C): δ (ppm) 0.52, 0.33 (s, C_H). 13C NMR (100 MHz, CDCl_3, 25 °C): δ (ppm) −25.52 (s, C_H). The total yield of the reaction of [LSc(μ-Cl)]_2 (200 mg, 0.19 mmol) with 115 mg of 2,2,3,3-tetradecuteroicyclopropyl lithium: 31% by weight, (1-2H, 2H, C_H). Anal. calcd (%) for C_{36}H_{54}N_2OSc: C, 75.10; H, 9.45; N, 4.87. Found. C, 75.08; H, 9.38; N, 5.03.

2,2,3,3-Tetradecuteroicyclopropyl 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-tetradecuteroicyclopropanocarbonylic 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. Na_2S_2O_3 and benzene were combined, and washed with 10 mL of brine, dried over anhydrous sodium sulfate and distilled under ambient pressure (b.p. 65–80 °C) to provide the 2,2,3,3-tetradecuteroicyclopropyl bromide/benzene mixture as a colorless liquid (1.31 g, 66% yield). 1H NMR (400 MHz, CDCl_3, 25 °C): δ (ppm) 7.16 (m, 6H, Ar_H), 4.93 (s, 1H, MeC[N](CH)), 3.45 (sept, 3H, J_H-H = 6.8 Hz, ArCHMe_2), 1.58 (s, 6H, MeC(N)), 1.45 (d, J_H-H = 6.8 Hz, 12H, ArCHMe_2), 1.20 (d, J_H-H = 6.8 Hz, 12H, ArCHMe_2), 0.61 (s, 2H, C_H). 3H NMR (60 MHz, C_6H_6, 25 °C): δ (ppm) −0.10 (s, C_H). 13C NMR (100 MHz, CDCl_3, 25 °C): δ (ppm) −80.6 (s, C_βH). The absorption correction was applied using the SADABS program. 28 The structures were solved by direct methods 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 programs. 29 Crystallographic data and refinement parameters are listed in Table S1 of the ESL.†

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 Ka radiation (λ = 1.34139 Å). The SMART program package was used to determine the unit cell parameters. The absorption correction was applied using the 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 programs. 29 Crystallographic data and refinement parameters are listed in Table S1 of the ESL.†

Computational details

Calculations were performed at the DFT level using the software Gaussian09, revision D.01. 30 Geometry optimizations were carried out without symmetry constraints in the gas phase using the PBE0 functional 31 and including dispersion corrections (GD3-BJ). 32 The scandium atom was described using the Stuttgart/Dresden ECP (SDD) pseudo-potential and its associated basis set 33 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 vibrational analysis within the harmonic approximation (1 atm and 298 K). Minima were identified as a full set of real frequencies.
Computation of the NMR coupling constants was realized with the IGLOII basis set for carbon and hydrogen atoms. NBO calculations were carried out using NBO6 as implemented in Gaussian09. Drawings were produced using the software Chemcraft.

Conflicts of interest

There are no conflicts to declare.

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