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click for updatesCite this: *Chem. Sci.*, 2016, 7, 803Received 24th August 2015
Accepted 16th September 2015

DOI: 10.1039/c5sc03138a

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Isolation, structure and reactivity of a scandium boryl oxycarbene complex†

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The reaction of a half-sandwich scandium boryl complex **1** with CO (1 atm) afforded a novel boryl oxycarbene complex **2**. The structure of **2** was characterized by ¹H, ¹³C and ¹¹B NMR, X-ray diffraction, and DFT analysis. Further reaction of **2** with CO (1 atm) yielded a phenylamido- and boryl-substituted enediolate complex **3** through C–C bond formation between CO and the carbene unit in **2** and cleavage and rearrangement of the Si–N bond in the silylene-linked Cp–amido ligand. Upon heating, insertion of the carbene atom into a methine C–H bond in the boryl ligand of **2** took place to give an alkoxide complex **4**. The reactions of **2** with pyridine and 2-methylpyridine led to insertion of the carbene atom into an *ortho*-C–H bond of pyridine and into a methyl C–H bond of 2-methylpyridine, respectively. The reaction of **2** with ethylene yielded a borylcyclopropyloxy complex **7** through cycloaddition of the carbene atom to ethylene.

Introduction

Carbon monoxide (CO) is an important C₁ building block in chemical industry, as it can be used for the production of synthetic lubrication oils and fuels *via* Fischer–Tropsch reactions.¹ So far, extensive studies on the reaction of CO with transition metal alkyls and hydrides have been reported in relevance to the Fischer–Tropsch process.^{1–3} The reaction of early transition-metal (including lanthanide and actinide) alkyls (or hydrides) with CO usually gives η²-acyl (or formyl) species that shows carbene-like characteristics in reactivity such as intramolecular 1,2-hydrogen migration, dimerization, and ketene formation.^{3–5} The analogous reactions of silyl, amido and phosphido complexes of some early transition metals with CO were also reported.⁶ In spite of extensive studies in this area, structurally characterized carbene-like species (or oxycarbene complexes) remains scarce. In 1980, Marks and co-workers reported that the reaction of a sterically demanding bis(pentamethylcyclopentadienyl) thorium neopentyl complex [(C₅Me₄)₂Th{CH₂C(CH₃)₃}Cl] with 1 equivalent of CO could afford a structurally characterizable oxycarbene complex [(C₅Me₅)₂Th{η²-OCCH₂C(CH₃)₃}Cl].^{4a} This is perhaps the only precedent of a well-defined oxycarbene complex.

Metal boryl complexes have received much attention in the last few decades because of their important roles in various chemical transformations.^{7–9} In this context, the reactions of metal boryl compounds with metal carbonyl complexes were recently reported, such as the nucleophilic addition of [(THF)₂Li{B(NDippCH)₂}] (Dipp = 2,6-diisopropylphenyl) to [Fe(CO)₅] and [Cr(CO)₆] as well as the intramolecular migratory addition of a boryl ligand to a carbonyl group in [(CO)₄Co{B(NDippCH)₂}]^{10a,b}. The reaction of metal carbonyl complexes such as K[[η⁵-C₅H₅]M(CO)₃] (M = Mo, W) with B₂(NMe₂)₂I₂ to give oxycarbene complexes was also reported.^{10c–e} In contrast, the reaction of gaseous CO with metal boryl compounds remains much less extensively explored.^{9b}

In 2011, we reported the reaction of a bis(amidinate)-ligated rare-earth boryl complex [(Me₃SiCH₂)C(N^{*i*}Pr)₂]₂Sc{B(NDippCH)₂} with gaseous CO (1 atm), which afforded a double CO insertion product. This reaction was proposed to proceed through a scandium borylacyl (or carbene) intermediate, but the isolation of such an acyl (or carbene) species was not achieved.^{9b} More recently, we found that a half-sandwich structure unit with a silylene-linked Cp–anilido ligand could serve as a useful platform for the isolation and transformation of rare-earth boryl species such as [Me₂Si(C₅Me₄)(NPh)Sc{B(NDippCH)₂}(μ-Cl)Li(THF)₃] (**1**).^{9c} In this paper, we report the isolation and structural characterization of a boryl oxycarbene complex [Me₂Si(C₅Me₄)(NPh)Sc{η²-OCB(NDippCH)₂}(THF)] (**2**) formed by reaction of the half-sandwich scandium boryl complex **1** with CO. The diverse reactivity of the boryl oxycarbene complex **2**, such as intra- and intermolecular sp² and sp³ C–H bond insertion, cyclopropanation with ethylene, and C–C bond formation with another molecule of CO is also described.

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† Electronic supplementary information (ESI) available: Synthesis, characterization of compounds 2–7. CCDC 981561–981563, 1042268 and 1042269. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc03138a



Results and discussion

Isolation and structure of a scandium boryl oxycarbene complex

When the half-sandwich scandium boryl (**1**) was exposed to a CO atmosphere (1 atm) at room temperature in benzene- d_6 , the insertion of CO into the Sc–boryl bond took place rapidly, selectively yielding the corresponding scandium borylacyl (or oxycarbene) complex **2** in 87% yield as dark blue crystals within 5 min (Scheme 1). The $(\text{THF})_3\text{LiCl}$ adduct in **1** is dissociated in this reaction. The reaction of **1** with ^{13}C -enriched CO afforded the ^{13}C -labeled analogue **2- ^{13}C** (eqn (1)). The ^{13}C NMR spectrum of **2** (or **2- ^{13}C**) in benzene- d_6 gave a singlet at δ 427.4 assignable to the CO group. This signal is considerably downfield shifted than those of reported transition-metal acyl complexes (δ 214.4–322.9),¹¹ and even lower than that of the thorium oxycarbene complex $[(\text{C}_5\text{Me}_5)_2\text{Th}\{\eta^2\text{-OCCH}_2\text{C}(\text{CH}_3)_3\text{Cl}\}]$ (δ 360.2),^{4a} clearly demonstrating the presence of a carbene species. The $^{11}\text{B}\{\text{H}\}$ NMR of **2** in benzene- d_6 showed a singlet at δ 16.9, which is 6.4 ppm up-field shifted from that of a cobalt Fischer-type boryl oxycarbene complex $[(\text{OC})_5\text{Cr}\{\text{C}(\text{OEt})\text{B}(\text{NDippCH})_2\}]$ (δ 23.3).^{10a}

Single crystals of **2** suitable for X-ray diffraction studies were obtained by recrystallization from a mixed hexane–benzene solution at -30°C . An X-ray diffraction study revealed that the Sc atom is bonded to the CO unit in a η^2 -fashion (Fig. 1). The Sc–O1 bond distance (2.114(2) Å) is significantly shorter than that of the Sc–C1 bond (2.194(2) Å), similar to what was observed in the thorium oxycarbene complex $[(\text{C}_5\text{Me}_5)_2\text{Th}\{\eta^2\text{-}$

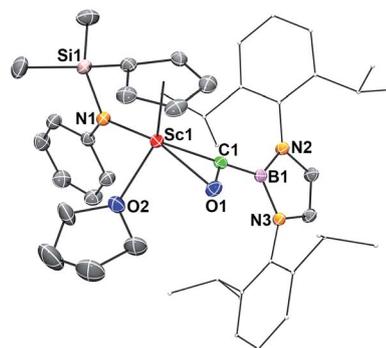
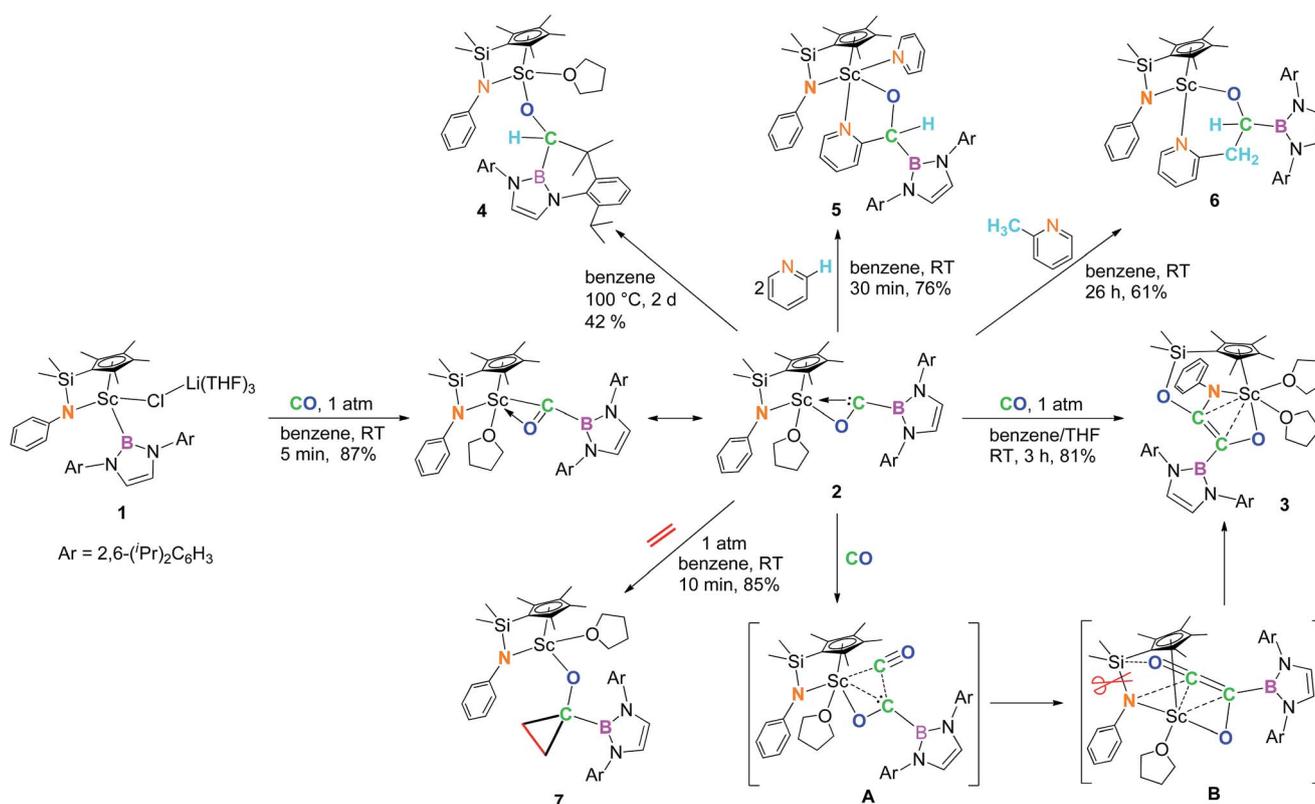


Fig. 1 ORTEP drawing of **2** with thermal ellipsoids at the 30% level except for the 2,6-(Pr) $_2\text{C}_6\text{H}_3$ groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Sc1–N1 2.130(2), Sc1–O1 2.114(2), Sc1–O2 2.199(2), Sc1–C1 2.194(2), C1–O1 1.266(3), C1–B1 1.577(3); Sc1–C1–O1 69.48(12), Sc1–O1–C1 76.40(12), Sc1–C1–B1 172.11(16).

$\text{OCCH}_2\text{C}(\text{CH}_3)_3\text{Cl}]$ (Th–O 2.37(2) Å, Th–C 2.44(2) Å).^{4a} The C1–O1 bond length (1.266(3) Å) in **2** is longer than that in $[(\text{C}_5\text{Me}_5)_2\text{Th}\{\eta^2\text{-OCCH}_2\text{C}(\text{CH}_3)_3\text{Cl}\}]$ (1.18(3) Å),^{4a} suggesting that the η^2 -CO unit in **2** is better considered as a carbene moiety than an acyl group.

In order to gain a better understanding about the nature of bonding of the boryl oxycarbene unit in **2**, DFT studies at the M06 level were carried out.¹² The calculated structure showed

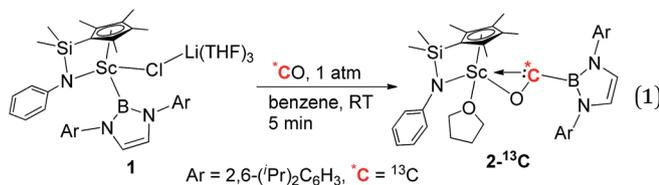


Scheme 1 Synthesis and reactivity of the boryl oxycarbene scandium complex **2**.



excellent agreement with the crystallographic structure, especially for the bond lengths of the Sc1–C1 (2.17 Å vs. 2.194(2) Å) and Sc1–O1 (2.12 Å vs. 2.114(2) Å) bonds.

The C1–O1 stretching frequency of **2** is difficult to assign experimentally due to overlapping bands with those of the boryl moiety. The computed C1–O1 stretching frequencies of **2** (1450 cm⁻¹) and 2-¹³C (1417 cm⁻¹) are comparable with the experimental IR values of the thorium oxycarbene complex [(C₅Me₅)₂Th{η²-OCCH₂C(CH₃)₃}Cl] (1469 cm⁻¹) and its ¹³CO analogue (1434 cm⁻¹), which are lower than those of transition-metal acyl complexes (1523–1666 cm⁻¹).¹¹ Further molecular orbital analysis of **2** suggests significant Sc1–O1 and Sc1–C1 bonding interactions with a minor contribution from the B1-2p orbital (see HOMO–1 in Fig. 2). HOMO–4 indicates π-bonding between C1, B1 and two N atoms of the boryl moiety (Fig. 2). The analysis of the donor–acceptor interactions on the basis of second-order perturbation theory¹³ revealed that the donation of σ(B1–C1) to Sc1 (177.7 kcal mol⁻¹) is significantly stronger than that of σ(O1–C1) (96.0 kcal mol⁻¹), and the donation of lone pair electrons of C1 to a vacant 3d orbital of Sc1 (170.3 kcal mol⁻¹) is higher than that of O1 to Sc1 (83.3 kcal mol⁻¹). In addition, the donation of the lone pair electrons of N2 (88.8 kcal mol⁻¹) and N3 (57.9 kcal mol⁻¹) atoms to B1 was also found in the boryl segment. Therefore, The boryl group plays an important role in stabilizing the Sc–(boryl)carbene moiety.



Reaction of carbene with CO

When being exposed to CO (1 atm) in a benzene–THF solution at room temperature for 3 h, **2** was completely consumed, and a phenylamido- and boryl-substituted enediolate complex **3** was obtained in 81% yield as yellow crystals after crystallization from a hexane–benzene solution (Scheme 1). An X-ray crystallographic study established that C–C bond formation between the carbene atom in **2** and CO occurred, accompanied by cleavage of the Si–NPh bond and formation of the O2–Si and C2–NPh bonds (Fig. 3). The resulting C1–C2 bond in **3** could be assigned as a double bond (1.364(5) Å), which shows some interactions with the Sc atom (Sc1–C1 2.519(3) Å, Sc1–C2 2.477(3) Å). The two oxygen atoms (O1 and O2) attached to the C1=C2 double bond are *trans* to each other, so are the boryl and PhN groups.

To further confirm the formation of **3**, the ¹³C-enriched complexes 3-¹³C, 3-¹³C' and 3-¹³C₂ were synthesized analogously, as shown in eqn (2)–(4). The ¹³C NMR spectrum of 3-¹³C₂ in benzene-*d*₆ showed a broad doublet at δ 134.6 and a sharp doublet at δ 136.7 for the OC=CO unit, whilst the ¹³C NMR spectra of 3-¹³C and 3-¹³C' gave a singlet at δ 136.7 and δ 134.7, respectively. The ¹¹B{H} NMR signal of **3** appeared at δ 23.8, which was 6.9 ppm downfield shifted compared to that of **2** (δ 16.9).

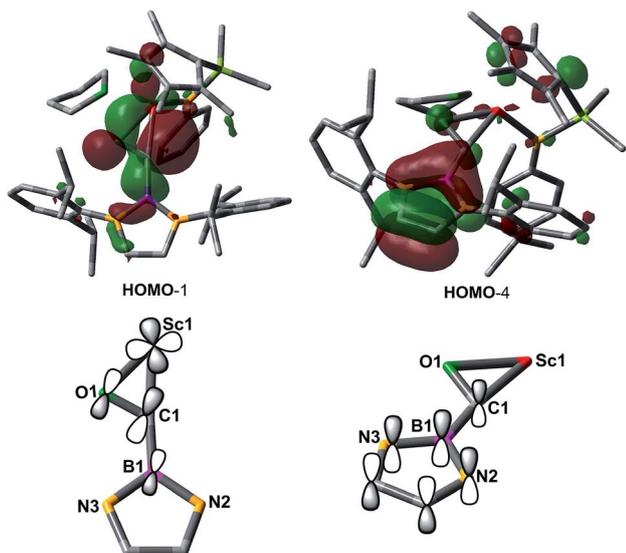
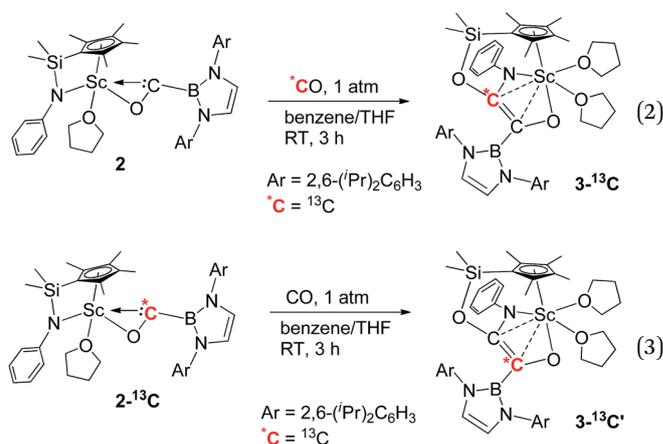


Fig. 2 Selected molecular orbitals for **2** (all H atoms are omitted for clarity).

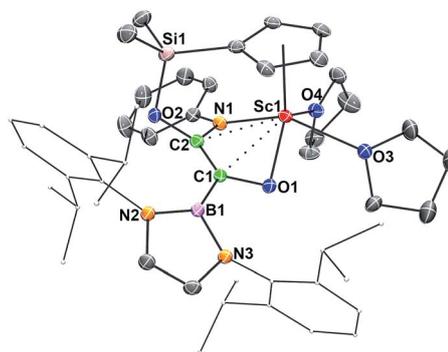
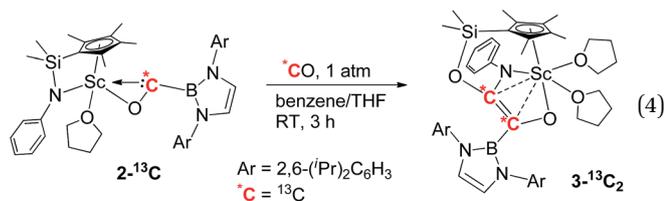


Fig. 3 ORTEP drawing of **3** with thermal ellipsoids at the 30% probability except for the 2,6-(*i*-Pr)₂C₆H₃ groups in the boryl unit. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Sc1–N1 2.086(3), Sc1–O1 2.005(2), Sc1–C1 2.519(3), Sc1–C2 2.477(3), Sc1–O3 2.335(3), Sc1–O4 2.291(2), C1–C2 1.364(5), C1–O1 1.383(4), C2–O2 1.390(4), C2–N1 1.405(4), B1–C1 1.567(5), Si1–O2 1.691(2).





The formation of **3** may be achieved by insertion of CO into the Sc–carbene bond in **2** to give a ketene unit,^{14a–c} followed by cleavage of the Si–N bond in the Cp–anilido ligand and formation of a Si–O bond and an N–C bond between the resulting silyl and PhN groups and the OCCO unit (*cf.* **A** and **B** in Scheme 1). Silylene-linked Cp–amido ligands have been used for the stabilization of various metal complexes, but examples of cleavage of the Si–N bond in these ligands are scarce.¹⁵ A possible driving force for the present Si–N cleavage could be the formation of stable Si–O and C–N bonds. A similar silyl migration reaction was also observed previously in the reaction of a bis(amidinate)-ligated scandium boryl complex with CO.^{9b} The reaction of transition-metal acyl complexes [M–C(=O)R] with CO were previously reported to give α -ketoacyl species such as [M–C(=O)C(=O)R].^{14d} The reaction of a metallocene cerium hydride complex Cp'₂CeH (Cp' = 1,2,4-(^tBu)₃C₅H₂) with CO was reported to yield an enediolate complex [Cp'₂CeOCH=CHOcCp'₂] without observation of an isolable mono-CO insertion product.^{5f}

Intra- and intermolecular insertion of carbene into C–H bonds

When complex **2** was heated at 100 °C in benzene for two days, intramolecular insertion of the carbene atom into a methine C–H bond in the boryl ligand took place to give the alkoxide complex **4** (Scheme 1). In this transformation, the Sc–carbene bond is broken, together with formation of a C54–H54 bond and a C54–C41 bond (Fig. 4). The Sc1–O1 bond distance in **4** (1.879(2) Å) is much shorter than that of the Sc–O1(oxy-carbene) bond in **2** (2.114(2) Å), whilst the O1–C54 bond distance in **4** (1.424(4) Å) is much longer than that of the O1–C1(oxy-carbene) bond in **2** (1.266(3) Å). The C–B bond distance in **4** (1.563(5) Å) is comparable with that in **2** (1.577(3) Å). The newly formed C54–C41 (1.561(5) Å) in **4** is best described as a single bond.

The hydrogen atom in the newly formed “HC(O)(B)C” unit in **4** gave a singlet at δ 3.91 in the ¹H NMR spectrum in benzene-*d*₆. The ¹¹B{H} NMR signal of **4** is located at δ 21.8, which is comparable to that of **3** (δ 23.8) and is 4.9 ppm upfield shifted compared to that of **2** (δ 16.9). The transformation of **2** to **4** could be viewed as a typical reaction (C–H insertion) of a carbene species.¹⁶

The reaction of **2** with two equivalents of pyridine in benzene-*d*₆ at room temperature yielded **5** as colourless crystals following recrystallization from hexane–benzene (Scheme 1; also see Fig. S1 in ESI†). In this reaction, the insertion of the carbene atom of **2** into an *ortho*-C–H bond of one molecule of pyridine took place, while another molecule of pyridine

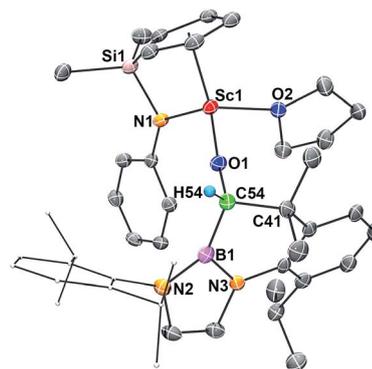


Fig. 4 ORTEP drawing of **4** with thermal ellipsoids at the 30% level except for a 2,6-(ⁱPr)₂C₆H₃ group in the boryl unit. Hydrogen atoms (except H54) and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sc1–O1 1.879(2), Sc1–O2 2.184(2), C54–O1 1.424(4), C41–C54 1.561(5), O1–C54 1.424(4), B1–C54 1.563(5), Sc1–O1–C54 169.5(2), B1–C54–O1 111.3(3), C41–C54–O1 110.3(3).

displaced the THF ligand of **2**. The ¹H NMR spectrum of the newly formed “HC(O)(Py)B” fragment in **5** showed a singlet at δ 5.75 in benzene-*d*₆. The ¹¹B{H} NMR spectrum of **5** showed a broad peak at δ 25.1 which is close to that of **3** (δ 23.8).

When **2** was allowed to react with 2-methylpyridine in benzene-*d*₆ at room temperature for 26 h, the insertion of a sp³ C–H bond in the methyl group of 2-methylpyridine occurred to give complex **6** in 61% isolated yield (Scheme 1 and Fig. 5). The ¹H NMR signals of the two protons on the resulting O–CH(B)–CH₂C₅H₄N moiety appeared at δ 2.74 (dd, 10.6 Hz, 14.6 Hz) and δ 2.95 (d, 14.6 Hz), whilst the one of O–CH(B)–CH₂C₅H₄N appeared at δ 4.50 (d, 10.6 Hz).

The molecular structures of **5** and **6** were also confirmed by X-ray crystallographic studies (Fig. S1† for **5** and Fig. 5 for **6**), although there were disorder problems in the case of **5**. The present C–H bond activation of pyridines by **2** is in contrast with what was observed previously in the reaction of conventional free carbene species with pyridines, in which a stable carbene–pyridine ylide complex was usually formed.¹⁷ The reason for the formation of the C–H activation products **5** and **6** is possibly because of facile coordination of the nitrogen atom of a pyridine unit to the electropositive Sc³⁺ centre, which could easily lead to activation of an *ortho*-C(sp²)–H or methyl C(sp³)–H bond by the highly active carbene species.^{18,5g} *ortho*-C–H activation of pyridine by a tantalum η^2 -acyl complex was reported previously.^{6a}

Cyclopropanation of carbene with ethylene

The reaction of **2** with ethylene (1 atm) in benzene-*d*₆ took place rapidly at room temperature, which was accompanied by a colour change from dark blue to colourless to give a borylcyclopropoxy product **7** *via* the cycloaddition of the carbene atom to ethylene (Scheme 1). The Sc–O_{CO} bond distance in **7** (1.9083(14) Å) (Fig. 6) is comparable with that in **6** (1.9175(12) Å), as are the C–O_{CO} bond distances (**7**: 1.402(2) Å; **6**: 1.412(2) Å). The bond distances and angles of the



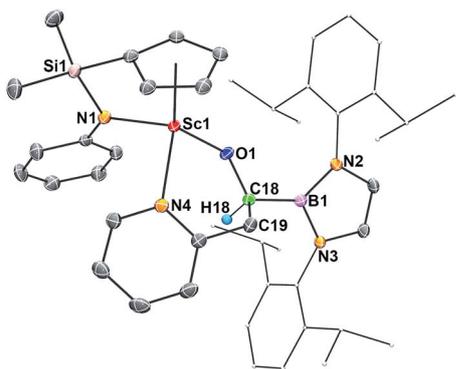


Fig. 5 ORTEP drawing of **6** with thermal ellipsoids at the 30% level except for a 2,6-(*i*-Pr)₂C₆H₃ group in the boryl unit. Hydrogen atoms (except H18) and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å): Sc1–O1 1.9175(12), Sc1–N1 2.0947(15), Sc1–N4 2.2811(15), O1–C18 1.412(2), C18–C19 1.550(2), B1–C18 1.595(3).

triangular carbon skeleton in **6** are typical for a cyclopropyl unit (Fig. 6).

The present formation of **7** represents a rare example of cyclopropanation of ethylene with a carbene species.¹⁹ It was known that carbenes could undergo cyclopropanation reactions with alkenes bearing polar substituents (either electron withdrawing or donating) but are usually inert towards simple alkenes such as ethylene.¹⁹ The cyclopropanation of ethylene with **2** may be promoted by coordination of ethylene to the electropositive Sc³⁺ center.²⁰ The cyclopropanation of a cationic iron carbene complex [$\{\text{Cp}(\text{CO})_2\text{Fe}=\text{CHC}_6\text{H}_5\}^+\{\text{PF}_6\}^-$] with ethylene was reported previously.^{19a} The reaction of a classical acyl species M–C(=O)R with ethylene usually gave a straightforward insertion product formulated as [M–CH₂CH₂C(=O)R].²¹

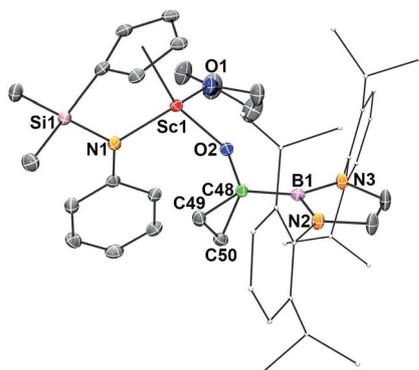


Fig. 6 ORTEP drawing of **7** with thermal ellipsoids at the 30% level except for the 2,6-(*i*-Pr)₂C₆H₃ groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sc1–N1 2.1238(18), Sc1–O1 2.1577(15), Sc1–O2 1.9083(14), O2–C48 1.402(2), C48–C49 1.514(3), C48–C50 1.533(3), C49–C50 1.492(3), C48–B1 1.569(3), C49–C48–C50 58.64(14), C50–C49–C48 61.33(14), C49–C50–C48 60.02(14).

Conclusions

We have demonstrated that the reaction of a half-sandwich scandium boryl complex such as **1** with CO (1 atm) can afford a structurally characterizable oxycarbene complex including **2**, which represents the first example of a well-defined boryl-substituted oxycarbene species. The scandium boryl oxycarbene complex **2** showed diverse reactivity, such as coupling with CO to form an enediolate complex **3**, intramolecular C–H bond activation to give **4**, insertion of the carbene atom into an *ortho*-C–H bond of pyridine or into a methyl C–H bond of 2-methylpyridine, and cyclopropanation with ethylene. The structure and reactivity of the carbene species in **2** are clearly affected by the scandium ion as well as the boryl substituent. Studies on the synthesis and reactions of other rare earth metal boryl complexes are in progress.

Acknowledgements

We appreciate financial support through a Grant-in-Aid for Scientific Research (B) (24350030) and a Grant-in-Aid for Scientific Research (S) (26220802) from JSPS and grants from the National Natural Science Foundation of China (21174023, 21137001 and 21429201). We thank Mrs Akiko Karube for micro-elemental analyses.

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