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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 ^{1}H, ^{13}C and ^{11}B 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 C_1 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 η^2-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 $[(C_5Me_4)_2Th\{CH_2C(CH_3)_3\}Cl]$ with 1 equivalent of CO could afford a structurally characterizable oxycarbene complex $[(C_5Me_5)_2Th\{\eta^2\text{-}OCCH_2C(CH_3)_3\}Cl]$.[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 $K[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, W) with $B_2(NMe_2)_2I_2$ to give oxycarbyne 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 $[\{(Me_3SiCH_2)C(N^iPr)_2\}_2Sc\{B(NDippCH)_2\}]$ 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 $[Me_2Si(C_5Me_4)(NPh)Sc\{B(NDippCH)_2\}(\mu\text{-}Cl)Li(THF)_3]$ (**1**).[9c] In this paper, we report the isolation and structural characterization of a boryl oxycarbene complex $[Me_2Si(C_5Me_4)(NPh)Sc\{\eta^2\text{-}OCB(NDippCH)_2\}(THF)]$ (**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 sp^2 and sp^3 C–H bond insertion, cyclopropanation with ethylene, and C–C bond formation with another molecule of CO is also described.

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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 $(THF)_3LiCl$ 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 $[(C_5Me_5)_2Th\{\eta^2\text{-}OCCH_2C(CH_3)_3\}Cl]$ (δ 360.2),[4a] clearly demonstrating the presence of a carbene species. The $^{11}B\{H\}$ 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 $[(OC)_5Cr\{C(OEt)B(NDippCH)_2\}]$ (δ 23.3).[10a]

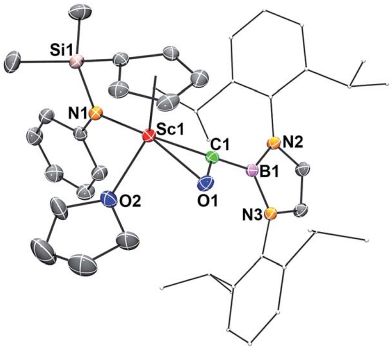
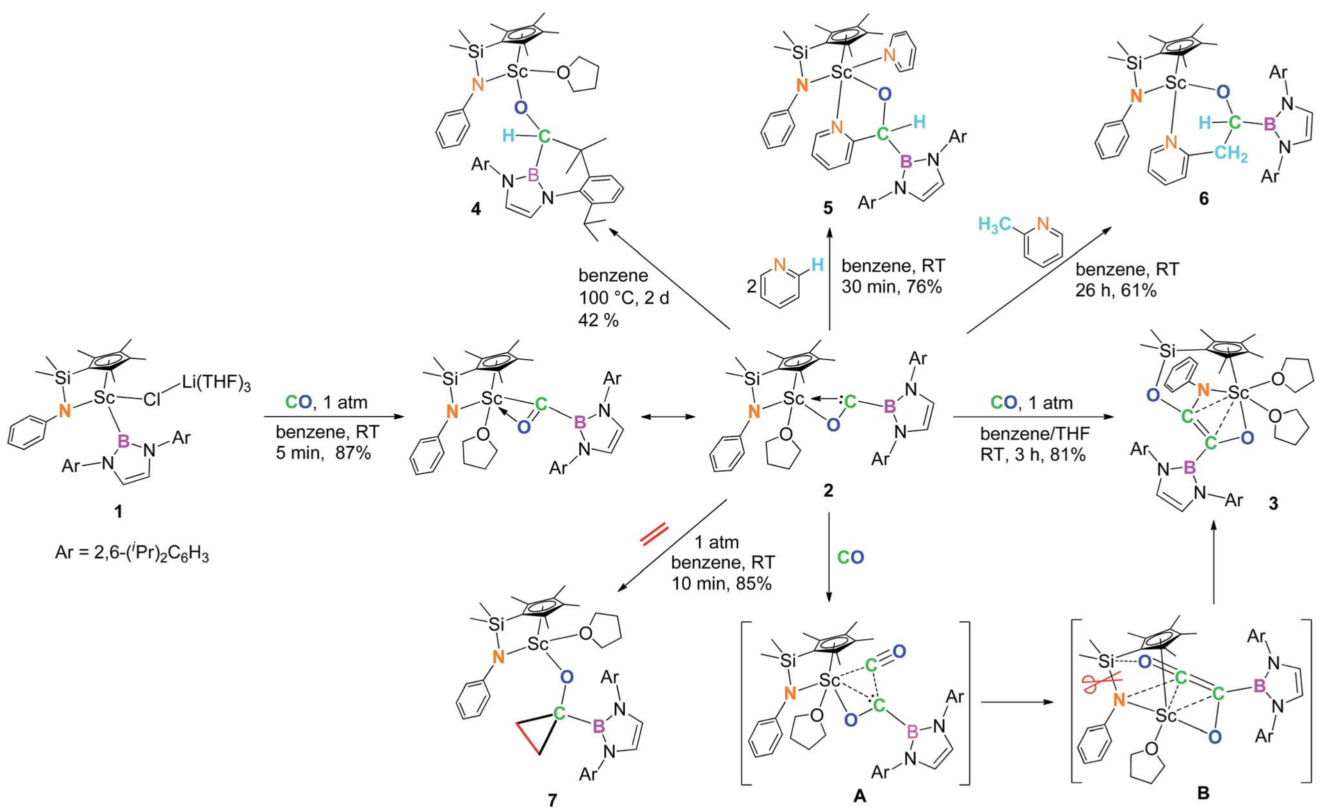


Fig. 1 ORTEP drawing of **2** with thermal ellipsoids at the 30% level except for the 2,6-$(^iPr)_2C_6H_3$ groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sc1–N1 2.130(2), Sc1–O1 2.114(2), Sc1–O2 2.199(2), 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).

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 $[(C_5Me_5)_2Th\{\eta^2\text{-}OCCH_2C(CH_3)_3\}Cl]$ (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 $[(C_5Me_5)_2Th\{\eta^2\text{-}OCCH_2C(CH_3)_3\}Cl]$ (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.

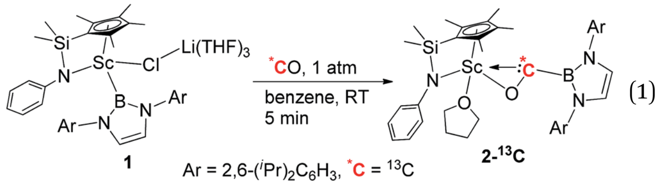
In order to gain a better understanding about the nature of bonding of the boryl oxycarbene unit in **2**, DFT studies at the M06 level were carried out.[12] The calculated structure showed



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-^{13}C** (1417 cm^{-1}) are comparable with the experimental IR values of the thorium oxycarbene complex $[(C_5Me_5)_2Th\{\eta^2\text{-}OCCH_2C(CH_3)_3\}Cl]$ (1469 cm^{-1}) and its ^{13}CO 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 theory[13] 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.



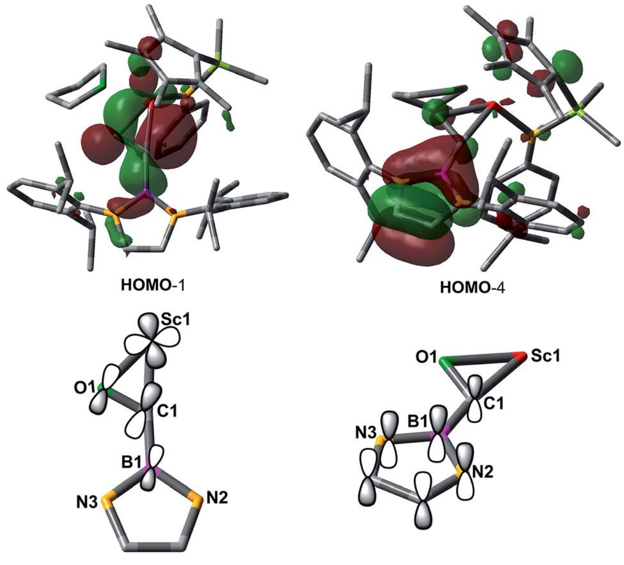
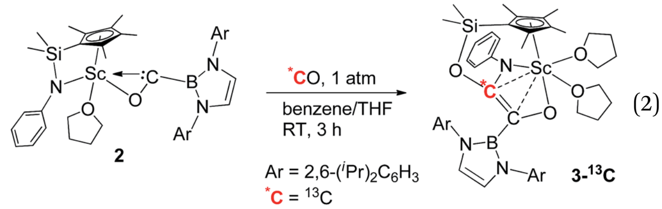


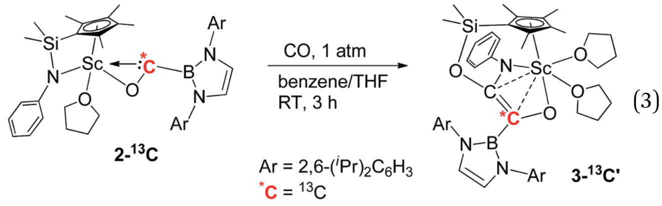
Fig. 2 Selected molecular orbitals for **2** (all H atoms are omitted for clarify).

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 ^{13}C-enriched complexes **3-^{13}C**, **3-^{13}C′** and **3-^{13}C$_2$** were synthesized analogously, as shown in eqn (2)–(4). The ^{13}C NMR spectrum of **3-^{13}C$_2$** 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 ^{13}C NMR spectra of **3-^{13}C** and **3-^{13}C′** gave a singlet at δ 136.7 and δ 134.7, respectively. The ^{11}B{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).





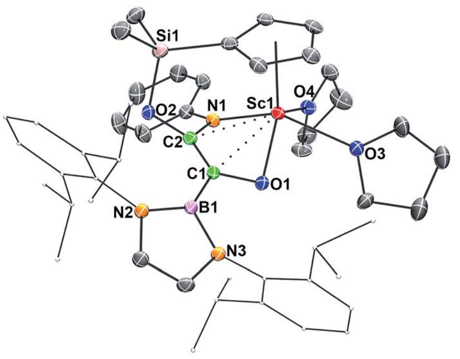
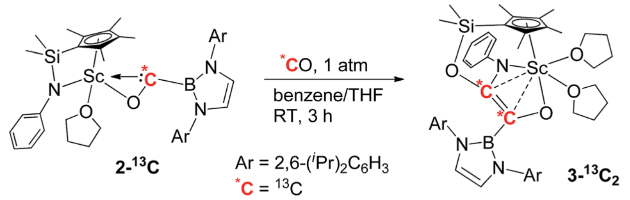


Fig. 3 ORTEP drawing of **3** with thermal ellipsoids at the 30% probability except for the 2,6-(^{i}Pr)$_2$C$_6$H$_3$ groups in the boryl unit. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Sc1–N1 2.086(3), Sc1–O1 2.005(2), Sc1–C1 2.519(3), Sc1–C2 2.477(3), Sc1–O3 2.335(3), 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).



(4)

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 ($Cp' = 1,2,4\text{-}(^tBu)_3C_5H_2$) with CO was reported to yield an enediolate complex $[Cp'_2CeOCH{=}CHOCeCp'_2]$ without observation of an isolable mono-CO insertion product.[5l]

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(oxycarbene) 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(oxycarbene) 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 $^{11}B\{H\}$ 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 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 $^{11}B\{H\}$ NMR spectrum of **5** showed a broad peak at δ 25.1 which is close to that of **3** (δ 23.8).

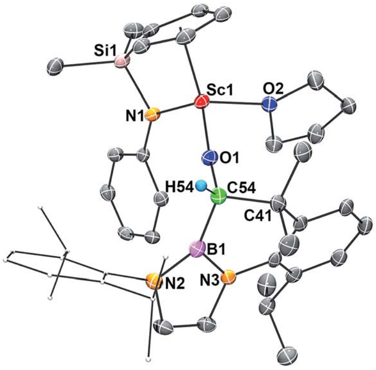


Fig. 4 ORTEP drawing of **4** with thermal ellipsoids at the 30% level except for a $2,6\text{-}(^iPr)_2C_6H_3$ group in the boryl unit. Hydrogen atoms (except H54) and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sc1–O1 1.879(2), Sc1–O2 2.184(2), 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).

When **2** was allowed to react with 2-methylpyridine in benzene-d_6 at room temperature for 26 h, the insertion of a sp^3 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 $O\text{–}CH(B)\text{–}CH_2C_5H_4N$ 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 $O\text{–}CH(B)\text{–}CH_2C_5H_4N$ 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 Sc^{3+} centre, which could easily lead to activation of an *ortho*-C(sp^2)–H or methyl C(sp^3)–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 borylcyclopropyloxy product **7** *via* the cycloaddition of the carbene atom to ethylene (Scheme 1). The $Sc\text{–}O_{CO}$ bond distance in **7** (1.9083(14) Å) (Fig. 6) is comparable with that in **6** (1.9175(12) Å), as are the $C\text{–}O_{CO}$ bond distances (**7:** 1.402(2) Å; **6:** 1.412(2) Å). The bond distances and angles of the

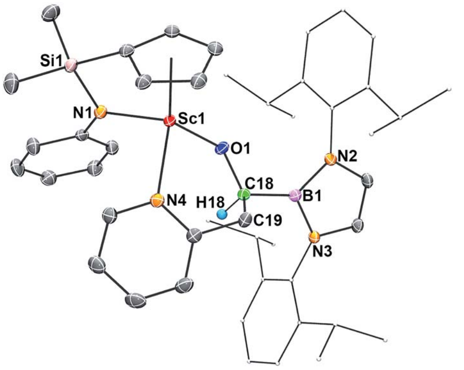


Fig. 5 ORTEP drawing of **6** with thermal ellipsoids at the 30% level except for a 2,6-(^{i}Pr)$_2$C$_6$H$_3$ group in the boryl unit. Hydrogen atoms (except H18) and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å): Sc1–O1 1.9175(12), Sc1–N1 2.0947(15), Sc1–N4 2.2811(15), 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 Sc^{3+} center.[20] The cyclopropanation of a cationic iron carbene complex [{Cp(CO)$_2$Fe=CHC$_6$H$_5$}$^+${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–CH$_2$CH$_2$C(=O)R].[21]

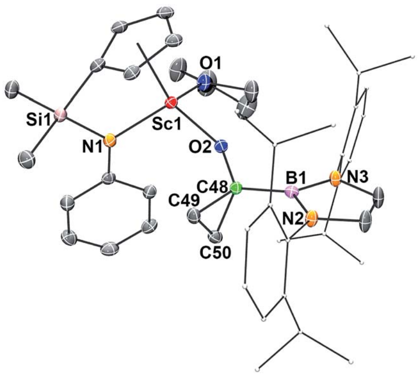


Fig. 6 ORTEP drawing of **7** with thermal ellipsoids at the 30% level except for the 2,6-(^{i}Pr)$_2$C$_6$H$_3$ groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (°): Sc1–N1 2.1238(18), Sc1–O1 2.1577(15), Sc1–O2 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

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