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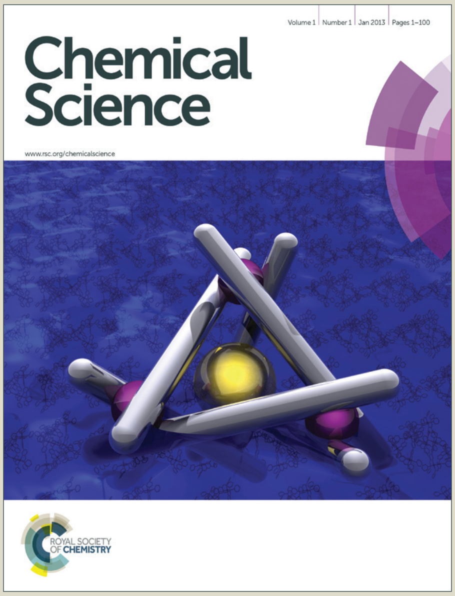

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Isolation, structure and reactivity of a scandium boryl oxycarbene complex†

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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, ^{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 gave η^2-acyl (or formyl) species that showed 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) remained 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 played 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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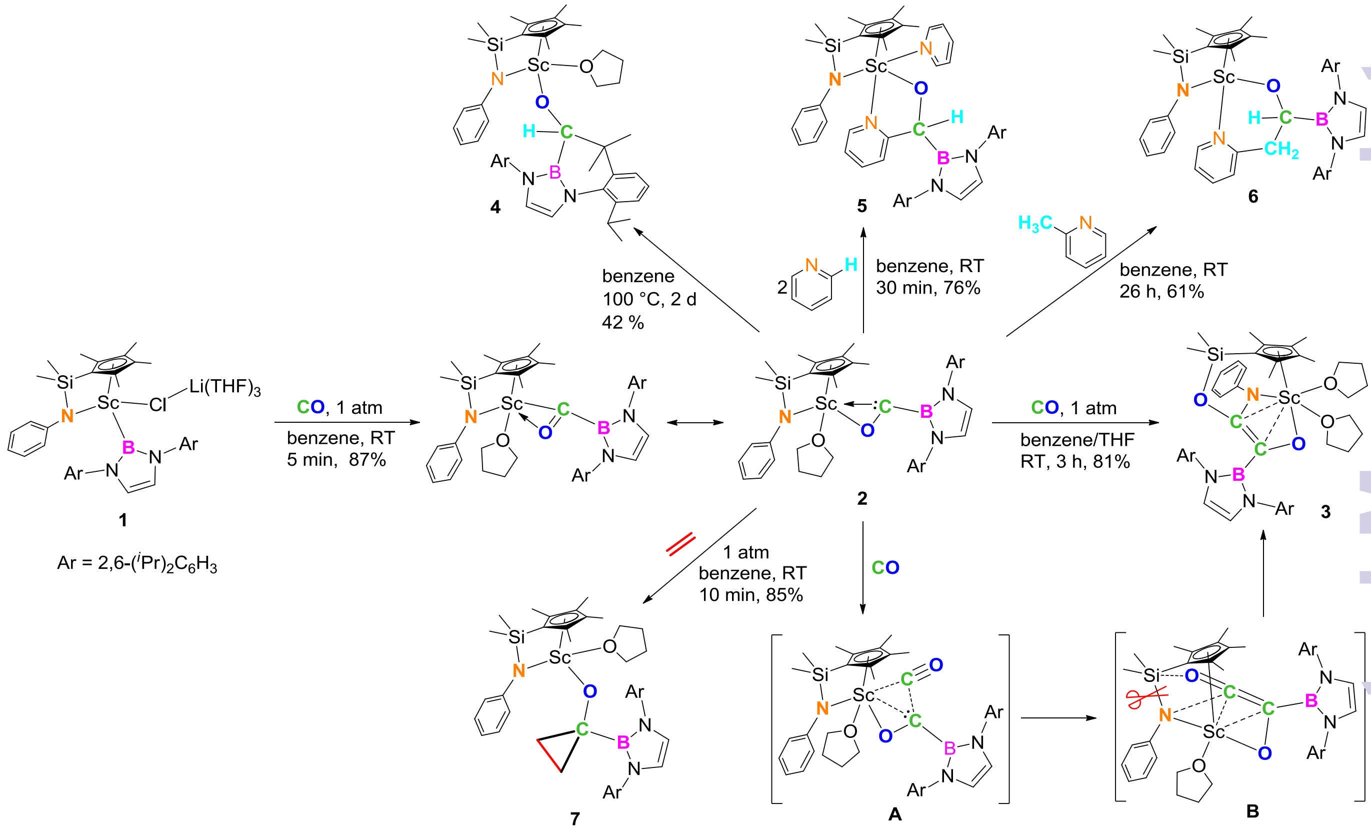
† Electronic Supplementary Information (ESI) available: Synthesis, characterization of compounds **2** to **7**. CCDC 981561 (**2**), 981563 (**3**), 981562 (**4**), 1042268 (**6**), and 1042269 (**7**) contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/



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

Results and discussion

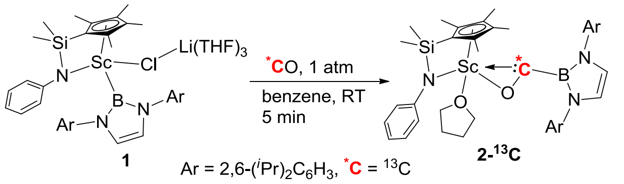
Isolation and structure of a scandium boryl oxycarbene complex

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 minutes (Scheme 1). The (THF)$_3$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** (Eq. 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 considerable down-field 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]

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 (Figure 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, and 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 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.* 2.115(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



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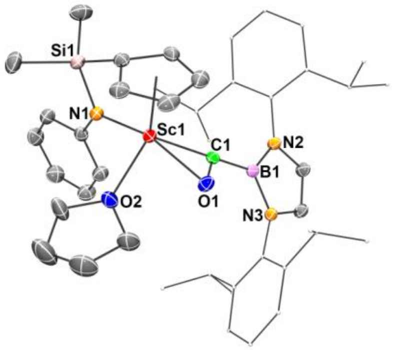


Figure 1 ORTEP drawing of **2** with thermal ellipsoids at the 30% level except for the 2,6-(^{i}Pr)$_2$C$_6$H$_3$ groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1–N1 2.130(2), Sc1–O1 2.114(2), Sc1–O2 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).

[(C$_5$Me$_5$)$_2$Th{η^2-OCCH$_2$C(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 Figure 2). HOMO-4 indicates π–bonding between C1, B1, and two N atoms of the boryl moiety (Figure 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 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 hours, **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 (Figure 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 Eqs 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).

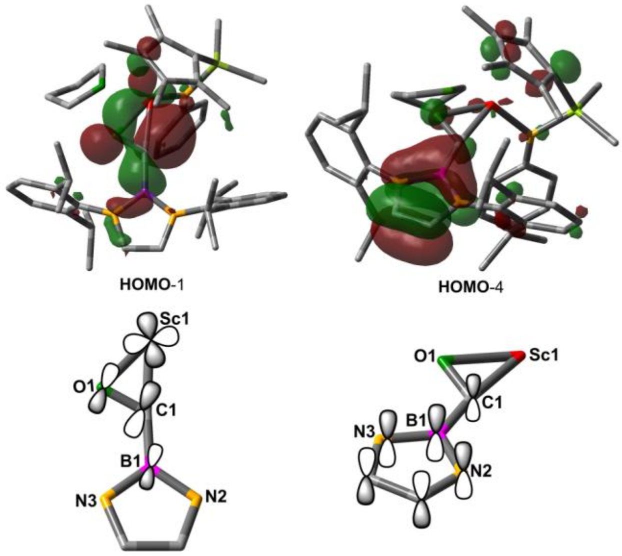
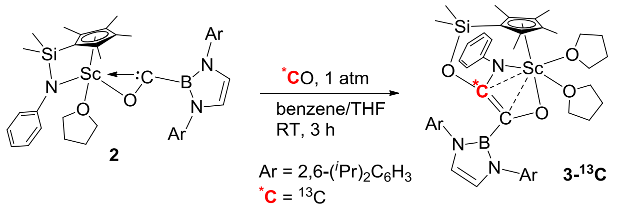


Figure 2 Selected molecular orbitals for **2** (all H atoms are omitted for clarify).

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 was 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′$_2$CeH (Cp′ = 1,2,4-(Me$_3$C)$_3$C$_5$H$_2$) with CO was reported to yield an enediolate complex [Cp′$_2$CeOCH=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 (Figure 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



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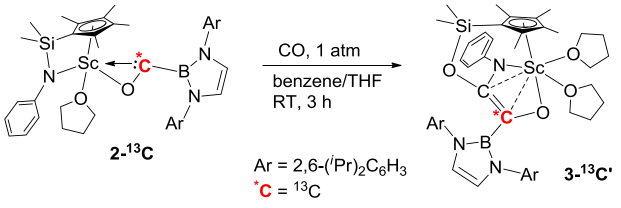

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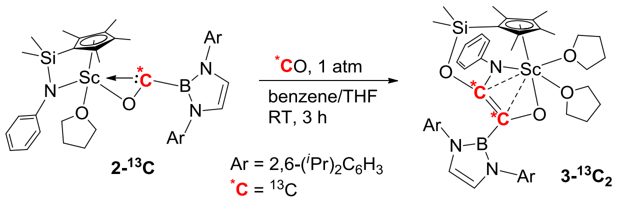

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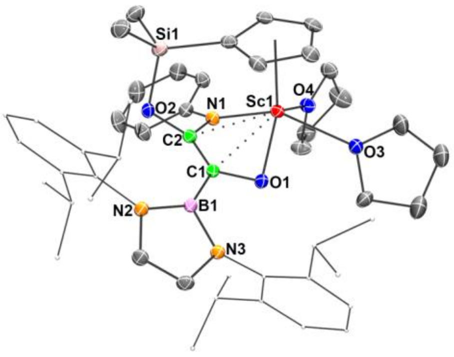

Figure 3 ORTEP drawing of **3** with thermal ellipsoids at the 30% probability except for the 2,6-(^{i}Pr)$_2$C$_6$H$_3$ groups in the boryl unit. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Sc1–N1 2.086(3), Sc1–O1 2.005(2), Sc1–C1 2.519(3), Sc1–C2 2.477(3), Sc1–O3 2.335(3),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

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 ^{1}H 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 up-field 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.[17]

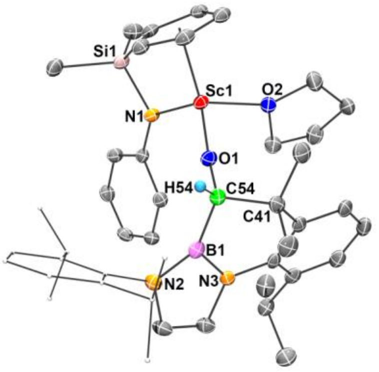

Figure 4 ORTEP drawings of **4** with thermal ellipsoids at the 30% level except for a 2,6-(^{i}Pr)$_2$C$_6$H$_3$ group in the boryl unit. Hydrogen atoms (except H54) and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1–O1 1.879(2), Sc1–O2 2.184(2), 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).

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 and benzene (Scheme 1; also see Figure 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 ^{1}H NMR spectrum of the newly formed "HC(O)(Py)B" fragment in **5** showed a singlet at *δ* 5.75 in benzene-D$_8$. 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).

When **2** was allowed to react with 2-methylpyridine in benzene-D$_6$ at room temperature for 26 hours, 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 Figure 5). The ^{1}H NMR signals of the two protons on the resulting O-CH(B)-C*H*$_2$C$_5$H$_4$N 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-C*H*(B)-CH$_2$C$_5$H$_4$N appeared at *δ* 4.50 (d, 10.6 Hz).

The molecular structures of **5** and **6** were also confirmed by X-ray crystallographic studies (Figure S1 for **5** and Figure 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

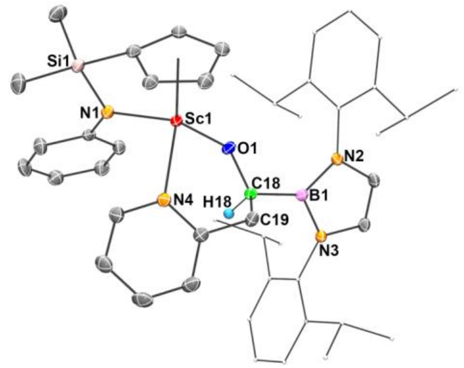

Figure 5 ORTEP drawings of **6** with thermal ellipsoids at the 30% level except for a 2,6-(^{i}Pr)$_2$C$_6$H$_3$ group in the boryl unit. Hydrogen atoms (except H18) and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1–O1 1.9175(12), Sc1–N1 2.0947(15), Sc1–N4 2.2811(15), O1–C18 1.412(2), C18–C19 1.550(2), B1–C18 1.595(3).

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–O_{CO} bond distance in **7** (1.9083(14) Å) (Figure 6) is comparable with that in **6** (1.9175(12) Å), as are C–O_{CO} bond distances (**7**: 1.402(2) Å; **6**: 1.412(2) Å). The bond distances and angles of the triangular carbon skeleton in **6** are typical for a cyclopropyl unit (Figure 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]

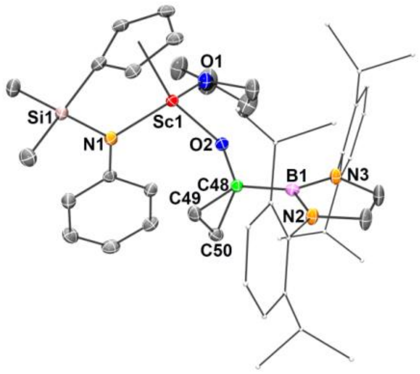

Figure 6 ORTEP drawing of **7** with thermal ellipsoids at the 30% level except for the 2,6-(^{i}Pr)2C6H3 groups in the boryl unit. Hydrogen atoms and the Me groups on the Cp ring have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sc1–N1 2.1238(18), Sc1–O1 2.1577(15), Sc1–O2 1.9083(14), 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 spieces 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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Notes and references

1 (a) C. K. Rofer-Depoorter, *Chem. Rev.*, 1981, **81**, 447; (b) A. Y. Khodakov, W. Chu and P. Fongarland, *Chem. Rev.*, 2007, **107**, 1692.

2 (a) K. Tatsumi, A. Nakamura, P. Hofmann, P. Stauffert and R. Hoffmann, *J. Am. Chem. Soc.*, 1985, **107**, 4440; (b) W. J. Evans, J. W. Grate and R. J. Doedens, *J. Am. Chem. Soc.*, 1985, **107**, 1671; (c) M. D. Curtis, K. B. Shiu and W. M. Butler, *J. Am. Chem. Soc.*, 1986, **108**, 1550; (d) J. B. Sheridan, J. R. Johnson, B. M. Handwerker, G. L. Geoffroy and A. L. Rheingold, *Organometallics*, 1988, **7**, 2404; (e) I. M. Arafa, K. Shin and H. M. Goff, *J. Am. Chem. Soc.*, 1988, **110**, 5228; (f) J. W. Bruno, M. C. Fermin, S. E. Halfon and G. K. Schulte, *J. Am. Chem. Soc.* 1989, **111**, 8738; (g) J. D. Debad, P. Legzdins, R. J. Batchelor and F. W. B. Einstein, *Organometallics*, 1993, **12**, 2094; (h) M. Gomez, P. Gomez-Sal, G. Jimenez, A. Martin, P. Royo and J. Sanchez-Nieves, *Organometallics*, 1996, **15**, 3579; (h) H. Shen and R. F. Jordan, *Organometallics*, 2003, **22**, 2080; (i) W. J. Evans, S. A. Kozimor, G. W. Nyce and J. W. Ziller, *J. Am. Chem. Soc.*, 2003, **125**, 13831; (j) M. L. Scheuermann, A. L. Rheingold and B. S. Williams, *Organometallics*, 2009, **28**, 1613; (k) O. Benaud, J. C. Berthet, P. Thuery and M. Ephritikhine, *Inorg. Chem.*, 2010, **49**, 8117; (l) J. L. Smeltz, P. D. Boyle and E. A. Ison, *J. Am. Chem. Soc.*, 2011, **133**, 13288;

3 (a) P. T. Wolczanski and J. E. Bercaw, *Acc. Chem. Res.*, 1980, **13**, 121; (b) T. J. Marks, *Science*, 1982, **217**, 4564; (c) L. D. Durfee and I. P. Rothwell, *Chem. Rev.*, 1988, **88**, 1059; (d) B. E. Kahn and R. D. Rieke, *Chem. Rev.*, 1988, **88**, 733.

4 (a) P. J. Fagan, J. M. Manriquez, T. J. Marks, V. W. Day, S. H. Vollmer and C. S. Day, *J. Am. Chem. Soc.*, 1980, **102**, 5393; (b) E. A. Maatta and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**,

3576; (c) P. J. Fagan, K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6959; (d) P. J. Fagan, J. M. Manriquez, S. H. Vollmer, C. S. Day, V. W. Day and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 2206; (e) K. G. Moloy, T. J. Marks and V. W. Day, *J. Am. Chem. Soc.*, 1983, **105**, 5696; (f) K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 7051; (g) K. G. Moloy, P. J. Fagan, J. M. Manriquez and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 56.

5 (a) W. J. Evans, A. L. Wayda, W. E. Hunter and J. L. Atwood, *J. Chem. Soc. Chem. Comm.*, 1981, 706; (b) K. Tatsumi, A. Nakamura, P. Hofmann, R. Hoffmann, K. G. Moloy and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 4467; (c) W. J. Evans and D. K. Drummond, *J. Am. Chem. Soc.*, 1988, **110**, 2772; (d) W. J. Evans, K. J. Forrestal and J. W. Ziller, *J. Am. Chem. Soc.*, 1995, **117**, 12635; (e) C. J. Schaverien, N. Meijboom and A. G. Orpen, *J. Chem. Soc. Chem. Comm.*, 1992, 124; (f) B. K. Campion, R. H. Heyn and T. D. Tilley, *Organometallics*, 1993, **12**, 2584; (g) B. J. Deelman, W. M. Stevels, J. H. Teuben, M. T. Lakin and A. L. Spek, *Organometallics*, 1994, **13**, 3881; (h) L. Lee, D. J. Berg, F. W. Einstein and R. J. Batchelor, *Organometallics*, 1997, **16**, 1819; (i) G. M. Ferrence, R. McDonald and J. Takats, *Angew. Chem. Int. Ed.*, 1999, **38**, 2233; (j) T. M. Cameron, J. C. Gordon, B. L. Scott and W. Tumas, *Chem. Comm.*, 2004, 1398; (k) T. Shima and Z. Hou, *J. Am. Chem. Soc.*, 2006, **128**, 8124; (l) E. L. Werkema, L. Maron, O. Eisenstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2007, **129**, 6662.

6 (a) J. Arnold and T. D. Tilley, *J. Am. Chem. Soc.*, 1985, **107**, 6409; (b) T. D. Tilley, *J. Am. Chem. Soc.*, 1985, **107**, 4084; (c) J. Arnold, T. D. Tilley, A. L. Rheingold, S. J. Geib and A. M. Arif, *J. Am. Chem. Soc.*, 1989, **111**, 149; (d) P. J. Fagan, J. M. Manriquez, S. H. Vollmer, C. S. Day, V. W. Day and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 2206; (e) P. L. Arnold, Z. R. Turner, R. M. Bellabarba and R. P. Tooze, *Chem. Sci*., 2011, **2**, 77; (f) M. Porchia, N. Brianese, F. Ossola, G. Rossetto and P. Zanella, *J. Chem. Soc. Dalton*, 1987, 691.

7 (a) G. J. Irvine, M. J. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell and L. J. Wright, *Chem. Rev.*, 1998, **98**, 2685; (b) S. Aldridge and D. L. Coombs, *Coord. Chem. Rev.*, 2004, **248**, 535; (c) L. Dang, Z. Lin and T. B. Marder, *Chem. Commun.*, 2009, 3987; (d) H. Braunschweig, R. D. Dewhurst and A. Schneider, *Chem. Rev.*, 2010, **110**, 3924; (e) I. A. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy and J. F. Hartwig, *Chem. Rev.*, 2010, **110**, 890; (f) J. Cid, H. Gulyas, J. J. Carbo and E. Fernandez, *Chem. Soc. Rev.*, 2012, **41**, 3558; (g) J. F. Hartwig, *Acc. Chem. Res.*, 2012, **45**, 864; (h) J. Cid, J. J. Carbo and E. Fernandez, *Chem. Eur. J.*, 2012, **18**, 12794.

8 (a) Y. Segawa, M. Yamashita and K. Nozaki, *Science*, 2006, **314**, 113; (b) T. B. Marder, *Science*, 2006, **314**, 69; (c) H. Braunschweig, *Angew. Chem. Int. Ed.*, 2007, **46**, 1946; (d) M. Yamashita, Y. Suzuki, Y. Segawa and K. Nozaki, *J. Am. Chem. Soc.*, 2007, **129**, 9570; (e) Y. Segawa, Y. Suzuki, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2008, **130**, 16069; (f) L. Weber, *Eur. J. Inorg. Chem.*, 2012, 5595; (g) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500; (h) N. Dettenrieder, H. M. Dietrich, C. Schadle, C. M. Mossmer, K. W. Tornroos and R. Anwander, *Angew. Chem. Int. Ed*., 2012, **51**, 4461; (i) N. Dettenrieder, C. Schadle, C. Mossmer, P. Sirsch and R. Anwander, *J. Am. Chem. Soc.*, 2014, **136**, 886; (k) R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams, and T. B. Marder, *J. Am. Chem. Soc.*, 1990, **112**, 9399; (l) K. M. Waltz and J. F. Hartwig, *Science*, 1997, **277**, 211; (m) Y. Segawa, M. Yamashita and K. Nozaki, *Angew. Chem. Int. Ed.*, 2007, **46**, 6710; (n) T. Kajiwara, T. Terabayashi, M. Yamashita and K. Nozaki, *Angew. Chem. Int. Ed.*, 2008, **47**, 6606; (o) Y. Segawa, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 9201; (p) T. Terabayashi, T. Kajiwara, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14162; (q) Y. Okuno, M. Yamashita and K. Nozaki, *Angew. Chem., Int. Ed.*, 2011, **50**, 920.

9 (a) L. M. Saleh, K. H. Birjkumar, A. V. Protchenko, A. D. Schwarz, S. Aldridge, C. Jones, N. Kaltsoyannis and P. Mountford, *J. Am. Chem. Soc.*, 2011, **133**, 3836 (b) S. Li, J. Cheng, Y. Chen, M. Nishiura and Z. Hou, *Angew. Chem. Int. Ed.*, 2011, **50**, 6360; (c) B. Wang, M. Nishiura, J. Cheng and Z. Hou, *Dalton Trans.*, 2014, 14215.

10 (a) R. Frank, J. Howell, R. Tirfoin, D. Dange, C. Jones, D. M. P. Mingos and S. Aldridge, *J. Am. Chem. Soc.*, 2014, **136**, 15730; (b) R. Frank, J. Howell, J. Campos, R. Tirfoin, N. Phillips, S. Zahn, D. M. P. Mingos, and S. Aldridge, *Angew. Chem. Int. Ed.*, 2015, **54**, 9586; (c) H. Braunschweig, M. Koster and K. W. Klinkhammer, *Angew. Chem. Int. Ed.*, 1999, **38**, 2229; (d) H. Braunschweig, C. Kollann, M. Koster, U. Englert and M. Muller, *Eur. J. Inorg. Chem.*, 1999, 2277; (e) H. Braunschweig, K. W. Klinkhammer, M. Koster and K. Radacki, *Chem. Eur. J.*, 2003, **9**, 1303.

11 (a) E. J. M. Deboer, L. C. T. Cate, A. G. J. Staring and J. H. Teuben, *J. Organomet. Chem*., 1979, **181**, 61; (b) J. Jeffery, M. F. Lappert, N. T. Luongthi, M. Webb, J. L. Atwood and W. E. Hunter, *J. Chem. Soc. Dalton*, 1981, 1593; (c) Z. Y. Guo, D. C. Swenson, A. S. Guram and R. F. Jordan, *Organometallics*, 1994, **13**, 766; (d) J. Vicente, M. T. Chicote, A. J. Martinez-Martinez, A. Abellan-Lopez and D. Bautista, *Organometallics*, 2010, **29**, 5693; (e) D. F. Chen, R. Scopelliti and X. L. Hu, *J. Am. Chem. Soc.*, 2010, **132**, 928.

12 DFT-M06: Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215.

13 F. Lavigne, E. Maerten, G. Alcaraz, N. Saffon-Merceron, C. Acosta-Silva, V. Branchadell and A. Baceiredo, *J. Am. Chem. Soc.*, 2010, **132**, 8864.

14 (a) W. A. Herrmann, J. Plank, M. L. Ziegler and K. Weidenhammer, *J. Am. Chem. Soc.*, 1979, **101**, 3133; (b) W. Sander, G. Bucher and S. Wierlacher, *Chem. Rev.*, 1993, **93**, 1583; (c) V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Angew. Chem. Int. Ed.*, 2006, **45**, 3488; (d) G. L. Geoffroy, J. B. Sheridan, S. L. Bassner and C. Kelley, *Pure Appl. Chem.*, 1989, **61**, 1723.

15 The Si–N bond cleavage of $[Me_2Si(C_5Me_4)(NPh)M(NMe_2)_3]$ (M = Nb, Ta) by photo-irradiation was reported: W. A. Herrmann and W. Baratta, *J. Organomet. Chem.*, 1996, **506**, 357.

16 (a) S. K. Zhao, C. Knors and P. Helquist, *J. Am. Chem. Soc.*, 1989, **111**, 8527; (b) H. M. L. Davies and T. Hansen, *J. Am. Chem. Soc.*, 1997, **119**, 9075; (c) J. L. Wood, B. M. Stoltz, H. J. Dietrich, D. A. Pflum and D. T. Petsch, *J. Am. Chem. Soc.*, 1997, **119**, 9641; (d) R. D. Haszeldine and J. G. Speight, *Chem. Commun.*, 1967, 995; (e) R. N. Haszeldine, R. Rowland, J. G. Speight and A. E. Tipping, *J. Chem. Soc. Perk. Trans.1*, 1979, 1943.

17 (a) J. E. Jackson, N. Soundararajan, M. S. Platz and M. T. H. Liu, *J. Am. Chem. Soc.*, 1988, **110**, 5595; (b) C. S. Ge, E. G. Jang, E. A. Jefferson, W. G. Liu, R. A. Moss, J. Wlostowska and S. Xue, *J. Chem. Soc. Chem. Comm.*, 1994, 1479; (c) A. Kuhn, C. Plug and C. Wentrup, *J. Am. Chem. Soc.*, 2000, **122**, 1945.

18 For examples of C-H activation of pyridines by rare-earth alkyl complexes, see: B. Guan and Z. Hou, *J. Am. Chem. Soc.*, 2011, **133**, 18086; (b) B. Guan, B. Wang, M. Nishiura and Z. Hou, *Angew. Chem. Int. Ed.*, 2013, **52**, 4418; (c) G. Song, W. O and Z. Hou, *J. Am. Chem. Soc.*, 2014, **136**, 12209.

19 (a) M. Brookhart, M. B. Humphrey, H. J. Kratzer and G. O. Nelson, *J. Am. Chem. Soc.*, 1980, **102**, 7802; (b) M. Brookhart, D. Timmers, J. R. Tucker, G. D. Williams, G. R. Husk, H. Brunner and B. Hammer, *J. Am. Chem. Soc.*, 1983, **105**, 6721;

(c) M. Brookhart and W. B. Studabaker, *Chem. Rev.*, 1987, **87**, 411; (d) D. F. Harvey and D. M. Sigano, *Chem. Rev.*, 1996, **96**, 271; (e) C. K. Murray, D. C. Yang and W. D. Wulff, *J. Am. Chem. Soc.*, 1990, **112**, 5660; (f) J. Pfeiffer and K. H. Dotz, *Angew. Chem. Int. Ed.*, 1997, **36**, 2828; (g) J. Pfeiffer, M. Nieger and K. H. Dotz, *Eur. J. Org. Chem.*, 1998, 1011.

20 For examples of reactions of alkenes with scandium alkyls, see: (a) M. Nishiura and Z. Hou, *Nature Chem.*, 2010, **2**, 257; (b) M. Nishiura, F. Guo and Z. Hou, *Acc. Chem. Res.,* 2015, **48**, 2209.

21 P. Braunstein, C. Frison and X. Morise, *Angew. Chem. Int. Ed.*, 2000, **39**, 2867.