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Homogeneous Catalysis

Selective Hydrosilation of CO_2 to a Bis(silylacetal) Using an Anilido Bipyridyl-Ligated Organoscandium Catalyst**

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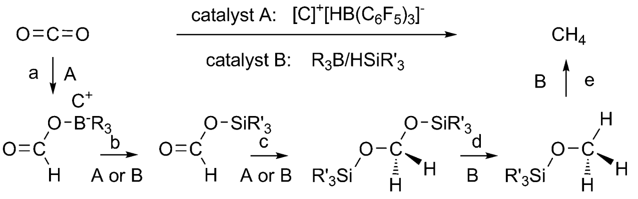
Abstract: *A rigid anilido bipyridyl ligand has been designed for use in an organoscandium-based carbon dioxide hydrosilation catalyst. Ligand attachment by alkane elimination results in metalation of an aryl C–H bond in a 3,5-di-tert-butylphenyl group installed on the pyridyl unit, thus rendering the ligand tetradentate. Insertion of CO_2 into the newly formed Sc–C bond leads to a κ^1 carboxylate which, when treated with the borane $B(C_6F_5)_3$, becomes hemilabile. In addition to activating the catalyst, the k^1 carboxylate effectively sequesters free $B(C_6F_5)_3$ and the ensemble is able to effectively hydrosilate CO_2, in the presence of excess Et_3SiH, almost exclusively to $R_3SiOCH_2OSiR_3$. A maximum turnover number of about 3400 (conversion of silane) is observed. Mechanistic experiments suggest that the sequestration of free $B(C_6F_5)_3$ by the hemilabile carboxylate contributes to the selectivity observed and prevents over reduction to methane.*

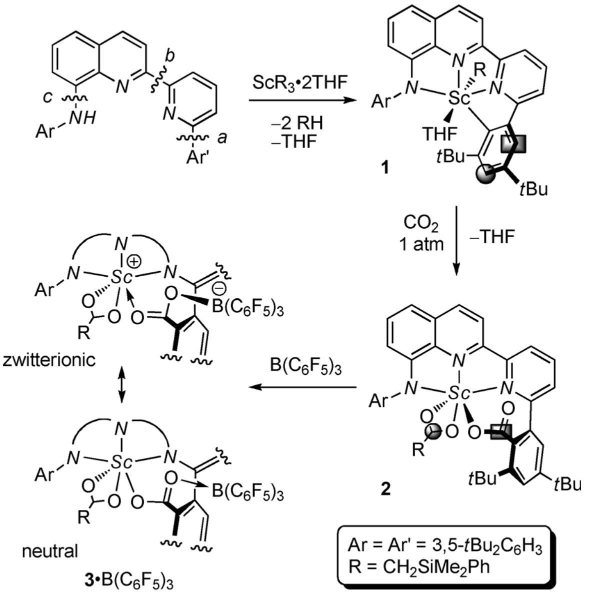
Carbon dioxide (CO_2) is a cheap, readily available source of carbon, and interest in its conversion into other, potentially more useful, organic molecules remains high.[1] In terms of reduction, effective homogeneous catalysts for hydrogenation to formic acid have been developed,[2] while reduction to methanol generally remains a challenge.[3] Selectivity in CO_2 reduction is thus a key consideration for both homo- and heterogeneous catalysts.[4]

Recently, we have described tandem catalysis[5] approaches to the hydrosilation of CO_2 to methane (Scheme 1).[6] The first transfer of hydride to CO_2 (step a) is mediated by an ion pair in which the cation is partnered with the hydridoborate counteranion $[HB(C_6F_5)_3]^-$.[7] Activation of the CO_2 through binding to the Lewis acid, $[C]^+$, enables this anion to deliver hydride to give a formatoborate which is rapidly converted into a silylformate (step b).[8] Subsequent steps (c–e) are well-documented $B(C_6F_5)_3$-catalyzed hydrosilation reactions,[9] with the ultimate CO_2-derived product being methane.



Scheme 1. Generalized tandem approach for hydrosilation of CO_2.

The observed accumulation of the bis(silylacetal) intermediate in tandem systems,[6b] where $[C]^+$ is $[Cp^*_2Sc]^+$ ($Cp^* = C_5Me_5$), suggests that step d (Scheme 1) is slow and raises the possibility of selective hydrosilation to this product, a formaldehyde equivalent. In this catalyst system, however, we were unable to develop reaction conditions wherein the reaction could be stopped at step d, mainly because of the inability to sequester free $B(C_6F_5)_3$ and prevent it from mediating the additional hydrosilation steps d and e.[9b] While a catalyst based on cationic β-diketiminato ("nacnac") organoscandium moieties[10] was moderately effective, this system was prone to degradation in the presence of CO_2 by transannular addition to the Sc(nacnac) ring.[11] We thus designed a new anilido bipyridyl (AbP) ligand system (Scheme 2) as a more robust ligand towards reactivity with CO_2 and with increased rigidity and denticity. This system is



Scheme 2. Synthesis of the complexes **1**, **2**, and **3**·$B(C_6F_5)_3$. THF = tetrahydrofuran.

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an effective platform for the selective hydrosilation of CO_2 to the bis(silylacetal) product.

The specific AbP ligand used here incorporates 3,5-di-*tert*-butylphenyl groups in the two aryl positions, but the synthesis of the ligand is modular and convergent, and provides gram quantities of the ligand in overall yields of 35–40% (see the Supporting Information for full details). The key starting material is 2,8-dibromoquinoline,[12] from which the bypyridyl portion of the ligand is constructed using a Negishi coupling to forge bond *b* (Scheme 2) from an in situ generated pyridyl zinc reagent.[12–13] The C–C bond *a* is made by a Kumada coupling from an aryl Grignard reagent and 2,6-dibromopyridine.[14] The final step installs the anilido donor by a Hartwig–Buchwald aniline arylation[12] at the 8-position of the quinoline building block. The free ligand is a crystalline and intensely yellow solid.

Ligand attachment proceeds smoothly using alkane elimination from the scandium tris(alkyl) complex $[Sc(CH_2SiMe_2Ph)_3{\cdot}2THF]$[15] as signaled by a rapid yellow to blue-green[16] color change upon mixing of the reagents (Scheme 2). However, instead of elimination of just one equivalent of RH to form a bis(alkyl) ligand complex, a second alkane is lost by metalation[17] of an aryl C–H bond in the pyridyl 3,5-di-*tert*-butyl group to form the monoalkyl complex **1**. This transformation is most apparent by the appearance of two mutually coupled ($^4J_{HH} = 1.1$ Hz) aryl resonances (each integrating to one proton) at $\delta = 7.97$ (rectangle) and $\delta = 7.59$ (circle) ppm in the ^1H NMR spectrum of this compound, and were assigned by using two-dimensional NMR correlation patterns to the inequivalent *tert*-butyl groups (see Figures S1 and S2 in the Supporting Information). Although the precise geometry at Sc in this molecule is not known, one THF ligand is retained, and it is likely that the rigidity of the ligand forces the NNNC framework to assume meridional coordination.

The compound **1** reacts rapidly and quantitatively with CO_2 to give the doubly inserted product **2**. The loss of the remaining THF solvate suggests that at least one of the carboxylates is bound in a κ^2 fashion. IR data was inconclusive (see Figure S3), but the ^{13}C NMR chemical shift of $\delta = 191.8$ ppm for the carboxylate carbon atom, highlighted with the circle (Scheme 2), is consistent with κ^2 coordination,[11] while the chemical shift of the carbon atom with the rectangle is quite different at $\delta = 173.1$ ppm. The compound **2** is marine blue in color and exhibits substantial thermal stability in solution, with no decomposition evident upon heating in C_7D_8 at 100 °C for several hours. Treatment of **2** with one equivalent of the electrophilic borane $B(C_6F_5)_3$ immediately results in complexation of the chelated carboxylate to form the adduct **3**$\cdot B(C_6F_5)_3$. The ^{13}C NMR shift of the alkyl carboxylate changes little ($\delta = 193.1$ ppm) in comparison to that of **2**, but the signal of the aryl carboxylate carbon atom shifts downfield to $\delta = 179.4$ ppm upon reaction with $B(C_6F_5)_3$. An X-ray structural analysis of **3**$\cdot B(C_6F_5)_3$ confirms this structure (Figure 1) and provides indirect corroboration of the assignments for **1** and **2**.

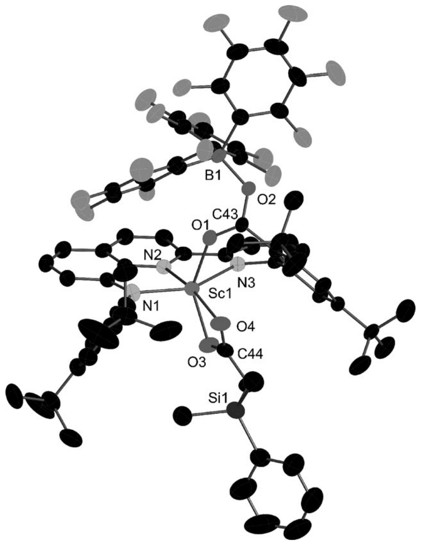
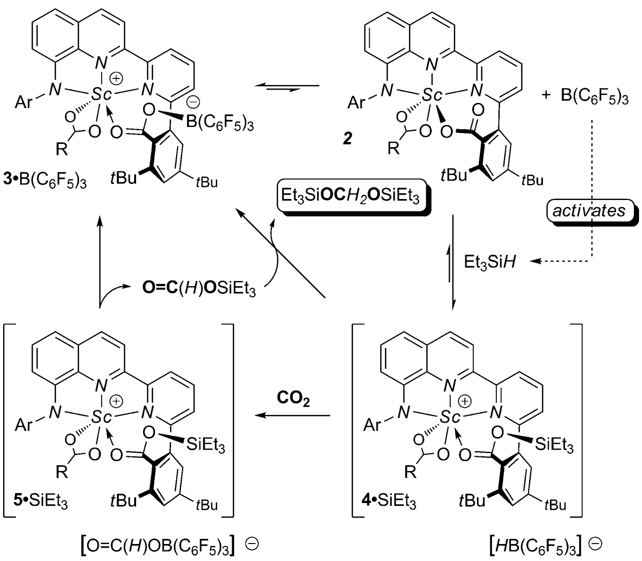


Figure 1. Thermal ellipsoid (50%) diagram of **3**$\cdot B(C_6F_5)_3$.[22] Selected bond lengths [Å]: Sc1–N1 2.096(3), Sc1–N2 2.214(3), Sc1–N3 2.329(3), Sc1–O1 2.076(2), Sc1–O3 2.129(3), Sc1–O4 2.129(2), O1–C43 1.240(4), C43–O2 1.276(4), O2–B1 1.553(4).

The scandium center in **3**$\cdot B(C_6F_5)_3$ exhibits distorted octahedral geometry with the NNN donors of the essentially planar anilido pyridyl pincer ligand occupying meridional sites. The amido bond Sc1–N1 is the shortest linkage, while the flanking Sc1–N3 pyridyl bond is 0.1 Å longer than the anchoring Sc1–N2 bond. The bond lengths along the Sc1-O1-C43-O2-B1 enchainment suggest that the structure is best represented as a zwitterionic structure as shown in Scheme 2, although contributions from a neutral structure through electron delocalization along this vector are probably significant. Even so, the Sc1-O1 length of 2.076(3) Å is longer than that found in a related scandium alkoxide (1.91 Å),[18] and the B1-O2 separation of 1.553(4) is slightly shorter than that of 1.594 Å in the $B(C_6F_5)_3$ adduct of ethyl benzoate.[19] Furthermore, the C43-O1 distance of 1.240(4) is shorter than the C43-O2 bond of 1.276(4) Å. The flexibility in the description of the core of the structure suggests a potential for reactivity with small molecules through hemilabile behavior of this linkage.[20]

The compound **3**$\cdot B(C_6F_5)_3$ is a robust catalyst precursor for CO_2 hydrosilation (Scheme 3), especially considering the generally high sensitivity associated with scandium-based catalysts. Catalytic runs employing a deficit of silane relative to CO_2 remained active even after the silane was fully depleted. Four sequential injections of a fresh charge of $[Et_3SiH]$ to the reaction resulted in resumed production of $Et_3SiOCH_2OSiEt_3$ at essentially the same rate (see Figure S6). Furthermore, a preparative scale reaction using 0.510 grams of Et_3SiH and 2.6 milligrams of **3**$\cdot B(C_6F_5)_3$ (0.1%) lead to isolation of 0.57 grams (94% yield) of pure product upon work up, thus representing a minimum turnover number (TON) of about 1000 (based on Et_3SiH consumed) under these reaction conditions. A TON of approximately 3400 was achieved using lower catalyst loadings (0.02%) and extended reaction times.

Monitoring a typical catalytic run by NMR spectroscopy (^1H, ^{11}B, ^{19}F) shows that **3**$\cdot B(C_6F_5)_3$ is rapidly converted into a new species in the presence of Et_3SiH. This species persists



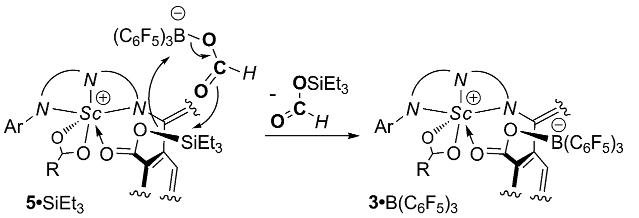
Scheme 3. Proposed mechanism for catalytic hydrosilation of CO_2: Rapid conversion of **3**·$B(C_6F_5)_3$ into **4**·$SiEt_3$ by hydrosilation of **2** leads to production of formatoborate. Silyl formate is eliminated from the postulated **5**·$SiEt_3$ to regenerate **3**·$B(C_6F_5)_3$, and is rapidly hydrosilated by **4**·$SiEt_3$.

through 50–100 turnovers and appears to be the resting state of the catalyst in the early stages of the catalysis, as long as $[Et_3SiH]$ is not zero. In low TON experiments, when the silane is fully depleted, **3**·$B(C_6F_5)_3$ is cleanly regenerated (see Figure S7).[21] We assign this new species as the ion pair **4**·$SiEt_3$ as shown in Scheme 3. Formation of this compound from **3**·$B(C_6F_5)_3$ is quantitative upon treatment with Et_3SiH in the absence of CO_2 and it has been fully characterized by multinuclear NMR spectroscopy (see Figures S8–S11). The presence of the $[HB(C_6F_5)_3]^-$ anion is clear from the ^1H, ^{11}B, and ^{19}F NMR data, while the cation features a ^{29}Si signal at $\delta = 41.7$ ppm and spectral data for the ligand framework similar to that of **3**·$B(C_6F_5)_3$.

We believe that **4**·$SiEt_3$ forms by $B(C_6F_5)_3$-catalyzed hydrosilation of **2**, which is in equilibrium[19] with **3**·$B(C_6F_5)_3$ by dissociation of borane from the neutral resonance structure of this compound (Scheme 2). Although this equilibrium lies far towards **3**·$B(C_6F_5)_3$, a slight deficit of $B(C_6F_5)_3$ leads to significant broadening of all NMR spectra, thus attesting to the dynamic nature of this system.

Formation of **4**·$SiEt_3$ from **2** and $B(C_6F_5)_3/Et_3SiH$ is rapidly reversible as demonstrated by the following two observations. First, treatment of the ion pair with Et_3SiD leads to rapid incorporation of deuterium into the $[HB(C_6F_5)_3]^-$ anion (see Figure S12). Second, when **4**·$SiEt_3$ is treated with an excess of a different silane (we used $EtMe_2SiH$), an equilibrium between **4**·$SiEt_3$ and **4**·$SiMe_2Et$ was rapidly established (see Figure S13). Although it may seem surprising that the carbonyl group of **4**·$SiEt_3$ is not fully hydrosilated by transfer of hydride from the hydridoborate counteranion, an examination of the structure of **3**·$B(C_6F_5)_3$ suggests that this carbonyl group is quite sterically protected on both faces by the *ortho tert*-butyl group and the NNN ligand framework.

Thus, within this system (i.e. **3**·$B(C_6F_5)_3 \rightleftarrows$ **2** + $B(C_6F_5)_3 \rightleftarrows$ **4**·$SiEt_3$) the free borane is effectively sequestered in **3**·$B(C_6F_5)_3$ or the hydridoborate anion and very little free borane is available for the hydrosilation of the product bis(silylacetal). This product is formed rapidly when mixtures of **4**·$SiEt_3$ and free silane are treated with CO_2 (Scheme 3). The intermediate **5**·$SiEt_3$ is not observed but we presume it forms through a low-barrier process in which CO_2 is activated by the cationic scandium center and accepts a hydride from the hydridoborate.[6b] The resulting formatoborate anion can then nucleophilically attack the $SiEt_3$ group, thus leading to formation of the silylformate $O{=}C(H)OSiEt_3$ and regeneration of **3**·$B(C_6F_5)_3$. This process is plausibly depicted in Scheme 4 and is consistent with the minimal free $[B(C_6F_5)_3]$ present in these solutions. Under catalytic conditions, the silylformate is not generally observed, and we believe that it is rapidly hydrosilated by **4**·$SiEt_3$ in the presence of excess silane. This notion is supported by the observation that when separately synthesized $O{=}C(H)OSiEt_3$ (see the Supporting Information for details) is reacted with in situ generated **4**·$SiEt_3$, $Et_3SiOCH_2OSiEt_3$, and **3**·$B(C_6F_5)_3$ are rapidly produced.



Scheme 4. Proposed nucleophilic attack of formatoborate on SiEt3, thus forming silylformate and regenerating **3**·$B(C_6F_5)_3$.

In conclusion, we present a robust scandium-based catalyst for the selective hydrosilation of CO_2 to the bis(silylacetal) $Et_3SiOCH_2OSiEt_3$ using triethylsilane. Over reduction to methane is avoided because free $B(C_6F_5)_3$, a known catalyst for the hydrosilation of O−C bonds, is minimized by its favorable interaction with the catalyst precursor **2** and the rapid, cooperative Si−H bond cleavage by **2** and $B(C_6F_5)_3$. The shuttling of $B(C_6F_5)_3$ and "$[SiEt_3]^+$" electrophiles across the κ^1 carboxylate group is a novel feature of this catalyst system and we seek to exploit it in next-generation catalysts based on this metalated AbP ligand system.

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[15] We employ this tris(alkyl) derivative because of its crystallinity, thermal stability, and availability in high yield.

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[21] In experiments with lower catalyst loadings, the NMR spectra indicate that **4**·$SiEt_3$ slowly converts to another major species which remains catalytically active. We believe this species arises by the gradual hydrosilation of the κ^2 carboxylate ligand to an alkoxide ligand, but there is a lack of definitive evidence for this proposal. Further work is necessary to determine the nature of this species, but the data indicates that the κ^1 $O{=}COER_3$ moiety [$E = SiEt_3$ or $B(C_6F_5)_3$] remains intact for continued catalytic turnover.

[22] CCDC 966857 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.