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Reactivity of Scandium β-Diketiminate Alkyl Complexes with Carbon Dioxide†

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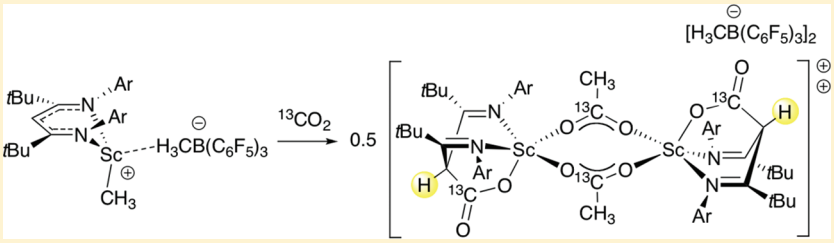
Supporting Information



ABSTRACT: The reactions of two highly air- and moisture-sensitive scandium bis(alkyls) supported by a bulky β-diketiminato (nacnac) ligand with carbon dioxide are described. [κ^2-ArNC(^{t}Bu)CHC(^{t}Bu)NAr]ScR$_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; R = CH$_3$, **1a**; R = CH$_2$SiMe$_3$, **1b**) react rapidly with CO$_2$ to give mixtures of mono- and bis(carboxylato) insertion products **2a**/**2b** and **3a**/**3b** depending on the stoichiometry and conditions of the reaction. Compound **2a** (R = CH$_3$) is a dimeric complex with bridging acetato groups, as determined by X-ray crystallography. These compounds were characterized by NMR spectroscopy, and **3a** could be isolated in pure form. Treatment of these compounds with excess CO$_2$ resulted in addition to the central carbon of the Sc(nacnac) six-membered ring and displacement of the nitrogen donors to yield dimeric scandium carboxylates **4a**/**4b**; compound **4b** was characterized by X-ray crystallography. Reactions of the nacnac scandium cations formed upon abstraction of one or two methides from **1a** using B(C$_6$F$_5$)$_3$ with CO$_2$ were also explored. Although the products were qualitatively more thermally robust, eventually ligand displacement occurred in these cationic acetato complexes as well. Nevertheless, insertion products were characterizable in solution using NMR spectroscopy. Overall, this study shows the facility with which CO$_2$ is taken up by scandium alkyls but that the nacnac ligand framework is too reactive to support chemistry aimed at catalytic conversion of CO$_2$ into other products.

INTRODUCTION

The activation and conversion of carbon dioxide (CO$_2$) into useful products has long been recognized by organometallic chemists as a desirable goal because of its plentitude and attractive economic attributes as a C$_1$ synthon.[1−4] More recently, activity in this area has also been motivated by the growing effect of high levels of atmospheric CO$_2$ on global climate trends.[5,6] New catalytic reactions involving CO$_2$ as a feedstock are, therefore, of considerable interest, although, realistically, the benefits of such reactions will (unfortunately) continue to be economic rather than environmental since the scales at which they must be run in order to mitigate atmospheric CO$_2$ are daunting even if they use more carbon than they generate.[7]

One of the most established reactivity modes of CO$_2$ is insertion into M−H or M−C bonds.[8,9] This is especially facile when M is an early transition metal or an alkaline earth metal;[10] indeed, the seminal work of Grignard[11] on the conversion of organomagnesium reagents to carboxylic acids exemplifies this chemistry. However, the high oxophilicity of these elements means that turnover by conversion of the resulting M−O bond is thermodynamically difficult,[12] and so these tend to be stoichiometric reactions for such metals, unless subsequent reactions also involve formation of M−O bonds.[13] In this context, a recent report by Kawaguchi et al.,[14] wherein a cationic organozirconium compound supported by a tridentate bis(phenoxide)-aryl ether ligand[15] was found to catalyze the hydrosilylation of CO$_2$ in the presence of the Lewis acidic cocatalyst B(C$_6$F$_5$)$_3$, is intriguing. While turnovers and activities were moderate, the B(C$_6$F$_5$)$_3$/silane reagent system[16,17] was able to provide a thermodynamic driver for the conversion of the zirconium carboxylate intermediates that presumably form upon reaction of the Zr−C bond with CO$_2$.[18,19] Mechanistic details for this system remain somewhat obscure, but it demonstrates that an early metal approach to hydrosilylation of CO$_2$ using B(C$_6$F$_5$)$_3$ as a cocatalyst is promising.

Inspired by this study, we have begun to examine organoscandium catalyst precursors for useful CO$_2$ conversion chemistry. A handful of CO$_2$ insertions into Sc−C[20,21] and Sc−Si[22] bonds have been reported, but subsequent chemistry of the carboxylate products has not been explored in detail. We have a long-standing interest in the chemistry of neutral[23−26] and cationic[27−30] organoscandium compounds supported by the β-diketiminato, or "nacnac", ligand framework[31] and report here some initial studies on the reactivity of compounds **1a**−**1d**, shown in Scheme 1, with CO$_2$. These compounds incorporate the

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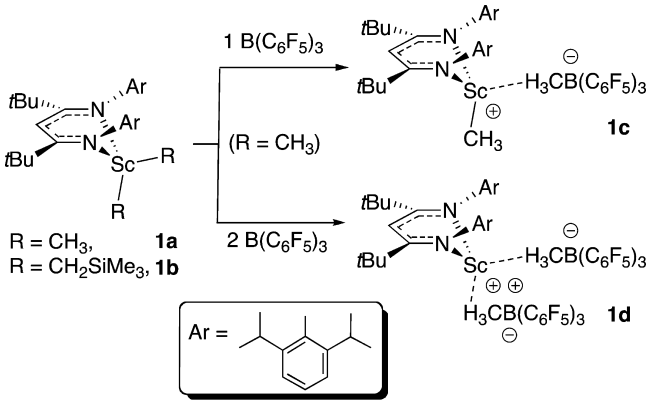
Scheme 1



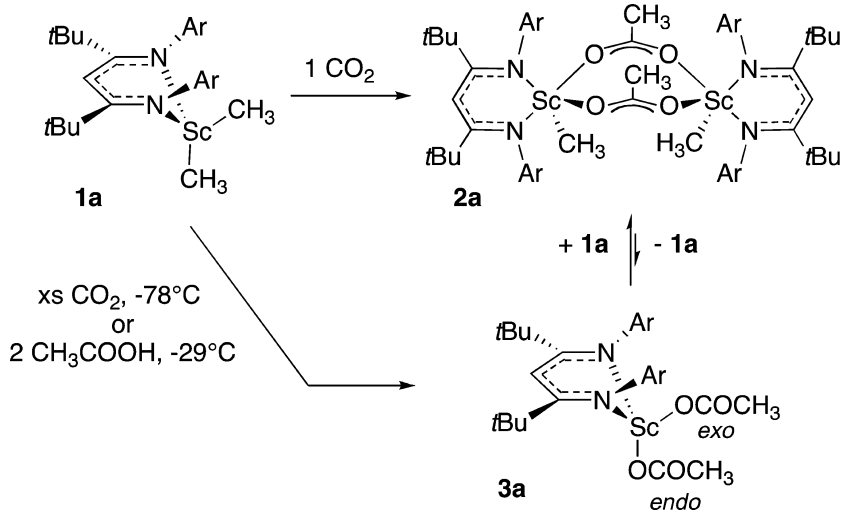
bulky nacnac ligand featuring 2,6-diisopropylphenyl groups on the nitrogen and *tert*-butyl groups on the imine carbons of the diketiminato backbone,[32] affording well-defined, base-free neutral dialkyl compounds, here the dimethyl (**1a**) and bis(trimethylsilyl)-methyl (**1b**) derivatives. When the dimethyl compound is treated with 1 or 2 equiv of the alkide abstracting[33] Lewis acid $B(C_6F_5)_3$,[34,35] the well-behaved mono- (**1c**) and dicationic (**1d**)[29] ion pairs are formed; together, these four compounds provide a well-understood platform for probing the reactivity of CO_2 with organoscandium compounds. Organoscandium compounds are notoriously Lewis acidic,[36] and exploration of their fascinating chemistry would not be possible without the foundational techniques for handling such compounds developed by Wilhelm Johann Schlenk.[37,38]

RESULTS AND DISCUSSION

Initial experiments on the reaction of dimethyl complex **1a** with excess CO_2 gas at room temperature gave complex product mixtures, so more careful investigations using stoichiometric quantities of CO_2 at lower temperatures were undertaken and the chemistry summarized in Scheme 2 was consequently revealed. Treatment of **1a** with 1 equiv of CO_2 in toluene at room temperature gave a mixture of compounds identified as the dimeric mono insertion product **2a** (70−80%) along with 10−15% each of the starting dimethyl complex and the bis insertion product, diacetate **3a**. This latter compound could be prepared and isolated as a pure compound via two methods. Treatment of **1a** with an excess of CO_2 at −78 °C, followed by removal of the CO_2 atmosphere prior to warming, led to excellent yields of **3a**; this reaction is sufficiently rapid that no intermediates or unreacted starting materials were detected by NMR spectroscopy on a sample maintained at −78 °C for the CO_2 addition and immediately inserted into a probe precooled to the same temperature. Compound **3a** was also synthesized independently by reaction of **1a** with 2 equiv of rigorously dried acetic acid at −29 °C (*ortho*-xylene/liq. N_2 bath). The precise coordination mode of the acetato ligands could not be established on the basis of a structural determination, but the high solubility of **3a** in aromatic solvents and its characteristic fluxional[24] NMR behavior are indicative of a monomeric structure. In the ^{1}H NMR spectrum at room temperature, there is a single resonance for the acetate methyl groups that broadens and decoalesces as the temperature is lowered, re-emerging as two singlets for the diastereotopic endo and exo groups now distinct on the NMR time scale. The barrier for this exchange was estimated to be $\Delta G^{\ddagger}$ = 10.5 kcal/mol at the temperature of coalescence (240 K), similar to values obtained for a variety of bis(alkyl) scandium nacnac derivatives.[24] A dimeric complex would be expected to exhibit a quite different dynamic behavior due to the presence of three diastereomeric forms (i.e., endo/endo, exo/exo, and endo/exo) for dimeric scandium nacnac compounds.[39]

Mixing equimolar amounts of pure **1a** and **3a** establishes the equilibrium with the dimeric mono insertion product **2a** through ligand metathesis; unfortunately, attempts to study the temperature dependence of this equilibrium were hampered by the poor solubility of **2a** in aromatic solvents at low temperatures and the tendency of **1a** to undergo metalation[24] at higher temperatures. Because dimer **2a** comprises 70−80% of the mixture at room temperature and is of lower solubility, it can be preferentially crystallized from these solutions, or those obtained by reaction of **1a** with 1 equiv of CO_2, as described above. X-ray analysis of crystals obtained in this way confirmed the dimeric structure of **2a**, featuring bridging acetato groups and terminal scandium methyl groups; redissolution of these crystals reproduces the equilibrium mixture of compounds indicated in Scheme 2. A thermal ellipsoid diagram of the molecular structure of **2a** is shown in Figure 1, along with selected metrical parameters. The molecule has a crystallographic C_2

Scheme 2



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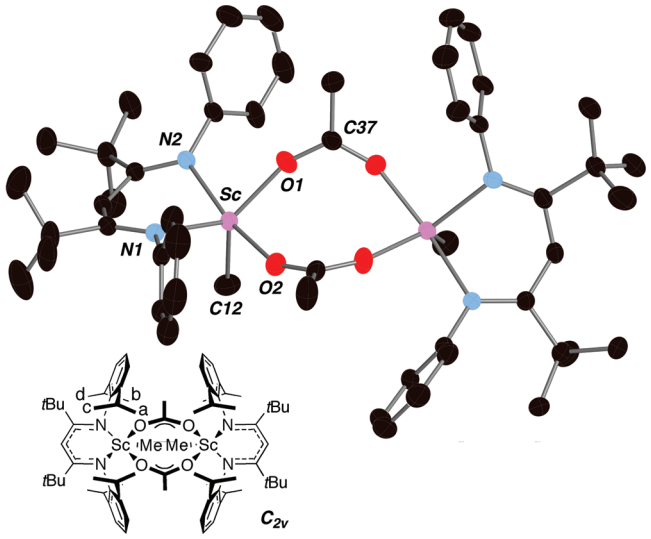


Figure 1. Thermal ellipsoid diagram (50%) of **2a**; isopropyl groups on the Ar substituents have been removed for clarity. The inset shows a stick depiction of the structure. Selected bond distances (Å): Sc–N(1), 2.1879(12); Sc–N(2), 2.1925(12); Sc–O(1), 2.0635(12); Sc–O(2), 2.0864(11); Sc–C(12), 2.2109(18). Selected bond angles (deg): N(1)–Sc–(N2), 88.22(5); O(1)–Sc–O(2), 83.45(5); N(2)–Sc–O(2), 167.18(5); N(1)–Sc–C(12), 104.84(6); O(1)–Sc–C(12), 128.58(7); N(1)–Sc–O(1), 126.57(5).

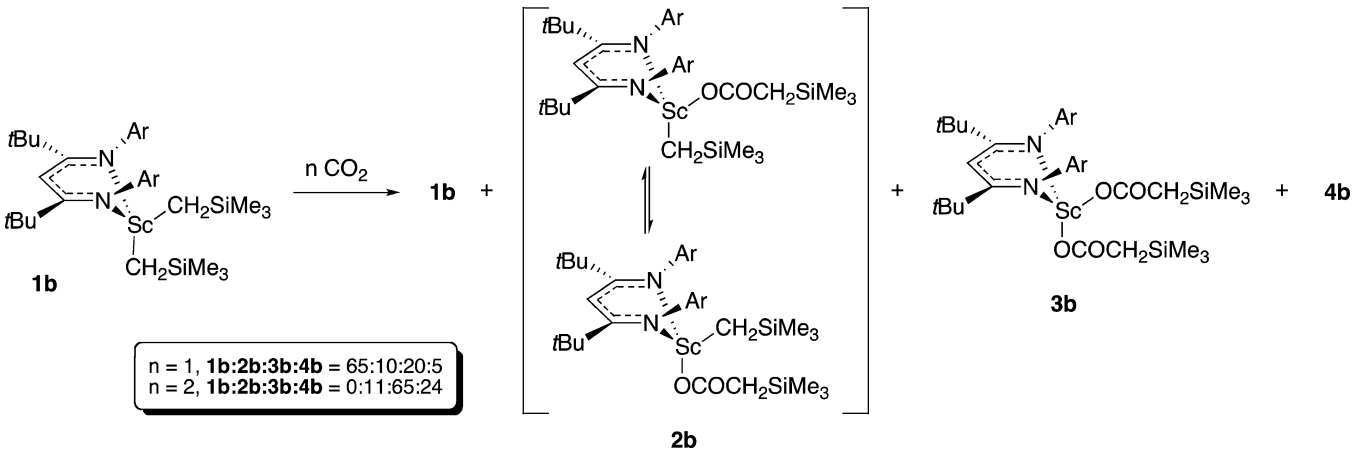
symmetry relating the two halves of the dimer, with a distorted trigonal-bipyramidal geometry at the scandium centers; N(1), O(1), and C(12) occupy the trigonal plane, while N(2) and O(2) are in the apical positions (N(2)–Sc–O(2) = 167.18(5)°). The axial atoms N(2) and O(2) exhibit slightly longer distances to Sc as compared with their equatorial counterparts, but all distances to scandium fall into typical ranges. As is common for scandium nacnac compounds, the scandium center lies out of the plane defined by the five essentially coplanar ligand atoms, here by 0.955 Å.

The solution behavior of **2a** is complex. In addition to the aforementioned equilibrium with **1a** and **3a**, dimer **2a** exists as a mixture of three isomers in solution, in an approximately 30:15:1 ratio. As mentioned above, this behavior is anticipated for dimeric scandium nacnac complexes.[39] Typically, exchange between the three possible diastereomers is slower on the NMR time scale than the exchange of endo and exo positions in monomeric compounds, and so all isomers are apparent in the room-temperature NMR spectra. A ^{1}H–^{1}H EXSY NMR experiment showed crosspeaks between the singlet resonances for the nacnac ligand CH protons, indicative of exchange between the major isomer and both minor isomers (Figure S1, Supporting Information). However, exchange peaks between the two minor isomers were not observed, indicating that this exchange is too slow to observe by NMR spectroscopy, or that the crosspeaks are not of high enough intensity to resolve. The lesser of the two minor isomers exhibited a higher degree of asymmetry than the others, giving rise to two ligand methyne resonances in a 1:1 ratio, but assignments and solution structure are difficult to comment on due to weak signal-to-noise ratios and/or overlapping signals. It appears, however, on the basis of 2D ^{1}H–^{1}H ROESY experiments, that the major isomer corresponds to the structure observed in the solid state, averaged into a C_{2v} symmetric structure. Of the four diastereotopic methyl groups (a–d, Figure 1, inset), one correlates with the acetate methyl groups (a) and one with the Sc-methyl group (b), while the others, which are pointed away from the molecular core, do not. The other two isomers are variations on this structure wherein the nacnac ligand ring "flips" its conformation relative to the other ligand in the dimer.[39]

When an analogous set of reactions was performed with **1b**, incorporating the bulkier CH_2SiMe_3 alkyl ligands, a slightly different chemistry was observed (Scheme 3). Reaction with 1 equivalent of CO_2 led to mixtures of unreacted starting material, mono insertion product **2b** and the bis(carboxylate) **3b**, along with the appearance of a further product, **4b** (vide infra), in a 65:10:20:5 ratio, indicating that the rate of insertion of CO_2 into the second Sc–C bond is competitive with that of the first. Even when 2 equiv of CO_2 were employed, the product mixture remained complex, although all of the starting material was consumed; a mixture of **2b**, **3b**, and **4b** was obtained in an 11:65:24 ratio.

Unlike the dimeric **2a**, it appears that **2b**, incorporating the bulkier substituted carboxylate group, remains monomeric, based on the following three observations. First, addition of **1b** to a mixture of **2b**, **3b**, and **4b** generated as described above did not perturb the ratio of the compounds as was observed in the "**a**" series, suggesting that ligand redistribution processes (which likely proceed via dimers) are suppressed in the CH_2SiMe_3 substituted compounds. Second, the ^{1}H NMR spectra for **2b** are broad at room temperature and, when cooled to 235 K, resolve into two distinct sets of resonances, consistent with the formation of diastereomers in which the two different groups

Scheme 3



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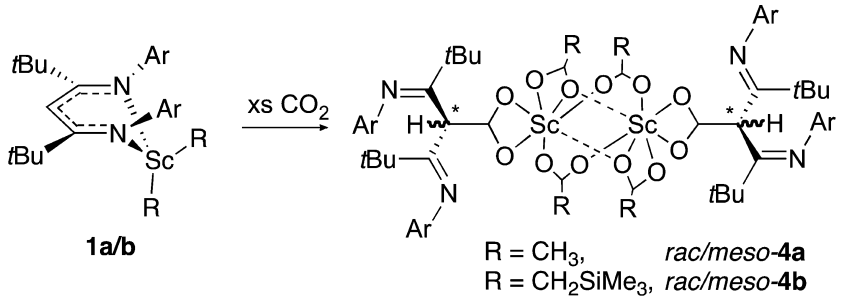
Scheme 4



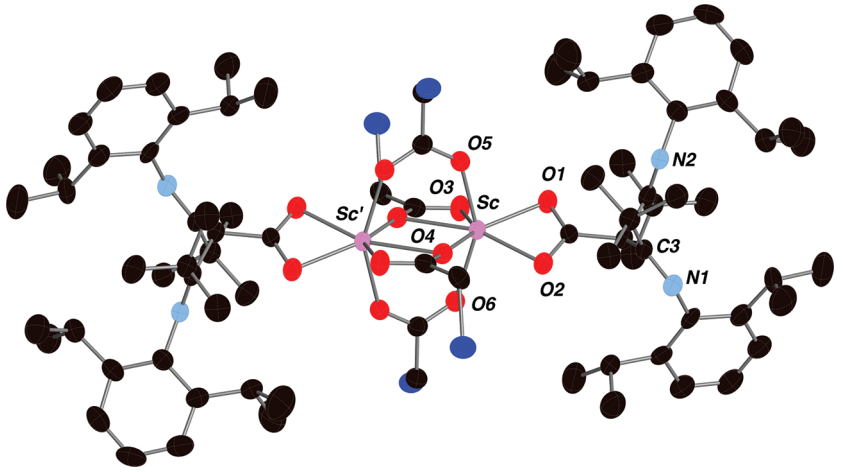


Figure 2. Thermal ellipsoid diagram (50%) of *rac*-**4b**; methyl groups attached to the silicon atoms have been removed for clarity. Selected bond distances (Å): Sc−O(1), 2.158(3); Sc−O(2), 2.175(3); Sc−O(3), 2.180(3); Sc−O(4), 2.2.110(3); Sc′−O(4), 2.337(3); Sc−O(5), 2.091(3); Sc−O(6), 2.116(3); C(3)−N(1), 1.273(5); C(5)−N(2), 1.260(5).

(alkyl and carboxylate) occupy the endo and exo coordination sites (see Scheme 3). This is commonly observed for scandium nacnac compounds with two different ligands R[24] and contrasts with the three different isomers typically observed for dimeric structures.[39] Finally, the chemical shifts for the carboxylate carbon atoms in these two diastereomers are nearly coincident (193.4 and 193.1 ppm) and are characteristic of terminal carboxylates, which occur further upfield than those in bridging carboxylates (cf. 178.2 ppm for **2a**). The bis(carboxylate) product **3b** is, like **2b**, monomeric and fluxional. At room temperature, ^{1}H NMR spectra consistent with an averaged C_{2v} symmetrical structure are observed, and lowering the temperature to 245 K freezes out the expected endo/exo fluxional behavior. The exchange between isomers occurs with an estimated barrier of $\Delta G^{\ddagger}$ = 11.6 kcal/mol, slightly higher than that found in **2a**, as anticipated due to the added bulk of the alkyl group.

The reactions of bis(alkyl) compounds **1a**/**1b** with an excess of CO_2 eventually produce compounds **4a**/**4b**, which derive from addition of a third equivalent of CO_2 to the ScN_2C_3 framework, followed by decoordination of the two nitrogen donors; the result is the formation of scandium carboxylate dimers, as shown in Scheme 4. This was assessed mainly via an X-ray analysis of the product **4b** (vide infra) but finds precedent in the addition of other unsaturated molecules to nacnac Al,[40] Ru,[41] and Pt[42] complexes in an analogous fashion. Here, the electropositive, Lewis acidic scandium center, in cooperation with the basic central carbon of the nacnac ligand, is able to activate the CO_2 ligand.[43,44] Addition of the CO_2 across the nacnac-Sc ring in this way triggers the decoordination of the two imine donors and formation of a (presumably) thermodynamically favored tris(carboxylate) complex, that by virtue of the removal of steric bulk around the metal imposed by the nacnac ligand is able to dimerize into a species with four bridging carboxylate ligands. These reactions proceed at room temperature over the course of a few hours to yield solutions of **4a**/**4b** that give complex proton NMR spectra (Figures S2 and S3, Tables S1−S4, Supporting Information).

The molecular structure of the CH_2SiMe_3-substituted derivative **4b** is shown in Figure 2 along with selected bond distances. The dimer has a crystallographic center of inversion, rendering the two halves of the dimer identical. Each scandium center is coordinated by seven carboxylate oxygen atoms; the ligand derived from the nacnac framework is a terminal κ^2O,O′carboxylato ligand, whereas those arising from the CH_2SiMe_3 groups bridge the two scandium centers via two distinct modes. In one mode, two carboxylato ligands bridge the scandium centers via a symmetrical μ-carboxylato-κO:κO′ span. The other mode is less symmetrical in the sense that one of the oxygen atoms, O(4), is tilted toward the second scandium center such that it forms a weak interaction and bridges the metal centers. The Sc−O(4) bond distance of 2.110(3)Å is similar to the others in the molecule, but the distance to the second scandium is substantially longer (Sc′−O(4), 2.337(3)Å).[45] As a consequence of this weaker interaction, the scandium centers are seven coordinate, with a distorted pentagonal-bipyramidal geometry in which the atoms of the symmetrically bridging carboxylato ligands, O(5) and O(6), occupy the apical sites.

In the decoordinated nacnac ligand, the C−N bonds are now clearly double bonds (C−N distances are 1.275(5) and

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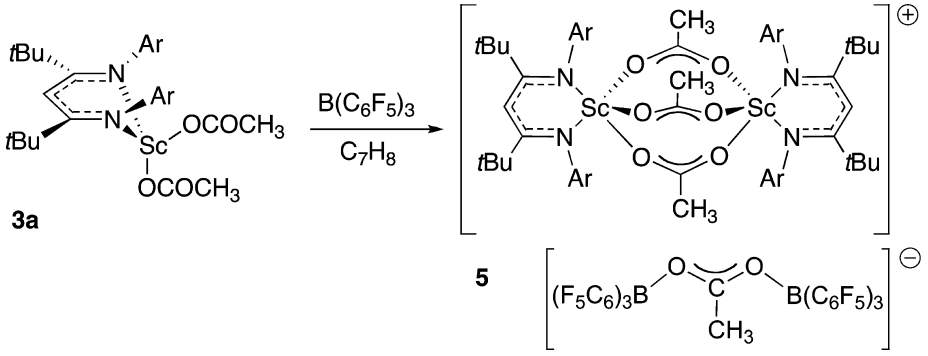
Scheme 5



1.260(5)Å). Additionally, the imine moieties differ in their geometry in that one features *trans*-*N*-aryl and *t*Bu groups, the other *cis*, as drawn in Scheme 4. Consequently, the diimine methyne carbons are chiral and the complexity of both the ^{1}H and the ^{13}C NMR spectra can be explained by invoking the presence of rac and meso diastereomers of **4a** and **4b**; the C_2 symmetric S:R/R:S diastereomer preferentially crystallizes and is the isomer depicted in Figure 2, assigning the *cis*-imine moiety as the higher priority group.[46] In solution, however, both diastereomers are in evidence; this is particularly evident in the ^{13}C NMR spectra, where a doubling of most of the resonances is observed for both compounds. Although it is not possible to assign the sets of resonances to a particular diastereomer, it is clear that they are both present in each case. A complete listing of the observed ^{1}H and ^{13}C NMR resonances for these compounds is given in Tables S1−S4 (Supporting Information).

The CO_2-induced decoordination process described above represents a potential catalyst degradation pathway in any reactions mediated by neutral compounds **1**, for example, hydrosilylation. Indeed, while turnover is observed in the hydrosilylation of CO_2 using $B(C_6F_5)_3$ as a cocatalyst in a similar way to that reported by Kawaguchi et al., the reactions terminate quite quickly. Since $B(C_6F_5)_3$ is known to form the monocationic **1c** and dicationic **1d** (Scheme 1), we postulated that the preformation of these cations might dissuade the ligand from undergoing displacement due to stronger Sc−N bonding. We therefore tested this postulate by preparing cations via reactions of **3a** with $B(C_6F_5)_3$ and treatment of cations **1c** and **1d** with CO_2.

Reaction of the well-defined neutral bis(acetate) compound **3a** with 1 equiv of $B(C_6F_5)_3$ indicated that the borane was capable of abstracting an acetate ligand from scandium. A single product was rapidly formed, which we assign as the dimeric cation **5** (Scheme 5).

Here, a putative monomeric ion pair of the formula $[(nacnac)Sc(O_2CCH_3)]^+[H_3CC(O)OB(C_6F_5)_3]^-$ probably forms, but the carbonyl group of the counteranion coordinates the remaining half equivalent of borane,[47,48] while the cationic scandium acetate dimerizes with the unreacted bis(acetate) **3a**. The use of an excess of $B(C_6F_5)_3$ (up to 5 equiv relative to scandium) had no effect on the outcome of the reaction. In ion pair **5**, the dimeric cation is overall C_s symmetric, with two five coordinate scandium centers bridged by two distinct acetate groups found in a 1:2 ratio. Signals for the acetato methyl groups are found at 2.03 and 1.03 ppm in the ^{1}H NMR spectrum, whereas acetate carbon nuclei appear in the region associated with bridging acetates at 181.3 and 181.0 ppm in the ^{13}C NMR spectrum. In 2D $^{1}H-^{1}H$ ROESY experiments, the methyl groups of the bridging acetates correlate to resonances for the aryl isopropyl groups; the strong upfield shift to 1.01 ppm of one set of acetate groups is likely due to the influence of a proximal aryl ring. Conversely, the signal for the methyl group of the bridging acetate group in the counteranion (2.10 ppm) shows no correlations to nacnac ligand resonances. The averaged C_s symmetry of the cation is also implied by the appearance of four septets and eight separate doublets for the aryl isopropyl groups, and two singlets for the *tert*-butyl groups on the ligand backbone. Attempts to isolate ion pair **5** resulted in recovery of oily, clathrate-like materials, a common phenomenon in early metal cation chemistry utilizing these perfluoroarylborates as weakly coordinating anions.[40,49−52] This material is stable in solution, but under an atmosphere of CO_2 at room temperature, conversion to a mixture of products is observed.

The above observations imply that, for acetato ligands, there is a strong tendency for the cations to dimerize, despite the considerable bulk of the nacnac ligand employed. This trend is also apparent in the products of the reactions of CO_2 with the cationic compound **1c**. When **1c** is generated in situ from $(nacnac)ScMe_2$ and $B(C_6F_5)_3$ and reacted with 1 equiv of CO_2 at temperatures near the freezing point of C_6D_5Br (−20 to −30 °C), clean formation of a new product formulated as the dimer **6** is observed (Figure 3). The precise structure of this compound is unknown, but a four coordinate, acetate bridged structure of high symmetry is indicated by the following spectroscopic observations. One septet and two doublets are observed for the *N*-aryl isopropyl groups in the ^{1}H NMR spectra, consistent with averaged C_{2v} symmetry; this pattern is observed to the freezing point of the C_6D_5Br solvent (245 K). ^{19}F NMR spectroscopy shows that the methylborate counteranions do not interact significantly with the scandium center by virtue of the small $\Delta_{m,p}$ value of 2.7 ppm.[35,53] Finally, the observed ^{1}H and ^{13}C NMR chemical shifts of 1.65 and 183.6 ppm, respectively, are consistent with bridging, rather than terminal, acetato groups.

The assignment of **6** as a dimer is also convincingly demonstrated by its reactivity with varying equivalencies of $^{13}CO_2$ (Figure 3; note that, when generated in situ in this way, the irreversibly formed briding acetato groups are also labeled with ^{13}C). The inset of Figure 3 shows the evolution of the region of the ^{1}H NMR spectrum associated with the ligand backbone C-*H* resonances, and the chemistry depicted outlines our interpretation of these observations. Upon introduction of 1 equiv of $^{13}CO_2$ to solutions of **6**, the singlet for the CH group in **6** (red dot) transforms into a singlet at 6.17 ppm (dark blue) and a doublet at 5.79 ppm ($^{2}J_{CH}$ = 6.8 Hz, light blue) in a 1:1 ratio, which we assign as the unsymmetrical dimer **7** in which one of

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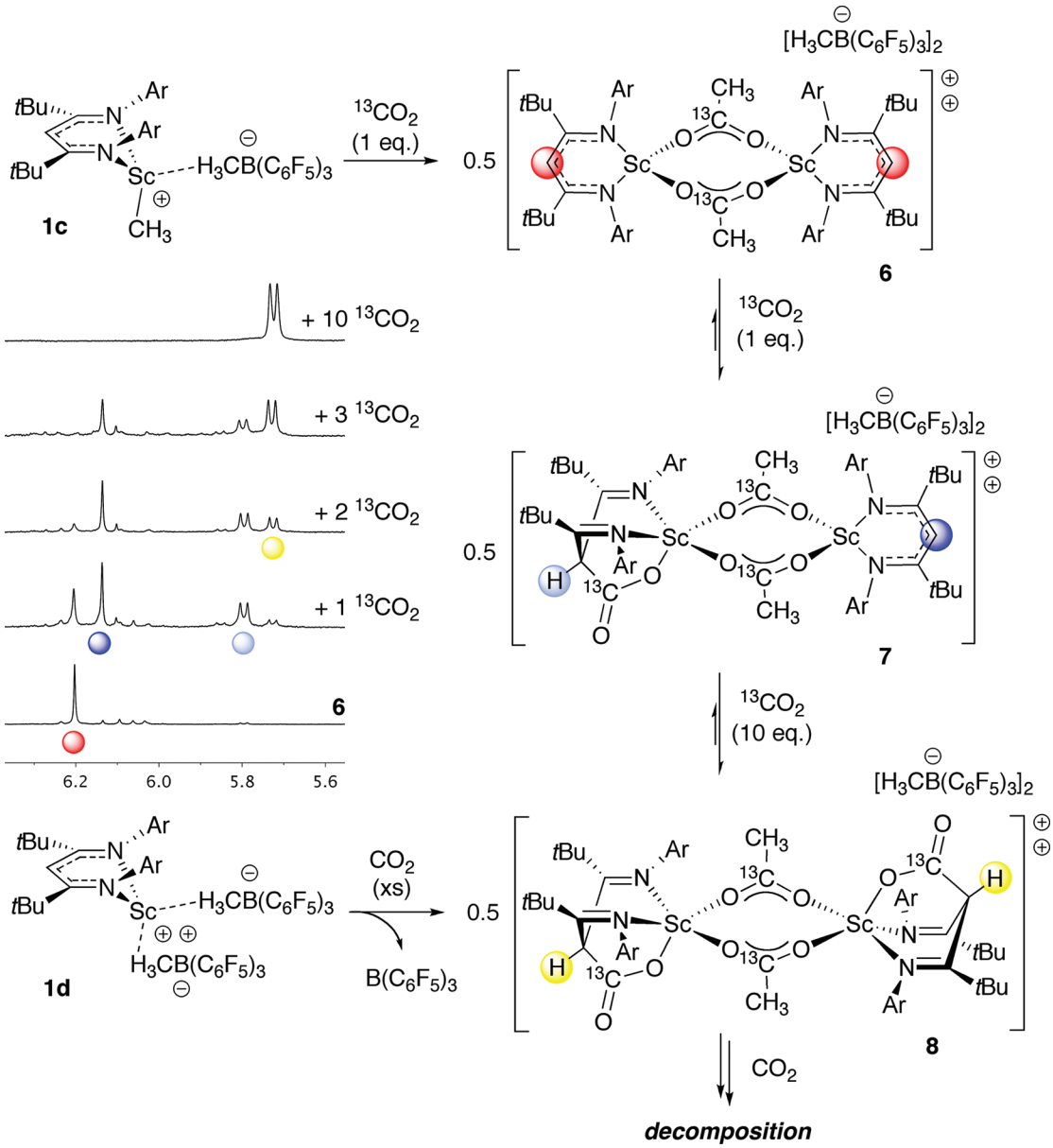

Figure 3. Reactions of nacnac scandium cations **1c** and **1d** with CO_2. Inset: a portion of the 400 MHz NMR spectrum of the reaction of **1c** with varying equivalencies of $^{13}CO_2$, showing the dimeric nature of the ionic complexes **6**, **7**, and presumably **8**.

the nacnac ligands has been modified through transannular bonding of CO_2, in a similar fashion to that proposed above in the formation of compounds **4a** and **4b**. Minor amounts of a second product are already in evidence, and as more $^{13}CO_2$ is added, the doublet for this species at 5.72 ppm grows in until it is the only compound present (yellow dot). In this product, **8**, $^{13}CO_2$ has added to both Sc(nacnac) rings of the dimer and is a highly symmetrical species on the basis of its ^{1}H NMR spectrum (see Figure S7, Supporting Information). It may also be formed directly from either **1c** or **1d** when treated with an excess of CO_2 and slowly decomposes, presumably via ligand displacement processes, upon prolonged residence in solution under an atmosphere of CO_2. The capture of CO_2 by the nacnac ligand framework is reversible; upon exposure of the ^{13}C-labeled **8** to an atmosphere of unlabeled CO_2, the doublet at 5.72 ppm disappears in favor of a singlet as the coupling to the ^{13}C nucleus is lost. None of the compounds **6**–**8** were isolable as solids, instead emerging as oily materials upon attempted workup procedures. Since the ^{19}F NMR data for each of these species indicate that the $[H_3CB(C_6F_5)_3]^-$ anions do not interact significantly with the scandium centers via the methide group ($\Delta_{m,p}$ = 2.5 ppm for both **7** and **8**), the poor crystallinity of these ionic compounds is not surprising.

Overall, these results suggest that cationic nacnac scandium methyl ions undergo rapid insertion of CO_2 to give acetates and subsequent addition of further CO_2 equivalents to the nacnac-Sc ring. Ligand displacement, although qualitatively slower in the cationic systems, is still the ultimate fate of these compounds. Nonetheless, it is clear that the oxophilic nature of scandium renders it highly reactive toward CO_2. For example, when the reaction of **1b** with 3 atm of CO_2 at 235 K was monitored by ^{1}H NMR spectroscopy, kinetic modeling of speciation plots indicated that the first insertion (to form **2b**) occurred with a pseudo-first-order rate constant of $\approx 2.3 \times 10^{-3}$ s^{-1}, and the second insertion (to form **3b**) took place at only slightly slower rates ($k_{obs} \approx 0.4 \times 10^{-3}$ s^{-1}). Unfortunately, the

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ligand displacement processes leading to compound **4b** also ensued to a significant degree under these conditions, again suggesting that more robust ancillary ligands are required for the development of scandium-based catalysts for reduction of CO_2 using, for example, silanes as the sacrificial reductant. Investigations along these lines are currently underway.

EXPERIMENTAL SECTION

General Procedures and Equipment. An argon atmosphere MBraun glovebox was employed for manipulation and storage of all oxygen and moisture-sensitive compounds. Reactions were performed on a double manifold high-vacuum line using standard techniques. Toluene and hexane were dried using the Grubbs/Dow purification system[54] and stored over sodium/benzophenone in evacuated glass vessels. Benzene and pentane were predried and distilled from 3 Å molecular sieves, then stored over sodium/benzophenone in evacuated glass vessels. Bromobenzene and d_5-bromobenzene were predried and distilled from 3 Å molecular sieves, then stored over fresh sieves in the glovebox. d_6-Benzene and d_8-toluene were predried and distilled from sodium/benzophenone and stored in a glass vessel in the glovebox. NMR spectra were obtained on Bruker DRX400, AVANCE 400 MHz, AVANCE III 400 MHz, or AVANCE III 600 MHz spectrometers. ^{1}H and ^{13}C{^{1}H} chemical shifts were referenced to residual proton, and naturally abundant ^{13}C resonances of the deuterated solvent, respectively, relative to tetramethylsilane. ^{11}B NMR spectra were referenced to an external standard of $BF_3{\cdot}OEt_2$, and ^{19}F NMR to an external standard of $CFCl_3$. NMR spectra were processed and analyzed with MestReNova software (v6.2.1-7569). Glacial acetic acid (EMD chemicals) was purified by refluxing at 110 °C over acetic anhydride and $KMnO_4$ under an argon atmosphere for 1.5 h, followed by fractional distillation into a Schlenk flask. Tris(pentafluorophenyl)-borane ($B(C_6F_5)_3$) was doubly sublimed at 65 °C under static vacuum and stored in the glovebox. Carbon dioxide, bone-dry grade 3.0, and $^{13}CO_2$ (99% ^{13}C) were obtained from Praxair and Cambridge Isotopes, respectively, and used as received. Compounds $LSc(CH_3)_2$ (**1a**), $LSc(CH_2Si(CH_3)_3)_2$ (**1b**), $[LScMe][H_3CB(C_6F_5)_3]$, and $[LSc][H_3CB(C_6F_5)_3]_2$ (L = 2,6-(*i*-Pr)$_2$C$_6$H$_3$)NC(*t*-Bu)}$_2$CH) were prepared according to reported literature procedures.[29] Elemental analyses were obtained by the Instrumentation Facility of the Department of Chemistry, University of Calgary.

Generation of 2a. A 10 mm diameter resealable tube was charged with **1a** (125 mg, 0.035 mmol) and 0.4 mL of C_6H_6. The resulting yellow solution was degassed by freeze−pump−thaw cycles. CO_2 was expanded into a 19.1 mL transfer bulb (34 mmHg, 0.035 mmol) and deposited into the tube at −196 °C. The tube was warmed to room temperature and allowed to stand for 4 h. The resulting yellow crystalline solid was isolated by filtration in the glovebox, then washed with cold benzene and hexanes (79 mg, 59%). ^{1}H NMR (400 MHz, C_7D_8) major isomer: δ 7.02, 6.91, 6.8 (m, C_6H_3), 6.07 (s, 1H, CH), 3.84, 2.96 (sp, 2H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 1.53, 1.38, 1.19, 0.90 (d, 6H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 1.17 (s, 18H, $C(CH_3)_3$), 0.26 (s, 3H, $ScCH_3$), 0.14 (s, 3H, $OCOCH_3$). ^{13}C NMR (101 MHz, C_6D_6): 178.2 ($OCOCH_3$), 177.1 ($NCC(CH_3)_3$), 144.9 (C_{ipso}), 142.1, 128.9, 128.8 (C_6H_3), 98.5 (CH), 45.03 ($C(CH_3)_3$), 33.6, 32.0 ($C(CH_3)_3$), 32.6 ($CH(CH_3)_2$), 28.7, 28.4 ($CH(CH_3)_2$), 22.6 ($OCOCH_3$). Anal. Calcd for $C_{82}H_{123}BrN_4O_4Sc_2$ (**1a,** containing 1 C_6H_5Br of solvation): C, 70.41; H, 8.86; N, 4.01. Found: C, 69.58; H, 8.94; N, 4.04.

Synthesis of 3a. Method A: A 50 mL flask was charged with **1a** (200 mg, 0.347 mmol) and 5 mL of toluene. CO_2 was expanded into the flask (1 atm), and the mixture was stirred for 3 h at −78 °C to ensure complete reaction. The flask was evacuated for 15 min at this temperature to remove unreacted CO_2, then warmed slowly to room temperature to remove the solvent in vacuo. The resulting yellow oil was triturated with pentane, and the solvent was removed to give a yellow powder (210 mg, 97%). Method B: A 50 mL two-neck flask was charged with **1a** (126 mg, 0.218 mmol) and toluene (25 mL) and cooled to −29 °C with an *ortho*-xylene/LN_2 cold bath. Rigorously dried acetic acid (25 μL, 0.437 mmol) was added to the solution via a gastight microsyringe and stirred for 1 h. The solution was then warmed to room temperature, and the solvent was evacuated in vaccuo. The resulting oily yellow solid was triturated with pentane to give a fine yellow solid (123 mg, 85%). ^{1}H NMR (400 MHz, C_7D_8): δ 7.04 (6H, C_6H_3), 6.08 (s, 1H, CH), 3.26 (sp, 2H, $CH(CH_3)_2$, $^2J_{HH}$ = 6.7 Hz), 1.60 (s, 3H, $OCOCH_3$), 1.36, 1.33 (d, 12H, $^2J_{HH}$ = 6.7 Hz, $CH(CH_3)_2$), 1.16 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (101 MHz, C_7D_8): 191.2 ($OCOCH_3$), 173.4 ($NCC(CH_3)_3$), 145.4 (C_{ipso}), 142.0 (C_6H_3), 124.7, 123.3 (C_6H_3), 96.2 (CH), 44.5 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 28.7 ($CH(CH_3)_2$), 26.2, 25.7 ($CH(CH_3)_2$), 22.6 ($OCOCH_3$). Anal. Calcd for $C_{39}H_{59}N_2O_4Sc_2$: C, 70.45; H, 8.94; N, 4.21. Found: C, 70.05; H, 8.72; N, 4.20.

Generation of 2b. A resealable NMR tube was charged with **1b** (10 mg, 0.014 mmol) and C_7D_8 and degassed at −78 °C. CO_2 was expanded into a 19.1 mL transfer bulb (14 mmHg, 0.014 mmol) and condensed into the tube at −196 °C. The tube was warmed to room temperature and allowed to stand for 1 h. The resulting solution contained a mixture of **2b**, **3b**, and **4b**. NMR spectra were recorded at 245 K, and assignments were made with reference to speciation plots and 2D NMR experiments. Endo/exo isomers were detected in solution; only one isomer is reported here. ^{1}H NMR (600 MHz, C_7D_8, 245 K): 7.06 (m, 6H, C_6H_3), 6.04 (s, 1H, CH), 3.87, 2.96 (sp, 4H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.6 Hz), 1.90 (s, 2H, $OCOCH_2$), 1.77, 1.53, 1.23, 1.15 (d, 6H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.6 Hz), 1.15 (s, $C(CH_3)_3$), 0.37, 0.10 (s, 9H, $SiC(CH_3)_3$), 0.24 (s, 2H, $ScCH_2$). ^{13}C NMR (151 MHz, C_7D_8, 245 K): 193.4 ($OCOCH_2$), 175.4 ($NCC(CH_3)_3$), 145.8 (C_{ipso}), 142.8, 141.5, 126.2, 124.9, 124.6 (C_6H_3), 94.8 (CH), 45.1 ($C(CH_3)_3$), 32.9 ($C(CH_3)_3$), 29.2 ($OCOCH_2$), 29.9, 29.0, 28.7, 27.03, 25.9, 25.2 ($CH(CH_3)_2$), 4.6 ($Si(CH_3)_3$), −0.5 ($OCOCH_2Si(CH_3)_3$). The Sc-CH_2 carbon nucleus was not detected.

Generation of 3b. A procedure identical to that for the synthesis of **2b** was used, but 2 stoichiometric equiv of CO_2 were employed (27 mmHg, 0.028 mmol). ^{1}H NMR (600 MHz, C_7D_8): 7.05 (m, 6H, C_6H_3), 6.06 (s, 1H, CH), 3.32 (br, 4H, $CH(CH_3)_2$), 1.62 (d, 4H, $ScCH_2$, $^2J_{HH}$ = 6.9 Hz), 1.40, 1.36 (d, 12H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.6 Hz), 1.19 (s, 18H, $C(CH_3)_3$), 0.05 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (151 MHz, C_7D_8): 192.8 ($OCOCH_2$), 173.5 ($NCC(CH_3)_3$), 145.8 (C_{ipso}), 142.25, 125.61, 124.60 (C_6H_3), 95.82 (CH), 44.60 ($C(CH_3)_3$), 32.33 ($C(CH_3)_3$), 29.10 ($OCOCH_2$), 28.60, 26.72, 25.81 ($CH(CH_3)_2$), −0.62 ($Si(CH_3)_3$).

Generation of 4a. A resealable NMR tube was charged with **1a** (16 mg, 0.028 mmol) and C_7D_8. The tube was degassed at −78 °C, and CO_2 was expanded into the tube (1 atm), which was allowed to stand at room temperature overnight. Isomerism is evident in the NMR spectra by nearly coincident or overlapping sets of peaks; only the major isomer is reported here. See Figure S2 and Tables S1 and S3 in the Supporting Information for a complete list of peaks. **4a**: ^{1}H NMR (400 MHz, C_7D_8): δ 7.21, 7.04 (m, C_6H_3), 5.49 (s, 1H, CH), 3.98, 3.78, 2.94, 2.85 (app p, 1H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 2.24, 2.02 (s, 3H, $OCOCH_3$), 1.78, 0.78 (s, 9H, $C(CH_3)_3$), 1.55, 1.42, 1.41, 1.36, 1.35, 1.34, 1.28, 1.22 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz). ^{13}C{^{1}H} NMR (101 MHz, C_7D_8): δ 191.6 (OCOSc), 188.5, 184.6, 184.0, 181.5 ($OCOCH_3$), 173.6, 168.9 ($NCC(CH_3)_3$), 145.7, 145.6 (C_{ipso}), 137.1, 135.3, 134.9, 133.2 ($CCH(CH_3)_2$), 124.0, 123.9, 123.8, 123.5, 123,1, 122.7 (C_6H_3), 56.7 (CH), 45.1, 43.5 ($C(CH_3)_3$), 31.2, 28.9 ($C(CH_3)_3$), 29.7, 28.3, 26.9, 26.6, 25.9, 23.9, 23.2, 21.8 ($CH(CH_3)_2$), 22.9 ($OCOCH_3$).

Generation of 4b. A procedure identical to that for the synthesis of **4a** was used, but beginning with **1b**. Isomerism is evident in the NMR spectra by nearly coincident or overlapping sets of peaks; only the major isomer is reported here. See Figure S3 and Tables S2 and S4 in the Supporting Information for a complete list of peaks. ^{1}H NMR (400 MHz, C_7D_8): δ 7.32, 7.06 (m, C_6H_3), 5.50 (s, 1H, CH), 4.02, 3.89, 2.94, 2.86 (sp, 1H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 1.98 (s, 2H, $OCOCH_2$), 1.98 (d, 2H, CH_2Si, $^2J_{HH}$ = 10.4 Hz), 1.79, 0.77 (s, 9H, $C(CH_3)_3$), 1.54, 1.46, 1.41, 1.36, 1.35, 1.32, 1.27, 1.22 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 0.19 (s, 18H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (101 MHz, C_7D_8): δ 192.6 (OCOSc), 185.2, 185.0 ($OCOCH_2$), 173.7, 169.5 ($NCC(CH_3)_3$), 146.2 (C_{ipso}), 137.3, 136.0, 135.8, 133.0 ($CCH(CH_3)_2$), 124.3, 124.1, 124.0, 123.8, 123.6, 123.5 (C_6H_3), 57.4 (CH), 45.7, 44.3 ($C(CH_3)_3$), 31.8, 29.3 ($C(CH_3)_3$), 30.1, 28.8, 27.4,

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27.3, 26.1, 24.1, 23.5, 22.2 ($CH(CH_3)_2$), 30.5 ($OCOCH_2$), −0.9 ($Si(CH_3)_3$).

Generation of 5. A resealable NMR tube was charged with **3a** (9 mg, 13 μmol), $B(C_6F_5)_3$ (7 mg, 14 μmol), and C_7D_8, then shaken briefly at room temperature to give a yellow solution. ^1H NMR (400 MHz, C_7D_8): δ 6.97 (m, 12H, C_6H_3), 6.01 (s, 2H, CH), 2.95, 2.84, 2.67, 2.36 (sp, 2H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 2.12 (BCH_3), 2.03 (s, 6H, $OCOCH_3$), 1.18, 1.09 (s, 18H, $C(CH_3)_3$), 1.33, 1.29, 1.23, 1.08, 1.03, 0.94, 0.87, 0.48 (d, 6H, $CH(CH_3)_2$, $^2J_{HH}$ = 6.6 Hz), 1.03 (s, 12H, $OCOCH_3$). ^{13}C NMR (101 MHz): δ 185.6 (OCOB), 181.3, 181.0 ($OCOCH_3$), 179.2, 170.0 ($C(CH_3)_3$), 146.3, 143.0 (C_{ipso}), 140.3, 139.9, 139.0, 137.4 ($CCH(CH_3)_2$), 127.5, 126.2, 125.5, 125.2, 124.9, 124.3 (C_6H_3), 97.6 (CH), 44.2, 44.0 ($C(CH_3)_3$), 31.3, 29.7 ($C(CH_3)_3$), 33.4, 28.7, 28.4, 27.1 ($CH(CH_3)_2$), 28.1, 27.9, 27.4, 26.8, 26.2, 24.6, 24.5, 24.4 ($CH(CH_3)_2$), 25.3, 23.3 ($OCOCH_3$), 23.4 (br, $BOCOCH_3$). ^{19}F NMR (376 MHz): δ −135.1 (app d, 6F, *o*-CF, $^3J_{FF}$ = 21 Hz), −160.0 (app t, 3F, *p*-CF, $^3J_{FF}$ = 20 Hz), −166.1 (br, 6F, *m*-CF, $^3J_{FF}$ = 20 Hz). ^{11}B NMR (128 MHz): −14.5.

Generation of 6. A d_5-bromobenzene solution of $[LScCH_3][CH_3B(C_6F_5)_3]$ was prepared in situ by mixing precooled solutions of **1a** (11 mg, 19 μmol) and $B(C_6F_5)_3$ (10 mg, 19 μmol) in a vial and storing in the freezer of the glovebox for 2 h. The resulting yellow/orange solution was transferred to a resealable NMR tube and quickly immersed in a cold bath (−20 to −30 °C). The tube was degassed with freeze−pump−thaw cycles; then $^{13}CO_2$ was expanded into a 19.1 mL transfer bulb (19 mmHg, 20 μmol) and deposited into the tube at −196 °C. The tube was warmed to room temperature and allowed to stand for 30 min. ^1H NMR (400 MHz, C_6D_5Br): δ 7.16, 7.02 (m, C_6H_3), 6.20 (s, 1H, CH), 2.14, (sp, 4H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 1.65 (d, 3H, $OCOCH_3$, $^2J_{HC}$ = 6.1 Hz), 1.13, 0.79 (d, 6H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7 Hz), 1.03 (s, 18H, $C(CH_3)_3$), 0.99 (s, BCH_3). ^{13}C NMR (101 MHz): 183.8 ($OCOCH_3$), 139.6, 138.44, 128.39, 125.03 (C_6H_3), 91.02 (CH), 44.46 ($C(CH_3)_3$), 31.18 ($C(CH_3)_3$), 30.14 ($CH(CH_3)_2$), 29.81, 25.24 ($CH(CH_3)_2$), 23.47 ($OCOCH_3$). Poor signal-to-noise resulted from the complex oiling out of solution. C_{ipso} carbon nuclei were not detected. ^{19}F NMR (376 MHz): δ −135.1 (br, 6F, *o*-CF), −160.0 (br, 3F, *p*-CF), −166.1 (br, 6F, *m*-CF). ^{11}B NMR (128 MHz): δ −14.5.

Generation of 8. A procedure similar to that for the synthesis of **6** was used, but 10 stoichiometric equiv of $^{13}CO_2$ were deposited (186 mmHg, 0.19 mmol), and NMR data were collected after 16 h. ^1H NMR (400 MHz, C_6D_5Br): δ 7.09, 6.98 (m, 6H, C_6H_3), 5.72 (d, 1H, CH, $^3J_{HC}$ = 6.8 Hz), 2.39, 2.30 (sp, 4H, $CH(CH_3)_2$, $^2J_{HH}$ = 6.6 Hz), 1.15, 1.05, 1.02, 0.95, (d, 6H, $CH(CH_3)_2$, $^2J_{HH}$ = 6.6 Hz), 1.09 (s, CH_3B), 0.95 (s, 18H, $C(CH_3)_3$), 0.33 (d, 3H, $^2J_{HC}$ = 6.2 Hz, $OCOCH_3$). $^{13}C\{^1H\}$ NMR (101 MHz): 182.8 (nondecoupled q, $^2J_{HC}$ = 6.2 Hz, $OCOCH_3$), 164.4 (nondecoupled d, $^3J_{HC}$ = 6.7 Hz, OCOSc), 129.7, 125.1 (C_6H_3), 29.1 ($C(CH_3)_3$), 30.25, 28.3 ($CH(CH_3)_2$), 26.8, 23.9, 23.4, 22.3 ($CH(CH_3)_2$), 20.6 ($OCOCH_3$). Poor signal-to-noise resulted from the complex oiling out of solution. Quaternary carbon nuclei were not detected. ^{19}F NMR (376 MHz): −131.8 (app d, 6H, *o*-CF, $^3J_{FF}$ = 21 Hz), 164.1 (app t, 3H, *p*-CF, $^3J_{FF}$ = 21 Hz), 166.6 (app t, 6H, *m*-CF, $^3J_{FF}$ = 21 Hz). ^{11}B NMR (128 MHz): δ −14.5.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data files for compounds **2a** and **4b** and Figures S1−S7 and Tables S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Biography

Warren Piers obtained his B.Sc. degree at the UBC in 1984 and continued there as a NSERC Postgraduate Scholar under the tutelage of Prof. Michael Fryzuk, graduating with a Ph.D. in 1988. He then spent two years at the California Institute of Technology as an NSERC and Killam Postdoctoral Fellow with Prof. John Bercaw. From 1990 to 1995, he was an Assistant Professor at the University of Guelph. He then moved back to western Canada to join the Chemistry Department at the University of Calgary as an Associate Professor. In July 2000, he was appointed to the S. Robert Blair Chair in Polymerization Catalysis and Polymer Synthesis, an endowed research chair sponsored by Nova Chemicals, and promoted to Full Professor. His research interests include the development of synthetic applications of perfluoroaryl boranes, mechanistic organometallic chemistry in catalysis, and the development of novel boron-based organometallic materials. Piers has more than 180 independent scholarly publications and several patents; in addition to the inaugural Schlenk Lecture Award, Piers' honors include the Province of Ontario's John C. Polanyi Prize in Chemistry (1991), an Alfred P. Sloan Foundation Research Fellowship (1996−2000), an NSERC E. W. R. Steacie Memorial Fellowship (2000−2002), the Royal Society of Canada Rutherford Medal in Chemistry (2000), the Merck Frosst Center for Therapeutic Research Award (2003), and the CSC Alcan Lecture Award (2005). In 2006, he became an Elected Fellow of the Royal Society of Canada and in January 2012 will take up a Canada Council of the Arts Killam Research Fellowship for two years. Other interests include music, wine, and mountaineering (not necessarily in that order).

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■ DEDICATION

[†]Dedicated to my friends and colleagues at the University of Tübingen for their hospitality during a three-week stay as the

inaugural Schlenk Lecturer and Guest Professor in October 2011.

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