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Early Metal Metallocenium Hydridoborate Catalysts for Carbon Dioxide Hydrosilation

Chiu, Frederick Sin Nang


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Early Metal Metallocenium Hydridoborate Catalysts for Carbon Dioxide Hydrosilation

by

Frederick Sin Nang Chiu

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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Abstract

A series of permethylmetalallocenium(III) hyridotris(pentafluorophenyl)borate complexes was synthesized and investigated as CO₂ hydrosilation catalysts in tandem with a B(C₆F₅)₃ co-catalyst. The increasing d electron count across the series of metals studied (Sc<sup>III</sup>: d⁰, Ti<sup>III</sup>: d¹, V<sup>III</sup>: d²) gave rise to contrasting kinetic behaviours as catalysts. The Sc- and Ti-based systems demonstrated sigmoidal hydrosilane consumption characteristic of two operative catalytic pathways. In particular, the activation of the secondary, more active catalytic pathway was attributed to the build-up of the hydrosilation intermediate, bis(triethylsiloxyl)methane in the initial stages of the reaction. This acetal species is capable of binding to the Sc<sup>III</sup> and Ti<sup>III</sup> centers, resulting in the observed reactivity. In the V<sup>III</sup> system, the electronic configuration precludes coordination of this acetal intermediate, resulting in the operation of only the initial pathway. In addition, carbonyl poisoning of the V<sup>III</sup> center allowed for insights to the role of the metal catalyst in the dual catalyst system.
Acknowledgements

I would like to thank Prof. Warren Piers for his guidance through my degree. Thank you for your continued effort and invaluable advice, which were of immense help in leading my project in the right direction. Under your supervision, I was trained with the highest level of rigor, where I was able to learn and grow as a scientific researcher. I would like to also thank Drs. Thomas Baumgartner and Roland Roesler for being part of my supervisory committee and offering valuable suggestions.

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During my time in the Piers group, I had the opportunity to work alongside talented coworkers and enjoy the company of great friends. Thanks to Matt Sloan, Bryan, Mike, Frankie, Denis, and Rich in assisting me through the continuous struggles in scientific research, and passing on the knowledge and expertise you have harnessed in your own scientific careers. I would also like to thank my chemistry friends, Chris, Aaron, Joel, Etienne, Adrian, Juan, Anjan, Rashi, Joy, and many others, for a great graduate experience out here in Alberta.

I wouldn’t have pursued a career in chemistry if it weren’t for my sisters Cindy, Alice and Lilian, who have piqued my scientific curiosity at a young age. Now we know what happened to the (annoying) little brother who was given an undergraduate chemistry textbook to play with at the age of seven. I’m grateful to my father, who continued to support my questionable hobby throughout high school that eventually led to me pursuing this degree. It would have been quite difficult making the important life choices that led to this degree without my supportive and loving parents.

Lastly, I am grateful to the University of Calgary and the Department of Chemistry for financial support during my studies.
For my dear sister Lilian,

1979 – 2000
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<td>br</td>
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<td>confer</td>
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<td>carbon monoxide dehydrogenase</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
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<td>pentamethylcyclopentadienyl</td>
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<tr>
<td>d</td>
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<td>DME</td>
<td>1,2-dimethoxyethane</td>
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<td>DMSO</td>
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<tr>
<td>ECP</td>
<td>effective core potential</td>
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<tr>
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<td>eq.</td>
<td>equivalent(s)</td>
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<td>Et</td>
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<tr>
<td>FLP</td>
<td>frustrated Lewis pair</td>
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<td>Fourier transform</td>
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Me  methyl
Mes  mesityl / 1,3,5-trimethylphenyl
mg  milligram(s)
MHz  megahertz
min  minute(s)
 mL  milliliter(s)
 mM  millimolar
mmHg  millimetres of mercury
mol  mole(s)
NHC  N-heterocyclic carbene
NMR  nuclear magnetic resonance
or  ortho
p  para
Ph  phenyl
pin  pinacolate
pm  picometer(s)
ppm  part(s) per million
PTA  1,3,5-triaza-7-phosphaadamantane
PTFE  poly(tetrafluoroethylene)
q  quartet
RT  room temperature
s  singlet (NMR)
str  stretch
sym  symmetric
t  triplet
t-Bu  tert-Butyl
Tf  Triflyl (OTf, triflate)
THF  tetrahydrofuran
TMP  2,2,6,6-tetramethylpiperidine
TOF  turnover frequency
TON  turnover number
TS  transition state
vib  vibration
w  weak
XRD  X-ray diffraction
°C  degrees Celsius
9-BBN  9-borabicyclo[3.3.1]nonane
Å  Ångstrom(s)
μeff  effective magnetic moment
μL  microliter(s)
μmol  micromole(s)
Chapter One: Introduction

1.1 The Chemistry of CO$_2$

CO$_2$ is a small, linear molecule. Despite being an overall nonpolar molecule, each C–O bond is polar, rendering CO$_2$ susceptible to nucleophilic attack at the carbon atom and electrophilic attack at oxygen. However, the activation of CO$_2$ is thermodynamically challenging, as seen in Eq. (1.1–1.6). The potentials for the half equations involving CO$_2$ reduction are invariably negative at pH 7, indicating that an energy penalty is required. In addition, CO$_2$ reduction causes a decrease in the C–O bond order by filling the π$^*$ orbital, resulting in the concomitant bending of the molecule. This reorganization energy, due to the change in geometry, is reflected in the very negative potential of the one-electron reduction of the linear CO$_2$ to the bent radical anion CO$_2$· (Eq. 1.1). However, in cases where the reduction steps are coupled with protonation (Eqs. 1.3–1.6), relatively mild reducing conditions are sufficient.

\[
\begin{align*}
\text{CO}_2 \text{ (aq)} + e^- & \rightarrow \text{CO}_2^- \text{ (aq)} \quad E^{\circ'} = -1.9 \text{ V} \quad (1.1) \\
\text{CO}_2 \text{ (g)} + 2\text{H}^+ + 2e^- & \rightarrow \text{CO} \text{ (g)} + \text{H}_2\text{O} \quad E^{\circ'} = -0.52 \text{ V} \quad (1.2) \\
\text{CO}_2 \text{ (g)} + \text{H}^+ + 2e^- & \rightarrow \text{HCO}_2^- \text{ (aq)} \quad E^{\circ'} = -0.43 \text{ V} \quad (1.3) \\
\text{CO}_2 \text{ (g)} + 4\text{H}^+ + 4e^- & \rightarrow \text{HCHO} \text{ (aq)} + \text{H}_2\text{O} \quad E^{\circ'} = -0.51 \text{ V} \quad (1.4) \\
\text{CO}_2 \text{ (g)} + 6\text{H}^+ + 6e^- & \rightarrow \text{CH}_3\text{OH} \text{ (aq)} + \text{H}_2\text{O} \quad E^{\circ'} = -0.38 \text{ V} \quad (1.5) \\
\text{CO}_2 \text{ (g)} + 8\text{H}^+ + 8e^- & \rightarrow \text{CH}_4 \text{ (g)} + 2\text{H}_2\text{O} \quad E^{\circ'} = -0.24 \text{ V} \quad (1.6) \\
\text{H}^+ + e^- & \rightarrow \frac{1}{2} \text{H}_2 \quad E^{\circ'} = -0.42 \text{ V} \quad (1.7)
\end{align*}
\]
In biological systems, the activation of CO$_2$ is facilitated by a combination of nucleophilic and electrophilic interactions towards CO$_2$ during the first reduction step. A well-studied example is [NiFe] CO dehydrogenase (CODH), which facilitates the reversible conversion between CO and CO$_2$. In the active site, CO$_2$ activation is assisted by the stabilization through a nucleophilic Ni center and an electrophilic hydrogen-bonding interaction with a neighbouring histidine residue. Subsequent reduction is brought about by reducing equivalents from a separate pathway involving the oxidation of dihydrogen. This yields the metallocarboxylate complex (Scheme 1-1B). Nucleophilic attack by an Fe-coordinated hydroxyl group yields intermediate C, which is followed
by β-elimination of the hydroxyl group from the nickelocarboxylic acid to form the carbonyl species D. Departure of coordinated CO completes the catalytic cycle. This cycle is completely reversible, and couples Eqs. (1.2) and (1.7) to give the overall reaction in Eq 1.8.

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO + H}_2\text{O} \quad (1.8)
\]

Early attempts in CO\(_2\) activation and functionalization have focussed on the more thermodynamically facile conversion to low energy products such as urea and alkyl carbonates (Scheme 1-2).\(^4^,^5\) The facile nature of such conversions allow these transformations to represent the most significant industrial applications of CO\(_2\) as a chemical feedstock to date.\(^6\) However, the versatility of these processes is limited to carbonates and derivatives, whereas reduction to methanol derivatives or methane, for example, would lead to a multitude of possible methods for utilizing this C\(_1\) fragment.

\[\text{Scheme 1-2 Various industrial transformations of CO}_2\]
1.2 Late Metal-catalyzed CO$_2$ transformations

1.2.1 Late-metal catalyzed hydrogenation of CO$_2$

In the development of new industrial scale uses of CO$_2$ as a C$_1$ feedstock, hydrosilation$^7$ or hydrogenation$^{8-11}$ to methanol or formic acid is one area of recent research, and the two methods represent the most common methods for CO$_2$ reduction. A variety of late metal complexes have been developed to catalyze the reduction of CO$_2$ to formate and other reduced species. Several notable CO$_2$ hydrogenation catalysts are depicted in Figure 1-1.

![Figure 1-1 Examples of late metal CO$_2$ hydrogenation catalysts](image)

In terms of free energy, the hydrogenation of carbon dioxide to neat formic acid is not favourable (Eq. 1.9). However, the same process carried out in aqueous solution is slightly exoergic (Eq. 1.10), whereas the stability of the formate salt in basic solutions is even more favourable (Eq. 1.11).$^{9,10,12}$

\[
\begin{align*}
\text{H}_2 \ (g) + \text{CO}_2 \ (g) & \rightarrow \text{HCO}_2\text{H} \ (l) \quad \Delta G(298 \text{ K}) = 33 \text{ kJ mol}^{-1} \quad (1.9) \\
\text{H}_2 \ (\text{aq}) + \text{CO}_2 \ (\text{aq}) & \rightarrow \text{HCO}_2\text{H} \ (l) \quad \Delta G(298 \text{ K}) = -4 \text{ kJ mol}^{-1} \quad (1.10)
\end{align*}
\]
H₂ (aq) + CO₂ (aq) + NH₃ (aq) → NH₄⁺ HCO₂⁻  \[ \Delta G(298 \text{ K}) = -35 \text{ kJ mol}^{-1} \]  (1.11)

In 1993, a catalytic system for CO₂ hydrogenation was developed (Figure 1-1A) by Leitner.¹³ A maximum turnover number (TON) of 3439 and turnover frequency of 287 h⁻¹ were achieved with this Rh⁺ phosphine complex, representing one of the earlier systems capable of carrying out the transformation, and was studied in great detail.⁹

![Scheme 1-3 Proposed mechanism of CO₂ hydrogenation by a Rh catalyst (Figure 1-1A)¹³](image)

As seen in Scheme 1-3, the chloro-complex shown is in fact not the active catalyst itself, but rather a pre-catalyst. In the presence of dimethylamine, the chloro-complex is converted under the reducing H₂ atmosphere to an active hydride catalyst. The proposed mechanism entails the CO₂
insertion into the hydride to yield a formate complex. After subsequent oxidative addition of dihydrogen, reductive elimination of the hydride and formate results in the formation of formic acid, regenerating the catalyst. Theoretical studies suggest a possible alternative pathway involving \( \sigma \)-bond metathesis between the coordinated dihydrogen and the formate ligand to generate formic acid and the hydride complex directly.\(^{14}\) In any case, the amine additive was found to be crucial not only to capture the formic acid produced, but more importantly in the formation of the active catalyst itself – the Rh hydride complex is only produced in the presence of the amine.

For Laurenczy’s Ru\(^{II}\) system shown in Figure 1-1B, different conditions are required. Instead of amine additives, bicarbonate additives are used to provide the basic aqueous conditions.\(^{15}\) Based on the pH dependence of the system, where a slightly acidic solution (pH 5.9) gives much faster catalytic activity (TOF = 70 h\(^{-1}\)) compared to more alkaline solutions (pH 7, TOF = 1.8 h\(^{-1}\)), the system was proposed to catalytically reduce bicarbonate, instead of CO\(_2\) directly. In addition, since Ru\(^{II}/Ru^{IV}\) is a less likely redox couple compared to Rh\(^{I}/Rh^{III}\), this suggests a different operative mechanism. The proposed mechanism (Scheme 1-4) involves similar exchange of the chloride ligand with a hydride under reducing conditions as with the Rh\(^{I}\) system, followed by dissociation of the second chloride ligand and subsequent coordination of bicarbonate. Intramolecular hydride attack of the carbonyl results in expulsion of water and generation of the formate ligand, which dissociates to give the CO\(_2\) reduction product. Coordination of bicarbonate, and deprotonation of a coordinated dihydrogen, result in the regeneration of the catalytic species. The Ru\(^{II}\) oxidation state is unchanged throughout the cycle.
Scheme 1-4 Proposed mechanism of CO₂ hydrogenation by a Ru catalyst (Figure 1-1B)\textsuperscript{15}

In the case of a related Ru complex developed by Jessop (Figure 1-1C),\textsuperscript{16} a number of mechanisms have been proposed. While the proposed mechanisms were quite similar, the primary difference lies in the number and type of spectator ligands on the catalytically active species. It is suggested that dissociation of a ligand is needed to generate the 5-coordinate active catalyst, though it is not clear which ligand dissociates. While phosphine ligands are known to be labile in solution, the experimental observation that excess phosphine does not inhibit the catalytic activity suggests that PMe₃ is not the ligand that is labilized to form the active catalyst. Reactions performed in various solvents led to observations that more acidic solvents (pentafluorophenol, 2,4-dinitrophenol) were more efficient promoters of the reaction than less acidic solvents (water, methanol). It was also found that in more acidic alcoholic solvents, the chloride ligand is labilized and the ionic species [Ru(η²-OAc)(PMe₃)₄]Cl could be isolated. This, along with the independent
synthesis of the highly active [Ru(η²-OAc)(PMe₃)₄]BPh₄, which shows no induction period, suggests that the chloride ligand is labilized and the cationic mechanism (Scheme 1-5) is most consistent with experimental observations.

![Scheme 1-5 Proposed mechanism of CO₂ hydrogenation by a Ru catalyst](image)

The cycle entails dihydrogen coordination to the empty site, followed by σ-bond metathesis producing formic acid (acetic acid in the first cycle). Subsequent coordination and activation of CO₂ regenerates the formate complex. Given the mechanistic information and experimental observations, the optimized conditions using triethylamine and pentafluorophenol in supercritical CO₂ at 50 °C led to TON and TOF as high as 31,667 and 95,000 h⁻¹, respectively.⁹,¹⁷

Recent advances have included the use of pincer ligands, which are a class of tridentate ligands occupying a meridional coordination mode. In addition to having fine control over the
coordination geometry, these ligands may participate in the catalytic cycle, exhibiting ligand cooperativity by facilitating H₂ activation, as seen in the case of the Ir complex in Figure 1-1D. With a TOF of 150,000 h⁻¹ and TON of 3,500,000, this system remains one of the most robust and efficient systems for CO₂ hydrogenation.

Scheme 1-6 CO₂ Hydrogenation by an Ir-pincer ligand catalyst (Figure 1-1D)²⁸,²⁹

The Ir catalyst operates via the cycle depicted in Scheme 1-6. CO₂ insertion into the trihydride complex yields the formate complex. Subsequent dissociation of formate is effected through deprotonation of the pendant arm of the pincer ligand. This coordinatively-unsaturated Ir complex then undergoes heterolytic cleavage of H₂ to regenerate the catalyst. However, under careful examination of the individual steps, and with support from theoretical investigations, each step was further elaborated to yield the proposed mechanisms as illustrated in Scheme 1-7.

Scheme 1-7a depicts CO₂ insertion proceeding through nucleophilic attack of the hydride on the carbon in a transition state with a bent CO₂ geometry. This leads to an H-bound formate that rearranges to give the O-bound formate complex, which is slightly exoergic compared to the
initial trihydride species. Scheme 1-7b shows the (rate-determining) dissociation of formate and subsequent coordination of hydroxide. Proton transfer from the pincer ligand backbone results in de-aromatization of the pyridine ring in the aqua complex in a slightly endoergic step, after which the aqua ligand easily dissociates.

![Scheme 1-7](image)

**Scheme 1-7** Mechanistic details of the catalytic cycle in Scheme 1-6 – a) CO$_2$ insertion into Ir-hydride complex, b) elimination of formate, and c) heterolytic splitting of dihydrogen$^{18,19}$

The calculated pathway for dihydrogen activation with two added molecules of water resulted in significantly lower computed barriers than the direct heterolytic cleavage of H$_2$ across the metal and ligand backbone (Scheme 1-7c). This is consistent with experimental observations.
that very polar solvents, especially water, accelerate the catalysis. Indeed, there has been literature precedence of computed pathways of dihydrogen activation with added molecules of water resulting in lower barriers for dihydrogen activation.20

As seen in the previous examples, late transition metal catalysts are capable of activation of dihydrogen either through a σ-complex or through oxidative addition, which results in CO₂ insertion to generate a formate moiety. The low oxophilicity of late metals and the propensity to reversibly form dihydrogen or dihydride complexes manifests as smooth energy profiles throughout the catalytic sequence, where no species is considerably more stable than all other intermediates, allowing the catalytic cycle to be driven efficiently with high TOF. It is also noteworthy that, as in the case of CO dehydrogenases, many complexes capable of hydrogenating CO₂ to formic acid or formates are also capable of the reverse reaction in acidic conditions (Eqs. 1.9, 1.10).19,21,22 Therefore late metal catalysts have potential applications for reversible hydrogen storage as formic acid. However, except for recently discovered systems using iron complexes,21,23 the majority of systems developed require the use of expensive noble metals such as Rh and Ir, which diminishes the economic attractiveness regarding potential industrial applications.

Electrochemical reduction methods have also been developed, where the use of redox catalysts or surface modification of the electrodes facilitates the selective reduction of CO₂ to desired products, bypassing the highly reactive CO₂•• radical anion formed in an uncatalyzed one-electron reduction process.11,12 In terms of the potentials required, limiting the reduction to the proton coupled multi-electron processes, which typically occur at less negative potentials than the one-electron reduction (Eqs. 1.1 – 1.6), also prevents side reactions arising from the highly reactive CO₂•• radical anion.
1.2.2 Late metal catalyzed hydrosilation of CO$_2$

Compared to hydrogenation of CO$_2$, which is slightly exoergic in basic conditions but thermodynamically unfavourable in acidic and solvent-free conditions, hydrosilation of CO$_2$ is thermodynamically favoured due to the reactivity of the Si-H bond and the strength of the Si-O bond.$^7$ Aside from this difference, many late transition metal systems developed for hydrosilation of CO$_2$ bear close resemblance to the systems previously described for CO$_2$ hydrogenation. Several notable examples are depicted in Figure 1-2.

![Figure 1-2 Late transition metal CO$_2$ hydrosilation catalysts](image)

The Ru$^{II}$ catalyst depicted in Figure 1-2A shows selective hydrosilation of CO$_2$ to silyl formates. Similar to the Ru–H$_2$ $\sigma$-complex formed in Scheme 1-5, a Ru–hydrosilane $\sigma$-complex is proposed to be formed in this case (Scheme 1-8). The activated hydrosilane reacts with CO$_2$ to form the silyloxy carbonyl-hydride oxidative addition intermediate, which quickly eliminates the silyl formate ester product. In addition to the ability to use a variety of hydrosilanes, including arylhydrosilanes, as stoichiometric reductants, the TON of 465 and TOF of 233 h$^{-1}$ represented the most active catalytic CO$_2$ hydrosilation system at the time.$^{24}$
Another system utilizing an Ir center with a pincer ligand has been reported by Brookhart (Figure 1-2B). The proposed mechanism suggests that the pincer ligand is innocent. However, the steric implications of the bulky pincer ligand stabilizes the uncommon terminal $\eta^1$-H-SiEt$_3$ coordination to the metal center, as well as selectivity in the reduction products based on the steric demands of the hydrosilane substrates. As in the case of hydrosilation catalyzed by the Lewis acid B(C$_6$F$_5$)$_3$ (vide infra), the interaction of the Si-H bond with the metal center results in polarization of said bond. The highly electrophilic Si center in the activated hydrosilane interacts not only with CO$_2$, but also with the O atoms of the partially reduced species, allowing for the exhaustive reduction of CO$_2$ to CH$_4$. This phenomenon parallels closely that observed with Lewis acid catalyzed hydrosilation, which often affords highly reduced species. The similarity of the two
systems have been compared in terms of the hydrosilation of organic substrates.\textsuperscript{26} While exhaustive reduction to CH$_4$ was observed with less sterically hindered silanes such as Et$_3$SiH and Me$_3$PhSiH, bulky silanes such as Ph$_3$SiH led to formation of products of incomplete reduction, such as bis(triphenylsiloxy)methane. Nevertheless, with optimized conditions, the catalyst was demonstrated to be efficient (TOF = 661 h$^{-1}$ at 60 °C with Me$_2$PhSiH) and robust (TON = 8293 at 23°C), and reductions can be performed on gram scales.

![Scheme 1-9 CO$_2$ hydrosilation catalyzed by an Ir$^{III}$ catalyst in Figure 1-2B\textsuperscript{25}]

Other late metal complexes have been investigated in catalytic CO$_2$ hydrosilation, including complexes of $d^{10}$ metals such as Cu$^+$ (Figure 1-2C) and Zn$^{II}$ (Figure 1-2D). The Cu$^+$ and Zn$^{II}$ hydride complexes were capable of CO$_2$ insertion to yield the respective formate complexes
(Scheme 1-10), the formate ligands coordinating in a monodentate fashion due to the steric hindrance by the bulky auxiliary ligands.\textsuperscript{27,28}

\textbf{Scheme 1-10} CO\textsubscript{2} hydrosilation with \textit{d}\textsubscript{10} metal hydride catalysts (Figure 1-2C and D)\textsuperscript{27,28}

These formate complexes react rapidly with hydrosilanes to produce the corresponding silyl formate and regenerate the hydride catalyst. It is interesting to note that (IPr)Cu(Ot-Bu) is not only a highly active catalyst for CO\textsubscript{2} hydrosilation (TOF = 1248 h\textsuperscript{-1}, TON = 7489), but NHC-Cu complexes are also known to facilitate various transformations of CO\textsubscript{2},\textsuperscript{29} including hydroboration
of CO$_2$\textsuperscript{30} as well as the incorporation of CO$_2$ into organic fragments, such as carboxylation of aromatic heterocycles\textsuperscript{31} and silacarboxylation of alkynes (Scheme 1-11).\textsuperscript{32} The versatility of the transformations highlight the functional group compatibility of these late metal systems.\textsuperscript{29}

\textbf{Scheme 1-11} Examples of CO$_2$ transformations catalyzed by NHC-Cu complexes\textsuperscript{29-32}
1.3 Lewis acid and Frustrated Lewis-Pair (FLP) catalysts for CO$_2$ transformations

A different approach towards CO$_2$ activation is to utilize the chemistry of Lewis acids. Interaction of Lewis acids with the oxygen atom of the CO$_2$ molecule facilitates attack by nucleophiles at the carbon atom (section 1.3.2). Lewis acids can also activate the hydrosilane Si-H bond towards reaction with CO$_2$, akin to the Ru (Scheme 1-8) and Ir (Scheme 1-9) complexes described previously. Introduction of a Lewis basic nucleophile, sterically precluded from interaction with the Lewis acid towards adduct formation, allows for synergistic CO$_2$ activation, in so-called frustrated Lewis pair (FLP) chemistry (section 1.3.1). These approaches have led to the discovery of various CO$_2$ hydrosilation and hydroboration catalysts (section 1.2), as well as tandem systems creatively utilizing two or more approaches in sequence (section 1.4).

With Lewis acid and FLP catalysts, hydrosilation and hydroboration produces reduced C1 fragments that are invariably protected as silyl ethers, silyl esters or boronate esters, which prevents the catalysts from being poisoned by otherwise incompatible products, e.g. formic acid, which is produced in hydrogenation reactions (cf. Section 1.2.1).

\[
\begin{align*}
\text{t-Bu} & \quad \text{t-Bu} \\
\text{t-Bu} & \quad \text{t-Bu} \\
\text{R} & \quad \text{B(C}_6\text{F}_5)_3 \\
\text{CO}_2 & \quad \text{1 atm, 25 °C} \\
& \quad \text{Vacuum, 80 °C}
\end{align*}
\]

\[
\begin{align*}
\text{Mes}_2\text{P} & \quad \text{B(C}_6\text{F}_5)_2 \\
\text{Mes}_2\text{P} & \quad \text{B(C}_6\text{F}_5)_2 \\
& \quad \text{1 atm CO}_2, 25 °C \\
& \quad \text{CH}_2\text{Cl}_2, > -20 °C
\end{align*}
\]

**Scheme 1-12** Reversible CO$_2$ binding by early FLP systems$^{34}$
1.3.1 FLP catalysts for CO$_2$ hydroboration

Since its discovery, FLP chemistry has extended beyond the well-developed dihydrogen activation chemistry$^{33}$ to include various stoichiometric and catalytic transformations of CO$_2$. Similar to the active site of [NiFe] CODH (section 1.1), the presence of both electrophilic and nucleophilic sites in close proximity allow for the facile activation of CO$_2$ without the use of overly strong Lewis acids or bases. Early FLP systems were only able to reversibly bind CO$_2$ (Scheme 1-12)$^{34}$ or stoichiometrically activate CO$_2$ (Scheme 1-13).$^{35}$

![Scheme 1-13 Irreversible CO$_2$ activation by early FLP systems$^{35}$](image_url)

Recent literature (Figure 1-3A and Figure 1-3B)$^{36,37}$ has provided examples of FLP systems capable of directly activating CO$_2$ in an intramolecular fashion to form boraphosphalactones (vide infra), the trapped C1 fragment of which is susceptible to further reduction by stoichiometric hydroboranes, regenerating the FLP system, thereby rendering the process catalytic. A third system (Figure 1-3C), derived from the heterolytic splitting of H$_2$ by an FLP, allows for the activation of CO$_2$ towards hydrosilation catalyzed by a Lewis acid in a tandem fashion.
The Fontaine system (Figure 1-3A), developed in 2013, activates CO₂ towards hydroboration by catecholborane. On activation of CO₂, successive hydroboration reactions give the methyl boronate ester as the final product (Scheme 1-14). Though the formation of the boraphosphalactone from CO₂ and the FLP was calculated to be thermodynamically unfavoured, the resulting steps were exoergic and proceed rapidly. Therefore, free boraphosphalactone was not detected spectroscopically in a solution of the FLP and CO₂, although the catalytic behaviour was clearly demonstrated on addition of a hydroborane. Optimized conditions resulted in TON over 2950, and TOF as high as 853 h⁻¹ at 70 °C using BH₃·SMe₂ as the stoichiometric reductant. In addition, the catalyst was found to be “living”, and resumes activity on adding additional CO₂ and hydroborane.

Figure 1-3 FLP systems for catalytic CO₂ reduction
Another catalytic FLP system developed by Stephan (Figure 1-3B)\textsuperscript{37} was synthesized unexpectedly through the reaction between the Lewis basic \(N\)-phosphorylated \(N\)-heterocyclic carbene (NHC) and the Lewis acidic 9-borabicyclo[3.3.1]nonane (9-BBN) (Scheme 1-15). This resulted in an intramolecular FLP capable of \(\text{CO}_2\) activation. On activation of \(\text{CO}_2\) to the lactone complex, reduction with pinacolborane (HBpin) and catecholborane (HBcat) generated the products \(\text{HCO}_2\text{Bpin}\) and \(\text{CH}_3\text{OBcat}\) respectively. Reduction with \(\text{BH}_3\cdot\text{SMe}_2\) resulted in the reduction to trimethylboroxine, \((\text{CH}_3\text{BO})_3\).
An FLP system consisting of 2,2,6,6-tetramethylpiperidine and B(C₆F₅)₃ was initially discovered by Sumerin and Rieger in 2008 to heterolytically cleave H₂, forming the ion pair in Figure 1-3C.³⁸ In 2009, Ashley and O’Hare discovered that this ion pair was capable of CO₂ activation to yield the formyloxytris(pentafluorophenyl)borate, and that thermolysis at 160 °C generates CH₃OH along with catalyst decomposition products (Scheme 1-16).³⁹ Although this process was not catalytic, it represented the first homogeneous non-metal system capable of conversion of CO₂ to methanol.
Scheme 1-16 CO₂ activation by an ion pair derived from an FLP system\textsuperscript{38,39}

Scheme 1-17 Tandem FLP / Lewis acid catalyzed CO₂ hydrosilation\textsuperscript{40}

In 2010, Berkefeld and Piers demonstrated that this ionic system can be used as a catalyst for CO₂ hydrosilation (Scheme 1-17),\textsuperscript{40} where the activation of CO₂ to form the formoxy moiety, in conjunction with the activation of the hydrosilane by the Lewis acidic B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, allows for the hydrosilation to generate the triethylsilyl formate, regenerating the ion pair CO₂ activation catalyst. Subsequent hydrosilation of the silyl formate proceeds rapidly under catalytic B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, representing a tandem system utilizing two catalysts – the FLP-derived ion pair for CO₂ activation, and the Lewis acidic borane-catalyzed hydrosilation of the resulting formyloxy fragment.

Albeit being a robust, living system, a low TOF of approximately 6 h\textsuperscript{-1} was observed at elevated temperatures (56 °C). It was also observed that the formyloxyborate anion was not detected under catalytic conditions. The authors therefore deduced the rate-limiting step to be a slow CO₂ addition across the B-H bond to generate the formyloxyborate.
1.3.2 Early transition metal-based Lewis acid catalysts for CO$_2$ hydrosilation

In a system developed by Kawaguchi et al. in 2006, a neutral bis(benzyl)zirconium complex undergoes alkyl abstraction by the strong Lewis acid B(C$_6$F$_5$)$_3$ to yield the ionic species shown in Figure 1-3C. This strongly Lewis acidic Zr is then capable of interaction with CO$_2$. Although an intermediate with coordinated CO$_2$ was not isolated, the presence of the cationic Zr species is required for catalytic CO$_2$ activation, which converts the C1 fragment to the doubly hydrosilated acetal product (Scheme 1-18). From this intermediate, reduction to CH$_4$ was mediated by catalytic B(C$_6$F$_5$)$_3$ alone, as demonstrated in control experiments without the Zr species.

![Scheme 1-18: Kawaguchi's cationic Zr catalyst for CO$_2$ hydrosilation](image)

It was found that product selectivity was dependent on the substituents on the hydrosilane reductant – bulky silanes such as Ph$_3$SiH yielded mostly the acetal product, whereas less bulky silanes such as Et$_2$MeSiH resulted in exhaustive reduction to CH$_4$, and proceeded somewhat more rapidly, achieving TOF of up to 7.3 h$^{-1}$ and TON of 211. However, decomposition of the anionic component of the catalyst was observed over time.
LeBlanc and Piers developed a system consisting of a strongly Lewis acidic cationic Sc center.\textsuperscript{42} This was prepared \textit{via} alkyl abstraction from a neutral dimethyl complex by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (Scheme 1-19) reminiscent of the Kawaguchi system above (Scheme 1-18). On treatment with CO\textsubscript{2}, coordination to the Sc center was observed in two different environments – insertion into the Sc-methyl bond to form the eventual bridging acetate ligands, and the FLP-type CO\textsubscript{2} activation by the Lewis-acidic Sc center and the nucleophilic carbon on the ligand backbone. However, for this system, only stoichiometric activation of CO\textsubscript{2} was achieved.

\textbf{Scheme 1-19} Stoichiometric CO\textsubscript{2} activation by a cationic Sc complex\textsuperscript{42}

With this preliminary result, the ligand was modified to produce a more robust coordination mode with less nucleophilic sites on the backbone, as presented by the anilido-bipyridyl ligand scaffold.\textsuperscript{43} While this scaffold was developed to be a tridentate ligand, metatation of an aryl C–H bond resulted in a tetradentate dianionic ligand (Scheme 1-20B). CO\textsubscript{2} insertion into the Sc-C bonds resulted in a doubly-inserted product C.
The details of the catalytic hydrosilation are depicted in Scheme 1-21. The equilibrium between the phenylenecarboxylate C and the B(C₆F₅)₃ adduct D (step a), though strongly favouring the adduct, allows for trace amounts of free B(C₆F₅)₃ to activate the Et₃SiH to form the cationic silyl ester with the hydridoborate counteranion E (step b). This step is reversible, as determined by the scrambling of silyl group when a different silane is added, or the formation of a deuterioborate anion on addition of Et₃SiD. In any case, this hydridoborate anion of C is capable of CO₂ insertion into the B-H bond to give the formyloxyborate anion F (step c). This eliminates the silyl formate ester, regenerating the borane adduct D (step d). The silyl formate ester generated can also be reduced by the hydridoborate anion in E to generate the bis(triethylsiloxy)methane (step e). This step proceeds rapidly, and triethylsilyl formate is not observed in the catalytic reaction. Also, since free B(C₆F₅)₃ is not present in significant quantities, further reduction to CH₄ can be avoided. TON of ~ 3400 and TOF of ~ 100 h⁻¹, selective for the bis(triethylsiloxy)methane, are achieved with this system.
Scheme 1-21 CO₂ hydrosilation catalyzed by an anilido-bipyridyl Sc catalyst⁴³

1.4 Tandem and cascade catalysis for sequential reduction of CO₂

Aside from the FLP-derived TMPH⁺ HB(C₆F₅)₃⁻ system (Scheme 1-17) and the Kawaguchi system (Scheme 1-18), which utilize two different catalysts for the initial activation of CO₂ and the successive hydrosilation of the partially reduced species, a number of systems have been developed that adopt multiple catalysts for the stepwise reduction of CO₂.
1.4.1 Cascade catalysis for CO₂ hydrogenation

A system developed by Sanford⁴⁴ utilizes three homogeneous catalysts to (i) convert CO₂ to methyl formate through the carboxylation of methanol, which is used as the solvent; (ii) a Lewis acid co-catalyst to accelerate this conversion; (iii) a catalyst to effect the hydrogenation of the formate ester to methanol. Screening of the various catalysts that were able to carry out the respective transformations and conditions resulted in the conditions as depicted in Scheme 1-22. The catalyst of choice for activation of CO₂ was a Ru-based catalyst described above (Scheme 1-5),¹⁶ which under alcoholic conditions results in the formation of the methyl formate ester. The activity was enhanced by the addition of the Lewis acid catalyst B.

![Scheme 1-22 Cascade catalysis for sequential CO₂ hydrogenation to CH₄](image)

Since catalyst C was deactivated by the Lewis acidic Sc(OTf)_3, and therefore incompatible with the A/B catalyst system, it was separately placed in the outer vessel, while the catalysts A and
were in an inner vessel, and the entire system was sealed in a Parr reactor. At elevated temperatures, the methyl formate product volatilizes and transfers from the inner vessel to the outer vessel containing catalyst C, where it is reduced further to methanol. $^{13}$CO$_2$ was used to allow for the detection of labelled methanol separately from the methanol solvent used. The authors determined the system to have a TON of 21 $^{13}$CH$_3$OH from $^{13}$CO$_2$.

1.4.2 A late-metal / B(C$_6$F$_5$)$_3$ tandem system for CO$_2$ hydrosilation

A system developed in the Turculet group$^{45}$ utilizes a Pt catalyst to activate CO$_2$ (Scheme 1-23). This activation is effected in conjunction with a Lewis acidic borane (B(C$_6$F$_5$)$_3$ or BPh$_3$), which generates a formyloxyborate species, quite reminiscent of the TMPH$^+$ HB(C$_6$F$_5$)$_3^-$ system employed by Piers in Scheme 1-17. This activated formyloxy moiety undergoes two successive hydrosilation reactions to generate the $\text{bis(trialkylsiloxy)methane.}$ If the more Lewis acidic B(C$_6$F$_5$)$_3$ is used, subsequent Lewis-acid catalyzed hydrosilation of the acetal results in the generation of CH$_4$. However, BPh$_3$, the weaker Lewis acid, results in the selective formation of the acetal without further reduction. This catalyst system achieved a TON of 2156 and a TOF of 956 h$^{-1}$ at 65 °C. However, catalyst activity was found to diminish with time. The Pd analogue was also found to be active, albeit with lower activities.

This provides a late-metal complement to the early metal-based tandem systems by Kawaguchi (Scheme 1-18) and the tandem FLP system by Piers (Scheme 1-17), and showcases selectivity for the acetal intermediate quite similar to the Sc-based system described by Piers (Scheme 1-21).
Scheme 1-23 Tandem Pt / Lewis acid catalyzed hydrosilation of CO$_2$ to CH$_4$\textsuperscript{45}

1.4.3 The Permethylscandocenium hydridotris(pentafluorophenyl)borate system

Another cationic Sc system developed in the Piers group utilizes a scandocenium framework (1-Sc, Scheme 1-24).\textsuperscript{46} This system, like the previously shown cationic Sc system in Scheme 1-21, is capable of CO$_2$ activation by the Sc center. However, the mechanism is vastly different, and the mode of CO$_2$ activation to a formyloxyborate moiety (2-Sc) and the resultant B(C$_6$F$_5$)$_3$-catalyzed exhaustive hydrosilation to yield CH$_4$ is more reminiscent of the TMPH$^+$ HB(C$_6$F$_5$)$_3$\textsuperscript{−} tandem system (Scheme 1-17) and the Turculet system (Scheme 1-23). The resulting formyloxy moiety is transferred to a B(C$_6$F$_5$)$_3$-activated Et$_3$SiH and subsequently reduced to CH$_4$. 
The system in its entirety is presented in Scheme 1-25. The catalyst 1-Sc serves to activate CO₂ to form 2-Sc (step a), which is in equilibrium with the neutral scandocene formate 3-Sc and free B(C₆F₅)₃ (step b). The formyloxy moiety is then transferred to a B(C₆F₅)₃-activated hydrosilane, regenerating 1-Sc (step d). Subsequent hydrosilation of triethylsilyl formate to CH₄ (steps e – g), as described in previous systems, occurs in the presence of B(C₆F₅)₃, which is produced in the equilibrium dissociation from 2-Sc to the neutral scandocene formate (3-Sc). However, the equilibrium formation of only small amounts of B(C₆F₅)₃ led to the observation of incomplete reduction products. Addition of excess B(C₆F₅)₃ facilitates the hydrosilation of the intermediates, favouring the formation of CH₄. This sequence represents the pathway that is operative at the initial stages of the reaction (Path A).
Scheme 1-25 The exhaustive reduction of CO₂ to CH₄ by catalyst 1-Sc⁴⁶
Close examination of the kinetics of the reaction allows the observation of an initial induction period, followed by a period of increased rate. The proposed mechanism of the reaction after the induction period is depicted as Path B in Scheme 1-25. The formyloxyborate species was proposed to be labilized from the Sc center in 2-Sc through coordination of the acetal intermediate to the Sc center. Evidence for this comes from treating the 2-Sc with a model acetal, which if added in large excess, can result in the observation of the coordinated complex in NMR spectroscopy (Scheme 1-26).

![Scheme 1-26 Acetal coordination to 2-Sc and labilization of the formyloxyborate](image)

Addition of the model acetal resulted in catalytic activity of the system without the induction period, providing good evidence for the acetal-mediated Path B. It is plausible that Path B would be faster than Path A due to the labilized formyloxyborate anion, which provides a much more sterically accessible formate moiety for transfer to the triethylsilyl group.

The duration of the induction period was found to be longer for increasing amounts of added B(C₆F₅)₃, which suggests the equilibrium $b$ is in place, and that the formate group is transferred from the 3-Sc – increasing B(C₆F₅)₃ concentrations would shift the equilibrium towards 2-Sc, slowing down the rate-determining formate transfer and hence the entire reaction. However, the precise equilibrium cannot be experimentally determined due to the oligomerization of 3-Sc.
In the presence of 4 eq. of $\text{B}(\text{C}_6\text{F}_5)_3$ relative to the Sc catalyst, the Sc catalyst after the induction period was estimated to have a TOF of 325 $\text{CO}_2$ h$^{-1}$, based on the stoichiometry of the reaction (Eq. 1.12) and the overall TOF of 1300 SiH h$^{-1}$ observed including the subsequent hydrosilation steps by $\text{B}(\text{C}_6\text{F}_5)_3$.

\[
\begin{align*}
\text{CO}_2 + 4 \text{Et}_3\text{SiH} & \quad \xrightarrow{\text{cat. } \text{Cp}^\ast_2\text{Sc}^\ast \text{ HB}(\text{C}_6\text{F}_5)_3^\ast, \text{B}(\text{C}_6\text{F}_5)_3} \\
& \quad \text{C}_6\text{D}_6 \text{ or } \text{C}_6\text{D}_3\text{Br} \\
& \quad \text{CH}_4 + 2 (\text{Et}_3\text{Si})_2\text{O} \\
\end{align*}
\]  

(1.12)

1.5 **Thesis Goals**

This introductory chapter described the different approaches towards homogenous catalytic chemical reductions of $\text{CO}_2$. Catalysts designs have ranged from early and late transition metals to main group elements, from single catalysts to tandem and cascade systems. In particular, the system recently developed in the Piers group utilizes the scandocenium hydridoborate framework ($1-\text{Sc}$) for $\text{CO}_2$ activation, showing a complex reactivity pattern with two pathways for $\text{CO}_2$ hydrosilation. The goal of the project is to investigate the possibility of using analogous systems with extra $d$ electrons (i.e. $\text{Ti}^{\text{III}}$ and $\text{V}^{\text{III}}$ systems in place of $\text{Sc}^{\text{III}}$) and examining the activity of the resulting compounds as catalysts, in order to determine whether the mechanism for $1-\text{Sc}$ is applicable to the other metals, possibly contributing to further understanding of the catalytic mechanism.
Chapter Two: Synthesis and reactivity of early metal metallocenium salts

2.1 Introduction

Since the discovery of ferrocene (Figure 2-1) by Pauson and Kealy in 1951, the scope of metallocene chemistry has been extended to include most transition metals and even main group elements. In particular, the metallocene chemistry of Lewis acidic early metals has been developed extensively due to their use in industrially relevant catalytic processes like olefin polymerization.

![Ferrocene](image)

**Figure 2-1** Ferrocene, the prototypical metallocene

These catalysts feature substituted and annulated cyclopentadienyl ligands, as well as cyclopentadienyl ligands with constrained geometries in order to create early metal metallocene catalysts with finely tuned steric and electronic properties suitable for polymerizing different olefins and creating polymers of desired tacticity (Figure 2-2). The catalysts are often activated to form cationic species to increase Lewis acidity.
Figure 2-2 Examples of metallocene catalysts for olefin polymerization.

In Chapter 1, the Lewis acidity of such early metallocenes was exploited in catalytic CO\textsubscript{2} hydrosilation by 1-Sc (Scheme 1-25). Here we sought to further investigate this type of early metal metallocene catalysed CO\textsubscript{2} reduction by extending the Sc\textsuperscript{III} chemistry to Ti\textsuperscript{III} and V\textsuperscript{III} systems.

In terms of structural knowledge of these complexes, both experimental and theoretical studies have been reported on the geometries of early metal metallocenes. Hessen \textit{et al.} have reported the synthesis and characterization of the solid-state structures of cationic permethylmetallocenium(III) compounds of scandium, titanium and vanadium partnered with weakly coordinating anions (\textit{vide infra}).\textsuperscript{58} The strong Lewis acidic character of the metal centers has led to observations of agostic interactions of the metal with the C-H bonds of the methyl substituents on the cyclopentadienyl ligand, or weak C-F interactions with the counteranions or solvent molecules. The exact nature of the coordination behaviour observed by Hessen varied among the three metals, and was dependent mostly on the $d$ electron count at the metal centers. Such electronic effects were rationalized through the theoretical studies by Green \textit{et al.} regarding the interplay between electronic configuration and preferred geometries, as described in the following section.\textsuperscript{59,60}
2.1.1 Bent metalocenes – electronic structure and coordination behaviour

In ferrocene, the overlap of the π orbitals of the cyclopentadieny1 moiety with the d orbitals of the iron center results in a d orbital splitting with the three highest occupied orbitals shown in Figure 2-3. On “bending” of the Cp rings, i.e. increasing the dihedral angle (α) between the rings, the molecular orbitals are perturbed both spatially and energetically. While the lowest energy 3a1 orbital decreases in energy, the 2b1 and 4a1 orbitals increase in energy.59 In addition, in the case of first and second row transition metals, the small energy difference between the three orbitals indicates that the highest multiplicity state is of lowest energy. This significantly affects the energy of the complexes on increasing the number of d electrons. A high spin configuration of the d2 and d3 systems leads to successive single occupation of the 2b1 and 4a1 orbitals, and as such, the preference for smaller α in the most optimal geometries of these metalocene systems, provided extra ligands are not present. On the other hand, d0 metalocenes without extra coordinated ligands will show little preference for bent or parallel sandwich structures, whereas the preference for a larger α will be expected for d1 systems. While interactions with additional ligands (as in 1-Sc and 2-Sc, refer to Scheme 1-24) will perturb the geometry around the metal center as well as the value of α, the high spin nature of these species and the spatial orientation of the available orbitals governs the coordination geometries seen with complexes of early transition metals.
Figure 2-3 Three highest occupied molecular orbitals of ferrocene on increasing dihedral angle $\alpha$
Figure 2-4 A variety of metallocenium complexes reported by Hessen$^{58}$
In the permethylmetallocenium systems studied by Hessen\textsuperscript{58} (Figure 2-4), the strongly Lewis acidic metalloccenium cations were isolated both base-free and with coordinated fluoroarene solvents or tetrahydrofuran (THF). In the base-free cases, the metal centers interact with C-H bonds. The strongly Lewis acidic Cp\textsuperscript{*}2Sc\textsuperscript{+} interacts with two C-H bonds from the counteranion, whereas Cp\textsuperscript{*}2Ti\textsuperscript{+} and Cp\textsuperscript{*}2V\textsuperscript{+} form agostic interactions with two and one methyl C-H bond(s) of a Cp\textsuperscript{*} ligand, respectively, consistent with the availability of two and one vacant orbital(s) on the respective metal for such interactions.

In the presence of coordinating solvents, the expected coordination mode was observed for Cp\textsuperscript{*}2Sc\textsuperscript{+} and Cp\textsuperscript{*}2V\textsuperscript{+}, while Cp\textsuperscript{*}2Ti\textsuperscript{+} only yields the mono-coordinated complex, even though two vacant orbitals are available for ligand coordination. The authors inferred that the smaller Ti\textsuperscript{3+} cation (ionic radius 67 pm) compared to Sc\textsuperscript{3+} (ionic radius 74.5 pm)\textsuperscript{61} presents greater steric hindrance preventing coordination of a second ligand to the Ti\textsuperscript{3+} center.

Finally, when the counteranion was B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}\textsuperscript{-}, a κ\textsuperscript{2}F-C\textsubscript{6}F\textsubscript{5} coordination was observed for Sc\textsuperscript{3+} and Ti\textsuperscript{3+}, while no contact was observed between Cp\textsuperscript{*}2V\textsuperscript{+} and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4} ions. This again agrees with the presence of at least two vacant orbitals in the case of Cp\textsuperscript{*}2Sc\textsuperscript{+} and Cp\textsuperscript{*}2Ti\textsuperscript{+} to interact with the coordinating molecules, whereas the high-spin Cp\textsuperscript{*}2V\textsuperscript{+} could not offer such a coordination mode.

As observed in this literature precedent, the structure and coordination behaviour of the bent metalloccene fragment can be correlated to the d electron count of the metal center. This theoretical and experimental knowledge of these early metal metalloccenes will serve as references as we explore the chemistry of the Ti\textsuperscript{III} and V\textsuperscript{III} analogues of the aforementioned 1-Sc catalytic system.\textsuperscript{46}
2.2 Results and Discussion

2.2.1 Synthesis and characterization of the permethylmetallocenium hydrotris(pentafluorophenyl)borates 1-M (M = Sc, Ti, V)

The syntheses of the hydridoborates 1-Ti and 1-V follow closely the method developed for 1-Sc.\textsuperscript{62} The general procedure entails the reaction of the respective chlorobis(pentamethylcyclopentadienyl) complex, Cp\textsuperscript{2}MCl, with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and Et\textsubscript{3}SiH (Scheme 2-1). The hydrosilane is activated through interaction with the Lewis acidic borane,\textsuperscript{63} resulting in a strongly polarized system with an electrophilic Si center and a nucleophilic hydride. This Lewis acidic activation by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} has been exploited in various organic transformations,\textsuperscript{63} including the exhaustive hydrosilation of otherwise unreactive substrates, such as ethers,\textsuperscript{64} primary alcohols,\textsuperscript{64} and ketones,\textsuperscript{65} to alkanes. Here, this activated Si–H bond reacts accordingly with the strongly polar M–Cl bond to produce the 1-M complexes in reasonable yields (68 – 91%).

Scheme 2-1 General synthesis of the metallocenium hydridoborates 1-M
The Cp₂MCl precursors were prepared from the respective THF adducts of the metal chlorides through different salt metathesis processes. For the synthesis of Cp*₂ScCl, the ultimate starting material is Sc₂O₃, which is digested with concentrated hydrochloric acid. The resulting oil containing hydrated ScCl₃ in conc. HCl was dehydrated by refluxing over a THF solution of thionyl chloride to produce ScCl₃·3THF (Scheme 2-2).⁶₆

\[
0.5 \text{Sc}_2\text{O}_3 + 3 \text{HCl (aq.)} \xrightarrow{\text{reflux}} \text{ScCl}_3 \cdot 6\text{H}_2\text{O}
\]

\[
\text{ScCl}_3 \cdot 6\text{H}_2\text{O} + 6 \text{SOCl}_2 \xrightarrow{\text{THF, reflux}} \text{ScCl}_3 \cdot 3\text{THF} + 6 \text{SO}_2 + 12 \text{HCl}
\]

\[
\text{ScCl}_3 \cdot 3\text{THF} + 2 \text{Cp}^*\text{Li} \xrightarrow{o\text{-xylene, reflux, 3 d}} \text{Cp}^*\text{₂ScCl} + 2 \text{LiCl} + 3 \text{THF}
\]

**Scheme 2-2** Synthesis of chlorobis(pentamethylcyclopentadieny1)scandium(III), Cp*₂ScCl

Subsequent salt metathesis with Cp*Li yields chlorobis(pentamethylcyclopentadienyl)-scandium(III), which is purified via sublimation, giving the product as yellow crystalline deposits.⁶⁷ Addition of a solution of B(C₆F₅)₃ and Et₃SiH to a dull yellow Cp*₂ScCl solution results in the bright yellow solution of **1-Sc**, from which pale yellow crystals of 1-Sc can be obtained by layering with hexanes.

The preparation of Cp*₂TiCl follows closely that of the Sc analogue, except that the use of Cp*MgCl·THF⁶⁸ instead of Cp*Li⁶⁹ for salt metathesis with TiCl₃·3THF was reported to give better yields and purity (Scheme 2-3). Indeed, the dark purple recrystallized product can be used directly for the synthesis of **1-Ti**. However, **1-Ti** is unstable at room temperature both in the solid state and in solutions of aromatic hydrocarbon solvents. A pure crystalline sample of the dark green 1-Ti was successfully obtained by leaving a slurry of B(C₆F₅)₃, Et₃SiH and Cp*₂TiCl in C₆H₆.
undisturbed for 8-12 hours, after which decomposition to an orange-brown oil is observed. Decomposition is slowed down by storage at -35 °C, where a sample can be kept for several days.

Bulk purity of a sample of 1-Ti was established through elemental analysis. Analysis by NMR spectroscopy was complicated by the paramagnetic nature of the Ti^{III} center. Nevertheless, $^1$H resonances for the Cp$^*$ methyl protons can be located as a paramagnetically-shifted and broadened resonance at $\delta$ 13.30 ppm ($\nu_{1/2} \approx 2250$ Hz), while the BH resonance was observed at $\delta$ 3.60 ppm, broadened due to coupling with the $^{11}$B and $^{10}$B nuclei as reported in 1-Sc.$^{62}$ A sharp $^{11}$B resonance was observed at $\delta$ -23.2 ppm comparable to $\delta$ -25.3 ppm observed in 1-Sc.$^{62}$ This resonance also agrees closely to those reported in literature examples for this anion paired with cations such as Na$^+$ (in DMSO-$d_6$, $\delta$ -25.2 ppm),$^{70}$ Bu$_4$N$^+$ (in CDCl$_3$, $\delta$ -25.4 ppm)$^{70}$, 2,6-Me$_2$C$_5$H$_3$NH$^+$ (in CD$_2$Cl$_2$, $\delta$ -24.7 ppm)$^{71}$ or (2,4,6-Me$_3$C$_6$H$_2$)$_3$PH$^+$ (in CDCl$_3$, $\delta$ -25.6 ppm).$^{72}$ The broad signal ($\nu_{1/2} \approx 180$ Hz) obtained in a proton-coupled spectrum compared to the sharper signal in the decoupled spectrum ($\nu_{1/2} \approx 120$ Hz) indicates coupling to the BH nucleus, consistent with the connectivity. $^{19}$F NMR resonances for 1-Ti were broadened significantly to afford one broad resonance ($\delta$ 157.3 ppm, $\nu_{1/2} \approx 1300$ Hz), suggesting interaction between the C$_6$F$_5$ groups and the paramagnetic Ti^{III} center in this hydridoborate complex in solution.

**Scheme 2-3** Synthesis of chlorobis(pentamethylenecyclopentadienyl)titanium(III), Cp$^*$$_2$TiCl
$^{19}$F NMR spectra acquired at lower temperatures (below 250 K) allowed for the observation of separate signals corresponding to the $o$-$m$-$p$-C$_6$F$_5$ resonances (Figure 2-5). The corresponding $^1$H NMR spectra feature a Cp$^*$ resonance that is broadened significantly on cooling and disappears into the baseline, and a new resonance is not observed, implying that 1-Ti remains paramagnetic within the range of temperatures studied. The observation of separate $^{19}$F resonances is likely due to the decreased fluxionality of this molecule at low temperatures, specifically with regards to the

Figure 2-5 Low-temperature $^{19}$F NMR spectra of 1-Ti in toluene-$d_8$. 
dynamic exchange between $C_6F_5$–Ti interactions. The broadening of resonances below 220 K was attributed to increased viscosity of the solvent at low temperatures.

Scheme 2-4 Synthesis of chlorobis(pentamethylcyclopentadienyl)vanadium(III), $\text{Cp}^*_2\text{VCl}$

For the $\text{V}^{III}$ analogue, a modified synthetic route was employed (Scheme 2-4). Salt metathesis of $\text{VCl}_3\cdot3\text{THF}$ with $\text{Cp}^*_\text{Li}$ results in the oxidation of $\text{Cp}^*_\text{Li}$ to $\text{bis}[\text{(1,2,3,4,5-pentamethyl)}-2,4$-$\text{cyclopentadienyl}], \text{Cp}^*_2$, with the concomitant reduction of $\text{V}^{III}$ to permethylvanadocene, $\text{Cp}^*_2\text{V}$.\textsuperscript{73} Both products have very high solubility in aliphatic solvents, which renders the separation by recrystallization unfeasible. Both products also have very similar volatility, with decamethylfulvalene being slightly more volatile. Repeated sublimations under reduced pressure are required to afford $\text{Cp}^*_2\text{V}$ in reasonable purity. Re-oxidation to $\text{V}^{III}$ is achieved by treatment with benzyl chloride, which affords chlorobis(pentamethylcyclopentadienyl)-vanadium(III), $\text{Cp}^*_2\text{VCl}$, as a dark blue solid after repeated recrystallizations to remove the bibenzyl by-product.\textsuperscript{74} The synthesis of 1-V was carried out in bromobenzene instead of benzene because its insolubility in benzene resulted in trapped impurities. Addition of a solution mixture of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Et}_3\text{SiH}$ to the dark blue $\text{Cp}^*_2\text{VCl}$ solution resulted in an instant colour change to dark red-brown, from which a dark red precipitate is formed in minutes. Needles of the
recrystallized product can be obtained by layering a dilute bromobenzene solution with hexanes and storage at -35 °C.

Unlike 1-Sc or 1-Ti, 1-V is insoluble in benzene or toluene, and only slightly soluble in bromobenzene. This may be due to the ionic nature of this species, where the lack of interaction between the C₆F₅ groups and the V³⁺ center prevents the formation of a contact ion pair in solution such as that in 1-Ti. Indeed, ¹⁹F resonances of 1-V were not perturbed dramatically by the paramagnetic V³⁺ center as seen in 1-Ti (Figure 2-6). A comparison of NMR characteristics of the three complexes is tabulated in Table 2-1.

Table 2-1  NMR data for the hydridoborate complexes 1-Sc, 1-Ti and 1-V

<table>
<thead>
<tr>
<th>Resonance</th>
<th>1-Sc⁰²</th>
<th>1-Ti</th>
<th>1-Vᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>¹H NMR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅(CH₃)₅</td>
<td>1.58 (s)</td>
<td>13.30</td>
<td>25.10</td>
</tr>
<tr>
<td>HB(C₆F₅)₃</td>
<td>4.13</td>
<td>3.60 (br, ν₁/₂ ≈ 2250 Hz)</td>
<td>4.20 (br, ν₁/₂ ≈ 500 Hz)</td>
</tr>
<tr>
<td></td>
<td>(br, ν₁/₂ ≈ 20 Hz)</td>
<td>(br, ν₁/₂ ≈ 500 Hz)</td>
<td>(br, ν₁/₂ ≈ 250 Hz)</td>
</tr>
<tr>
<td><strong>¹⁰/¹¹B NMR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>¹⁰B{¹H} / ¹¹B{¹H}</td>
<td>- 25.3 (s)b / - 25.3 (s) /</td>
<td>- 23.4 (s)b / - 23.2 (s) /</td>
<td>- 24.7 (s) / - 24.6 (s) /</td>
</tr>
<tr>
<td>(HBAr₃)</td>
<td>- 25.3</td>
<td>- 23.2 (br, ν₁/₂ ≈ 180 Hz)b</td>
<td>- 24.6</td>
</tr>
<tr>
<td></td>
<td>(br, ν₁/₂ ≈ 220 Hz)b</td>
<td>(br, ν₁/₂ ≈ 180 Hz)b</td>
<td></td>
</tr>
<tr>
<td><strong>¹³C{¹H} NMR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅(CH₃)₅</td>
<td>126.5, 10.2</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td><strong>¹⁹F{¹H} NMR</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-C₆F₅</td>
<td>- 133.9</td>
<td>-157.3 (br, ν₁/₂ ≈ 145 Hz)</td>
<td>- 131.7 (br, ν₁/₂ ≈ 130 Hz)</td>
</tr>
<tr>
<td></td>
<td>(br, ν₁/₂ ≈ 145 Hz)</td>
<td>(br, ν₁/₂ ≈ 130 Hz)d</td>
<td>(br, ν₁/₂ ≈ 130 Hz)</td>
</tr>
<tr>
<td>m-C₆F₅</td>
<td>- 166.8</td>
<td></td>
<td>- 160.0</td>
</tr>
<tr>
<td></td>
<td>(br, ν₁/₂ ≈ 145 Hz)</td>
<td></td>
<td>(br, ν₁/₂ ≈ 600 Hz)</td>
</tr>
<tr>
<td>p-C₆F₅</td>
<td>- 160.3</td>
<td>- 163.0 (br, ν₁/₂ ≈ 25 Hz)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(t, J = 21 Hz)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

¹ Recorded in C₆D₆ at room temperature. ² Recorded in C₆D₅Br at room temperature. ³ Not observed due to paramagnetism. ⁴ One broad peak is observed in the ¹⁹F NMR spectrum (see text).
The structures of the hydridoborate complexes 1-M in the solid state have been elucidated using single crystal X-ray diffraction (XRD) (Figure 2-7). They were found to resemble closely those of the permethylmetallocenium tetrakis(pentafluorophenyl)borate complexes reported by Hessen (vide supra). Similar $\kappa^2$-F coordination of the perfluorophenyl group was seen in both 1-
Sc$^{62}$ and 1-Ti (Figure 2-7). Except for a somewhat less distorted interaction between the Sc and the C$_6$F$_5$ group, as indicated by a smaller angle between the C$_6$F$_5$ and the F-Sc-F planes (Table 2-2), metrical data around the Cp$^*$_2Sc$^+$ center agree closely with the respective B(C$_6$F$_5$)$_4^-$ complexes reported by Hessen$^{58}$, although the bidentate coordination was afforded by the o- and m-F rather than the m- and p-F as observed for the B(C$_6$F$_5$)$_4^-$ complexes. Hessen has suggested that the weak M–F interactions are mainly electrostatic, as underlined by two observations.$^{58}$ First, the coordinated anion is easily displaced by fluoroarene solvents in solution. Second, the X-ray structures reveal a shortening of M–F distances by 0.08 – 0.13 Å as compared to optimized geometries from calculations, which the authors attributed to increased Coulombic stabilization manifesting as crystal packing forces in the solid state. Therefore it is likely that in the solid state structures of 1-Sc and 1-Ti, the o- and m-ArF bidentate coordination mode may stem from a slight preference for the coordination to the fluorine atoms closer to the negatively-charged boron center, maximizing the electrostatic attraction between the opposite charges. Due to the steric hindrance bought about by four C$_6$F$_5$ rings, this coordination mode is not accessible with the B(C$_6$F$_5$)$_4^-$ anion, and the m-/p-F coordination is observed instead.

**Table 2-3** Selected metrical data for 1-Ti and Cp$^*$_2Ti$^+$ B(C$_6$F$_5$)$_4^-$

<table>
<thead>
<tr>
<th></th>
<th>1-Ti</th>
<th>Cp$^*$_2Ti$^+$ B(C$_6$F$_5$)$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti–F</td>
<td>2.317(1) (o-F), 2.363(2) Å (m-F)</td>
<td>2.325(5) (m-F), 2.370(5) Å (p-F)</td>
</tr>
<tr>
<td>C–F</td>
<td>1.383(3) (o-F), 1.369(2) Å (m-F)</td>
<td>1.365(10) (m-F), 1.346(10) Å (p-F)</td>
</tr>
<tr>
<td>Cp$^*$–Ti$^+$</td>
<td>2.033 / 2.034 Å</td>
<td>2.052 / 2.039 Å</td>
</tr>
<tr>
<td>∠Cp$^<em>$–Ti–Cp$^</em>$</td>
<td>143.02°</td>
<td>144.9°</td>
</tr>
<tr>
<td>∠Cp$^<em>$–Cp$^</em>$ (α)</td>
<td>35.73°</td>
<td>32.90°</td>
</tr>
<tr>
<td>∠F–Ti–F</td>
<td>67.01(5)°</td>
<td>67.62(18)°</td>
</tr>
<tr>
<td>∠(C$_6$F$_5$B, TiF$_2$)</td>
<td>14.24°</td>
<td>20.3°</td>
</tr>
</tbody>
</table>

$^a$ Distance between Ti and the centroid of the Cp$^*$ ring. $^b$ Defined as the angle between the C$_6$F$_5$B and F-Ti-F planes.
Figure 2-7 Thermal ellipsoid diagrams of the solid state structures of 1-Sc\textsuperscript{62}, 1-Ti and 1-V (bottom) at 50\% probability. All Cp\textsuperscript{*} hydrogens (except for the agostic CH\textsubscript{3} in 1-V) and cocrystallized C\textsubscript{6}H\textsubscript{6} (for both 1-Sc and 1-Ti), are removed for clarity.
In 1-V, however, bidentate coordination of the anion to the V center was not observed, in accordance with a high-spin \(d^2\) metal center with only one spatially accessible vacant orbital.\(^{59}\) One \(\text{CH}_3\) group (C8, see Figure 2-7 and Table 2-4) of one \(\text{Cp}^+\) ligand is distorted out of the plane of the five-membered ring towards the metal center by 10.5°, reminiscent of the analogous \(\text{B(C}_6\text{F}_5)_4^-\) and \(\text{BPh}_4^-\) complexes reported by Hessen (Figure 2-4), albeit with a smaller magnitude of bending. The V1–C8 distance (2.963 Å) is considerably shorter than the distances between other \(\text{Cp}^+\) methyl C atoms and the V1 center (3.203 – 3.440 Å). This may imply a single C–H agostic interaction with the \(\text{V}^{\text{III}}\) center in 1-V as observed in \(\text{Cp}^+\text{V}^+\) complexes by Hessen. The V–H distance of 2.7(1) Å was long compared to typical M–H agostic interactions (1.8 –2.3 Å)\(^{75}\), although the M–H–C angle (92.6°) was consistent with such an interaction (90 - 140°)\(^{75}\).

In solution, paramagnetism of the \(\text{V}^{\text{III}}\) center results in a broad, paramagnetically shifted singlet (δ 25.10 ppm, \(w_{1/2} \approx 500\) Hz) observed for the \(\text{Cp}^+\) protons in the solution \(^1\text{H NMR}\) spectrum. This, in addition to the known fluxionality of the \(\text{Cp}^+\) ring, allows very little observable detail on the possibility of an agostic interaction in solution by NMR spectroscopy.

**Table 2-4** Selected metrical data for 1-V compared with the literature-reported \(\text{Cp}^+\text{V}^+\text{BPh}_4^-\) and \(\text{Cp}^+\text{V}^+\text{B(C}_6\text{F}_5)_4^-\)\(^{58}\)

<table>
<thead>
<tr>
<th></th>
<th>1-V</th>
<th>(\text{Cp}^+\text{V}^+\text{B(C}_6\text{F}_5)_4^-)</th>
<th>(\text{Cp}^+\text{V}^+\text{BPh}_4^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp}^+\text{–V}^a)</td>
<td>1.878 / 1.888 Å</td>
<td>1.885 / 1.907 Å</td>
<td>1.885 / 1.923 Å</td>
</tr>
<tr>
<td>(\angle \text{Cp}^+\text{–V–Cp}^+)</td>
<td>159.42°</td>
<td>154.82°</td>
<td>155.00°</td>
</tr>
<tr>
<td>(\angle \text{Cp}^+\text{–Cp}^+ (\alpha))</td>
<td>13.48°</td>
<td>15.62°</td>
<td>14.49°</td>
</tr>
<tr>
<td>(\angle \text{C8–C3–Cp})(^b)</td>
<td>10.5°</td>
<td>26.9°</td>
<td>26.1°</td>
</tr>
</tbody>
</table>

\(^a\) Distance between V and the centroid of the \(\text{Cp}^+\) ring. \(^b\) Defined as the angle between the \(\text{Cp}^+\) plane and the \(\text{Cp–CH}_3\) bond for the presumed agostic \(\text{CH}_3\) group.
The absence of interactions between the metal center and the C₆F₅ groups allowed for a solid state packing mode with arene-perfluoroarene interactions governed by the quadrupole interactions between the electron-rich aromatic Cp* ring and an electron-poor perfluorophenyl ring, albeit with a small dihedral angle (10.48°) between the two arene rings. The distance between the centroids is 3.65 Å, comparable to the solid phase π–π stacking in arene-hexafluorobenzene addition compounds\textsuperscript{76} (interplanar distances 3.43 – 3.55 Å) or in selectively fluorinated diphenylbutadiynes\textsuperscript{77} (3.69 Å) (Figure 2-8).

\[ \text{Figure 2-8 Arene-perfluoroarene interactions.} \]
The FT-IR spectra of the three complexes of the series 1-M were very similar (Figure 2-9, Table 2-5). Multiple C–H stretch absorptions manifest as three weak-intensity bands in the region 2980 – 2870 cm\(^{-1}\). The weak B–H stretch at \(\approx 2385\) cm\(^{-1}\) is also observed, along with two intense bands at \(\sim 1510\) cm\(^{-1}\) and \(\sim 1470\) cm\(^{-1}\) corresponding to deformation vibrations of the perfluorophenyl ring seen in compounds bearing the functionality.\(^{78,79}\) While the possibility of a C–H agostic interaction with the V center in 1-V suggests a lower frequency C–H stretch in the 2700 – 2350 cm\(^{-1}\) region may be present,\(^{80}\) the region also corresponds to the frequency of the B–H stretch of the 1-M series, and a discernable peak assignable to the C–H agostic interaction was not located for 1-V. Such lower frequency peaks were also not observed by Hessen in the related metallocenium complexes.\(^{58}\)
Table 2-5 IR data for the hydridoborate complexes 1-M

<table>
<thead>
<tr>
<th>Compound</th>
<th>Region (cm(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Comments(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Sc</td>
<td>2980, 2917, 2870</td>
<td>w</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>2385</td>
<td>w</td>
<td>B–H str</td>
</tr>
<tr>
<td></td>
<td>1511, 1466</td>
<td>s</td>
<td>C(_6)F(_5) def vib</td>
</tr>
<tr>
<td>1-Ti</td>
<td>2970, 2920, 2871</td>
<td>w</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>2387</td>
<td>w</td>
<td>B–H str</td>
</tr>
<tr>
<td></td>
<td>1511, 1466</td>
<td>s</td>
<td>C(_6)F(_5) def vib</td>
</tr>
<tr>
<td>1-V</td>
<td>2963, 2920, 2871</td>
<td>w</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>2380</td>
<td>w</td>
<td>B–H str</td>
</tr>
<tr>
<td></td>
<td>1511, 1470</td>
<td>s</td>
<td>C(_6)F(_5) def vib</td>
</tr>
</tbody>
</table>

\(^{a}\) w = weak, s = strong; \(^{b}\) str = stretching, def vib = deformation vibrations

2.2.2 Synthesis and characterization of the permethylmetallocenium formyloxytris(pentafluorophenyl)borates 2-M (M = Sc, Ti, V)

Treatment of the hydridoborate complexes 1-M with CO\(_2\) (2 atm) leads to the rapid formation of the respective formyloxyborate complexes 2-M (Scheme 2-5), presumably due to the cooperation of the Lewis acidic metal center and the nucleophilic hydride in the counteranion in activating CO\(_2\). More evidence of this cooperativity is described in Section 2.2.4 with the use of inactivated metal centers. These reactions were instantaneous, as observed from the changes in colour and solubility.
Scheme 2-5 CO$_2$ insertion into the hydridoborate complexes 1-M (M = Sc, Ti, V)

 Addition of CO$_2$ to a suspension of the sparingly soluble 1-Sc in C$_6$H$_6$ results in instant dissolution of the bright yellow solid to a straw coloured solution, from which 2-Sc can be obtained as a dull yellow crystalline precipitate on layering the solution with hexanes. The hydridoborate $^1$H resonance at $\delta$ 4.13 ppm disappears, yielding to a new resonance at $\delta$ 8.77 ppm corresponding to a formyloxy CH proton (Table 2-6). The use of $^{13}$CO$_2$ results in the splitting of this resonance into a doublet ($^{1}J_{C-H} = 217$ Hz), as well as the amplification of the corresponding $^{13}$C resonance at $\delta$ 172.9 ppm, a region typical for carboxylic acid derivatives. The $^{11}$B{$^1$H} NMR spectrum also sees a change from the characteristic HB(C$_6$F$_5$)$_3$$^-$ resonance at $\delta$ -25.3 ppm to a broader feature at $\delta$ -0.7 ppm ($\nu_{1/2} \approx 630$ Hz). Similar chemical shifts and peak broadness have been reported in
literature for this anion paired with the dimethylbenzylammonium cation (in C₆D₆, δ -2.2 ppm, ν₁/₂ ≈ 200 Hz), and the tetramethylpiperidinium cation (in toluene-d₈, δ -2.41 ppm, br).³⁹

Both 1-Sc and 2-Sc feature ¹⁹F resonances with ³J_F-F ≈ 20 Hz, allowing the identification of o-, m-, and p-C₆F₅ resonances. The chemical shift difference between m-F and p-F (Δδₗp) is ≈ 6 ppm, characteristic of C₆F₅ groups bound to a four-coordinate boron center.⁶³ For 2-Sc, an equilibrium with 3-Sc (see Scheme 1-25, step b) can be observed in the ¹⁹F{¹H} NMR spectrum (Figure 2-10).⁴⁶

As for 1-Ti, introduction of CO₂ to a dark green solution in C₆H₆ or C₆H₅Br immediately afforded 2-Ti, which were first isolated as deep red crystals on slow evaporation of the C₆H₆ solution into toluene by Dr. Matthew Sloan. Alternatively, layering a C₆H₅Br solution with hexanes and cooling to -35 °C was found to be an effective recrystallization method. Although broadened due to the paramagnetic Ti³⁺ center, the Cp*-methyl ¹H resonance of 2-Ti was observed to shift from δ 13.3 ppm in 1-Ti (ν₁/₂ ≈ 2250 Hz) to δ 14.8 ppm in 2-Ti (ν₁/₂ ≈ 2700 Hz). ¹¹B{¹H} NMR spectroscopy again offered the characteristic disappearance of the sharp hyridoborate resonance (δ -23.2 ppm) in favour of the broader formyloxyborate resonance (δ – 2.0 ppm, ν₁/₂ ≈ 400 Hz) as seen similarly from 1-Sc to 2-Sc.⁴⁶ The similarities in the chemical shifts and peak widths of the ¹¹B{¹H} resonances between 2-Sc and 2-Ti suggest that the boron center is not significantly influenced by the paramagnetic nature of the Ti³⁺ center. Similar ¹⁹F NMR resonances were also observed when comparing 2-Sc and 2-Ti, although the ortho-ArF resonances of 2-Ti were broadened (ν₁/₂ ≈ 350 Hz), perhaps due to increased rate of spin relaxation aided by the paramagnetic Ti³⁺ center, either conveyed through orbital overlap or through the magnetic field of the paramagnetic center through space. Since the transmission of spin information over seven
bonds is unlikely, it is conceivable that the broadening of the \( o \)-F resonance is due to through space effects. Indeed, from the X-ray structure of 2-Ti (Figure 2-13), three \textit{ortho}-F atoms are at 4.791, 5.203 and 5.234 Å away from the Ti center, the closest of which lies in the plane of the three lowest energy \( d \) orbitals of Ti. Assuming that the contact ion-pair structure is intact in solution, it is conceivable that the rotation around the B–O bond and the B–C(Ar) bonds would allow for the \( o \)-F atoms to align with the singly-occupied orbital of the Ti center in solution. A close observation of the \( ^{19} \text{F} \) spectra of 2-Ti reveals that the \( m \)- and \( p \)- ArF resonances are similarly broadened, but to a lesser extent (\( \nu_{1/2} \approx 50 \) Hz and 45 Hz, respectively). This is reasonable since through space effects of paramagnetic nuclei are known to decrease with distance (\( r \)) in an inverse-cube relationship (\( 1/r^3 \)).

On addition of CO\(_2\) to a red-brown suspension of 1-V in C\(_6\)H\(_5\)Br, dissolution to a deep blue solution of the more soluble 2-V was observed instantly, from which deep blue crystals were formed on standing. This is accompanied by the disappearance of the characteristic \( ^1 \text{H} \) and \( ^{11} \text{B} \) hydridoborate resonances at \( \delta \) 4.20 ppm and \( \delta \) -24.64 ppm respectively, in favour of the formyloxyborate resonance observed in the \( ^{11} \text{B} \) NMR spectrum (\( \delta \) -0.19 ppm), although the accompanying \( ^1 \text{H} \) resonance was not located. A comparison of the \( ^{19} \text{F} \) \( o \)-F resonances of the 2-M series in Table 2-6 and Figure 2-10 reveals a downfield shift and broadening of this signal in 2-V (\( \nu_{1/2} \approx 200 \) Hz) than the \( m \)- and \( p \)-F resonances (\( \nu_{1/2} \approx 50 \) Hz), similar to 2-Ti.
Figure 2-10 $^{19}$F NMR spectra of 2-M (376.5 MHz, C$_6$D$_3$Br), from top to bottom – 2-Sc (resonances of the reversibly formed B(C$_6$F$_3$)$_3$ are marked with an asterisk), 2-Ti and 2-V.
Table 2-6 NMR data for the formyloxyborate complexes 2-Sc, 2-Ti and 2-V

<table>
<thead>
<tr>
<th>Resonance a</th>
<th>2-Sc</th>
<th>2-Ti</th>
<th>2-V</th>
</tr>
</thead>
<tbody>
<tr>
<td>^1H NMR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_5(CH_3)_5</td>
<td>1.67 (s)</td>
<td>14.80 (br, ν_{1/2} ≈ 2700 Hz)</td>
<td>10.40 (br, ν_{1/2} ≈ 850 Hz)</td>
</tr>
<tr>
<td>HCO_2B(C_6F_5)_3</td>
<td>8.77 (s)</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>^11B (^1H) NMR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO_2BAr_3</td>
<td>- 0.7 (br, ν_{1/2} ≈ 630 Hz)</td>
<td>- 1.95 (br, ν_{1/2} ≈ 400 Hz)</td>
<td>- 0.19 (br, ν_{1/2} ≈ 500 Hz)</td>
</tr>
<tr>
<td>^13C (^1H) NMR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_5(CH_3)_5</td>
<td>124.2, 10.4</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>HCO_2B</td>
<td>172.9</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>^19F (^1H) NMR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-C_6F_5</td>
<td>- 132.8 (m) (br, ν_{1/2} ≈ 350 Hz)</td>
<td>- 130.4 (br, ν_{1/2} ≈ 200 Hz)</td>
<td>- 128.3</td>
</tr>
<tr>
<td>m-C_6F_5</td>
<td>- 163.1 (m) (br, ν_{1/2} ≈ 50 Hz)</td>
<td>- 163.1</td>
<td>- 163.2</td>
</tr>
<tr>
<td>p-C_6F_5</td>
<td>- 156.4 (t, J = 21 Hz)</td>
<td>- 156.4 (s)</td>
<td>- 156.6</td>
</tr>
</tbody>
</table>

a Recorded in C_6D_5Br at room temperature except for 1-Sc (C_6D_6). b Not observed due to paramagnetism.

The FT-IR spectra again have very similar features between the three analogous complexes. A summary of distinct IR features is presented in Table 2-7. The similar bands for Cp*-C–H stretch (≈ 2900 cm\(^{-1}\)) and the two intense bands from the C_6F_5 ring deformation (≈ 1500 cm\(^{-1}\)) vibrations are observed as in 1-M. The hydridoborate B–H stretch is no longer observed, and the asymmetric C–O stretch of the formyloxy moiety is seen at ≈ 1640 cm\(^{-1}\). The location of the medium intensity symmetric stretch was not immediately obvious, since there are multiple bands in the 1450 – 1300 cm\(^{-1}\) region. ^13C-labelling of the formyloxy carbon atom of the 2-M series gave the labelled series (2-M'). FT-IR spectra of this series were otherwise identical to the unlabelled compound except for two peaks shifted to lower frequencies, allowing the identification of the
symmetric C–O stretch (Figure 2-11). The band at \( \simeq 1640 \text{ cm}^{-1} \) was also observed in the 1-M series, albeit much weaker, which is attributed to the brief exposure of the sample KBr pellet to air before insertion into the spectrometer, allowing for reaction with atmospheric CO\(_2\) to form traces of 2-M.

Table 2-7 IR data for the formyloxyborate complexes 2-M and 2-M’

<table>
<thead>
<tr>
<th>Compound</th>
<th>Region (cm(^{-1}))</th>
<th>Intensity(^a)</th>
<th>Comments(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Sc (2-Sc’)</td>
<td>2959, 2916, 2850</td>
<td>w</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>1621 (1597)(^c)</td>
<td>s</td>
<td>Asym C=O str</td>
</tr>
<tr>
<td></td>
<td>1518, 1467</td>
<td>s</td>
<td>C(_6)F(_5) def vib</td>
</tr>
<tr>
<td></td>
<td>1340 (1328)(^c)</td>
<td>w</td>
<td>Sym C=O str</td>
</tr>
<tr>
<td>2-Ti (2-Ti’)</td>
<td>2975, 2912, 2865</td>
<td>w</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>1618 (1579)(^c)</td>
<td>s</td>
<td>Asym C=O str</td>
</tr>
<tr>
<td></td>
<td>1516, 1468</td>
<td>s</td>
<td>C(_6)F(_5) def vib</td>
</tr>
<tr>
<td></td>
<td>1337 (1327)(^c)</td>
<td>w</td>
<td>Sym C=O str</td>
</tr>
<tr>
<td>2-V (2-V’)</td>
<td>2908, 2860</td>
<td>w</td>
<td>C–H str</td>
</tr>
<tr>
<td></td>
<td>1635 (1591)(^c)</td>
<td>s</td>
<td>Asym C=O str</td>
</tr>
<tr>
<td></td>
<td>1517, 1467</td>
<td>s</td>
<td>C(_6)F(_5) def vib</td>
</tr>
<tr>
<td></td>
<td>1321 (1307)(^c)</td>
<td>w</td>
<td>Sym C=O str</td>
</tr>
</tbody>
</table>

\(^a\) w = weak, s = strong; \(^b\) str = stretching, asym = asymmetric, sym = symmetric, def vib = deformation vibrations; \(^c\) values in brackets correspond to the isotopically labelled \(^{13}\)C=O stretch of the 2-M’ series
Figure 2-11 Top: FT-IR spectrum of 2-V representative of the 2-M series. Bottom: Expansion of the ν(C=O) region of 2-V and 2-V’ showing the effect of isotopic substitution.
The solid state structures of the 2-M series have been elucidated through single crystal XRD. Coordination of the formyl oxygen to the metal centers were observed for all three analogous complexes. The bridging formyloxy C-O bonds are not equal – the slightly shorter C21–O1(–M1) bond compared to the C21–O2(–B1) bond (Table 2-8) indicates a small preference for the zwitterionic resonance structure (left) over the neutral B(C₆F₅)₃ adduct structure (right) (Figure 2-12).

![Figure 2-12 Possible resonance forms of 2-M](image)

<table>
<thead>
<tr>
<th></th>
<th>2-Sc⁴⁶</th>
<th>2-Ti</th>
<th>2-V</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1–O1</td>
<td>2.088(3) Å</td>
<td>2.034(3) Å</td>
<td>2.077(3) Å</td>
</tr>
<tr>
<td>O1–C21</td>
<td>1.236(5) Å</td>
<td>1.241(3) Å</td>
<td>1.228(6) Å</td>
</tr>
<tr>
<td>C21–O2</td>
<td>1.272(5) Å</td>
<td>1.269(3) Å</td>
<td>1.273(7) Å</td>
</tr>
<tr>
<td>O2–B1</td>
<td>1.560(5) Å</td>
<td>1.560(3) Å</td>
<td>1.548(6) Å</td>
</tr>
<tr>
<td>Cp*–M1</td>
<td>2.133 / 2.127 Å</td>
<td>2.038 / 2.038 Å</td>
<td>1.824 / 2.175 Å</td>
</tr>
<tr>
<td>∠O1–C21–O2</td>
<td>122.7(3)°</td>
<td>122.6(2)°</td>
<td>124.0(5)°</td>
</tr>
<tr>
<td>∠M–O1–C21</td>
<td>151.2(3)°</td>
<td>155.2(2)°</td>
<td>145.69°</td>
</tr>
<tr>
<td>∠C21–O2–B1</td>
<td>129.2(3)°</td>
<td>129.4(2)°</td>
<td>128.13°</td>
</tr>
<tr>
<td>∠Cp*–Cp* (α)</td>
<td>34.24°</td>
<td>34.51°</td>
<td>32.14°</td>
</tr>
<tr>
<td>∠Cp*–M–Cp* a</td>
<td>144.23°</td>
<td>144.34°</td>
<td>150.24°</td>
</tr>
<tr>
<td>∑∠M</td>
<td>359.85°</td>
<td>359.99°</td>
<td>359.20°</td>
</tr>
</tbody>
</table>

*a Distance / Angle between the metal and the two centroids of the Cp* rings. b Sum of the three angles around the metal center, connecting to O1 and to the centroids of the Cp* rings.
The difference in the C–O bond lengths (C21–O1 and C21–O2) is larger for 2-Sc (0.036 Å) and 2-V (0.045 Å), but smaller in 2-Ti (0.028 Å), perhaps implying slightly more delocalization of negative charge in 2-Ti. This pattern correlates with the shorter M1–O1 bond in 2-Ti compared to 2-Sc or 2-V, suggesting that the stronger M1–O1 interaction may be related to the higher degree of charge delocalization across the formyloxy bridge. However, contraction of the ionic radii across the period (Sc$^{3+}$: 74.5 pm; Ti$^{3+}$: 67 pm; V$^{3+}$: 64 pm$^{61}$ prevents meaningful interpretation of the M–O bond changes.

A comparison of the M1–O1 bond length with the series of THF complexes reported by Hessen$^{58}$ reveal that the 2-M complexes have consistently shorter M–O bond lengths for all three metals from the coordination of the formyloxy moiety, when compared to the coordination of a THF ligand (Table 2-9). This is indicative of the contributions from the neutral resonance form (Figure 2-12) towards the increased strength of the formyloxy coordination relative to a coordination bond.

Table 2-9 M–O bond lengths in the formyloxyborate complexes 2-M and in THF complexes$^{58}$

<table>
<thead>
<tr>
<th>M</th>
<th>[Cp$_2$M(THF)$_n$]$^+[\text{BPh}_4]$</th>
<th>Cp$_2$MOC(H)OB(C$_6$F$_5$)$_3$ (2-M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>2.2964(14) / 2.2652(14) Å$^a$</td>
<td>2.088(3) Å</td>
</tr>
<tr>
<td>Ti</td>
<td>2.116(3) Å</td>
<td>2.034(3) Å</td>
</tr>
<tr>
<td>V</td>
<td>2.1189(8) Å</td>
<td>2.077(3) Å</td>
</tr>
</tbody>
</table>

$^a$ n = 1 for Sc, n = 2 for Ti, V. The two values for Sc indicate the M–O bond lengths to the two coordinated THF molecules
Figure 2-13 Thermal ellipsoid diagrams of the solid state structures of 2-M (from top, M = Sc, Ti, V) at 50% probability. All hydrogens except for H21, and cocrystallized C₆H₆ in 2-Sc and 2-Ti, are removed for clarity. 2-Ti was crystallized by Dr. Matthew Sloan.
CO₂ activation by the 1-M complexes to generate the 2-M complexes were instantaneous, which rendered the kinetic properties of this reaction difficult to study. More insight to the mechanism of CO₂ activation was probed through DFT computations by Dr. Ludovic Castro and Prof. Laurent Maron (University of Toulouse).

**Figure 2-14** Gibbs energy profile of the reaction of 1-Sc and CO₂ to form 2-Sc. (Adapted from Ref. 46 with permission from The Royal Society of Chemistry.)
Figure 2-15 Gibbs energy profile of the reaction of 1-Ti and CO$_2$ to form 2-Ti.

A comparison between the computed pathways for 1-Sc (Figure 2-14) and 1-Ti (Figure 2-15) shows a very similar pathway and energy profile between the two systems. The initial endoergic step involves slippage of the bidentate Ar–M interaction and concomitant coordination of CO$_2$. In 1-Sc, this results in a monodentate ArF coordination, whereas in 1-Ti, complete dissociation of the anion was found to be the lowest energy pathway. The optimized geometries
of the intermediates \textbf{INT1} in both cases are such that the hydride is in close proximity to the CO$_2$ carbon center. The subsequent hydride attack on the CO$_2$ passes through a slightly endoergic transition state (TS$_A$), where the linear geometry of CO$_2$ is perturbed to facilitate the transformation. The systems then evolve to \textbf{INT2}, the neutral formate species 3-M and the free B(C$_6$F$_5$)$_3$, which is exoergic with respect to the reactants (-15.5 kcal mol$^{-1}$ and -13.1 kcal mol$^{-1}$ for 1-Sc and 1-Ti, respectively), presumably due to the proximity of the positive and negative charges$^{46}$ and the entropically favourable bidentate coordination of the formate ligand to the early metal centers in 3-M. Subsequent interaction of B(C$_6$F$_5$)$_3$ with the formate oxygen atoms results in the abstraction of the coordinated formate ligand to form 2-M. The energy barriers from \textbf{INT2} to 2-M are low (9.8 kcal mol$^{-1}$ for Sc, 8.8 kcal mol$^{-1}$ for Ti), suggesting a kinetically facile step. The difference in Gibbs free energy between \textbf{INT2-Sc} and 2-Sc is only 6.4 kcal mol$^{-1}$. This energy difference is comparable to the experimental Gibbs free energy difference of 1.2 kcal mol$^{-1}$ favouring 2-Sc derived from the observation of both B(C$_6$F$_5$)$_3$ and 2-Sc resonances integrating to a ratio of approximately 1:7 in the $^{19}$F NMR spectrum of 2-Sc (Figure 2-10). The computed energy difference between \textbf{INT2-Ti} and 2-Ti is greater (10.7 kcal mol$^{-1}$), which supports the spectroscopic evidence that B(C$_6$F$_5$)$_3$ was not observed in the $^{19}$F NMR spectrum of 2-Ti at room temperature.

The energy profile of 1-V (Figure 2-16) shows that the CO$_2$ activation barriers are much lower. While the optimized geometry of 1-V possesses a monodentate ArF coordination, this coordination was not observed in the crystallographically-determined solid state structure of 1-V. Hessen has reported the similar calculation that fluoroarene coordination to Cp$^*$$_2$V$^+$ was slightly exoergic, but lower than the expected 10 kcal mol$^{-1}$ loss of entropy on coordination.$^{58}$ Here we can see that dissociation of the monocoordinated anion to allow for coordination of CO$_2$ (\textbf{INT1-V}) is only endoergic by 0.3 kcal mol$^{-1}$. Moreover, \textbf{INT2-V} is much higher in energy (+ 17.6 kcal mol$^{-1}$
compared to \textbf{2-V}) than \textbf{INT2-Sc} (+ 6.4 kcal mol$^{-1}$ from \textbf{2-Sc}) or \textbf{INT2-Ti} (+ 10.7 kcal mol$^{-1}$ from \textbf{2-Ti}), presumably due to the lack of two coordination sites in the $d^2$ V$^{\text{III}}$ center of \textbf{3-V} for bidentate formate coordination, as observed in the monodentate optimized geometry. This geometry allows for facile interaction of the non-coordinating formate oxygen with the free borane in a low energy \textbf{TS2} ($\Delta G^\ddagger = 2.8$ kcal mol$^{-1}$ compared to 9.8 kcal mol$^{-1}$ for Sc, 8.8 kcal mol$^{-1}$ for Ti). Compared to Sc and Ti, the V system has the lowest overall energy barrier from \textbf{1-M} to \textbf{2-M}, the primary contribution arising from the aforementioned lability of the HB(C$_6$F$_5$)$_3^-$ anion in \textbf{1-V}.

\textbf{Figure 2-16} Gibbs energy profile of the reaction of \textbf{1-V} and CO$_2$ to form \textbf{2-V}.
2.2.3 Catalytic activity of the hydridoborate complexes towards CO$_2$ hydrosilation

As described in Section 1.4.3, 1-Sc is a CO$_2$ hydrosilation catalyst, in tandem with B(C$_6$F$_5$)$_3$, selective for the exhaustive reduction to CH$_4$ (Scheme 1-25). Experiments suggest the operation of two pathways responsible for the slow induction period and subsequent fast hydrosilane consumption. The role of the metallocene catalyst is to activate CO$_2$ and transfer the resulting formyloxy moiety to a stoichiometric hydrosilane reductant, where further reductions are catalyzed by B(C$_6$F$_5$)$_3$. In section 2.2.1 it is demonstrated that CO$_2$ activation is observed with all three hydridoborate complexes 1-M. Since the rate determining step of the initial, slow pathway is proposed to be the transfer of the formyloxy moiety to the B(C$_6$F$_5$)$_3$-activated hydrosilane, we hypothesized that increasing the number of $d$ electrons on the metal would weaken the formyloxy coordination to the metal center and possibly lead to higher initial rates. However, this is found to be a considerable oversimplification of the catalytic system. Scheme 2-6 shows the generalized catalytic mechanism based on 1-Sc, incorporating the results from 1-Ti and 1-V, which were observed to show somewhat similar but distinct behaviour, as will be described below in greater detail.

In the rate determining step, an equilibrium between 2-Sc and 3-Sc and free B(C$_6$F$_5$)$_3$ has been implicated, where the C1 fragment is transferred from the 3-Sc (Scheme 2-6, step d). A similar scheme can be proposed for 2-Ti, as depicted in Scheme 2-7. 3-Ti, depicted as a monomer, possibly consists of oligomers of varied nuclearity in solution similar to 3-Sc. This adds to the difficulty in tracking discrete paramagnetic formate species in this mixture by NMR spectroscopy.
Scheme 2-6 Catalytic CO$_2$ hydrosilation by the 1-M catalysts
Scheme 2-7 Possible CO₂ activation and formate transfer mechanism for 1-Ti.

Step b in Scheme 2-7 depicts an equilibrium between 2-Ti and the neutral titanocene formate 3-Ti. This equilibrium is proposed based on observations from 2-Sc, where the equilibrium is observed by $^{19}$F NMR spectroscopy, and that the equilibrium can be shifted on adding excess B(C₆F₅)₃, which led to slower formate transfer due to the decrease in the concentration of 3-Sc.

The independent synthesis of 2-Ti from 3-Ti and B(C₆F₅)₃ (Scheme 2-8) demonstrates the reverse direction of step b. Salt metathesis of dark purple Cp*$₂$TiCl with methylmagnesium chloride yields dark-green methylbis($η^5$-pentamethylcyclopentadienyl)titanium(III), Cp*$₂$TiMe. Treatment with dihydrogen (4 atm) gives the deep red hydride complex via a σ-bond metathesis.
reaction.\textsuperscript{83} CO\textsubscript{2} insertion into the Ti-H bond yields the pale blue permethyltitanocene formate, \textbf{3-Ti}. When this was treated with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, \textbf{2-Ti} was identified as the major product by \textsuperscript{1}H, \textsuperscript{11}B and \textsuperscript{19}F NMR spectroscopy, and residual B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} was not detected, establishing the complete conversion to \textbf{2-Ti}. Compared to \textbf{2-Sc}, which is in equilibrium with the formate complex and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, \textbf{2-Ti} does not appear to be in an analogous equilibrium, since B(C\textsubscript{6}F\textsubscript{5}) was not observed in the \textsuperscript{19}F NMR spectrum of \textbf{2-Ti}. This phenomenon was also supported by computational results (Figure 2-14 and Figure 2-15).

\begin{center}
\begin{align*}
\text{Cp}^*\text{2TiCl} & \xrightarrow{\text{MeMgBr, Et}_2\text{O, -78 °C}} \text{Cp}^*\text{2TiMe} & \xrightarrow{(i) \text{H}_2; (ii) CO}_2 \text{C}_6\text{H}_6 & \xrightarrow{\text{B(C}_6\text{F}_5)_3, \text{ Hexanes}} \text{2-Ti} \\
& & & \text{Cp}^*\text{2Ti}(\kappa^2\text{-O}_2\text{CH}) & \text{3-Ti}
\end{align*}
\end{center}

\textbf{Scheme 2-8} Alternative synthetic route to the formation of \textbf{2-Ti}

Nevertheless, treatment of excess Et\textsubscript{3}SiH with CO\textsubscript{2} in the presence of catalytic amounts of \textbf{2-Ti} and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} resulted in the formation of (Et\textsubscript{3}Si\textsubscript{2})O and CH\textsubscript{4} as observed by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy. The only observable intermediate during the course of the catalytic reaction was \textit{bis}(triethylsiloxy)methane, CH\textsubscript{2}(OSiEt\textsubscript{3})\textsubscript{2}, the acetal species that results upon addition of two equivalents of hydrosilane to CO\textsubscript{2}. The absence of observable concentrations of triethylsilyl formate is consistent with observations from the \textbf{1-Sc} system, where its absence is attributed to its rapid reduction to CH\textsubscript{2}(OSiEt\textsubscript{3})\textsubscript{2} in the presence of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and Et\textsubscript{3}SiH.\textsuperscript{46} Hydrosilation of the acetal is slower and therefore this species builds up in concentration in these reactions.

Similar to the \textbf{1-Sc} catalyzed system,\textsuperscript{46} a sigmoidal curve was observed with catalytic \textbf{1-Ti} on monitoring the rate of hydrosilane consumption with time in a CO\textsubscript{2} hydrosilation experiment.
When conditions identical to that employed for 1-Sc were used, a comparison of the two Et$_3$SiH consumption curves from 1-Sc and 1-Ti revealed a longer induction period and a generally less effective catalysis by 1-Ti.

![Graph showing Et$_3$SiH consumption](image)

**Figure 2-17** Et$_3$SiH consumption in CO$_2$ hydrosilation catalyzed by 1-Sc and 1-Ti with B(C$_6$F$_5$)$_3$.

Conditions: 120 μmol Et$_3$SiH, 4 μmol 1-M, 4 μmol B(C$_6$F$_5$)$_3$, 40 μmol toluene (internal standard), made up to 550 μL with C$_6$D$_5$Br and added 313 μmol CO$_2$.

The rate determining step of Path A was proposed to be formate transfer from a metal formate-containing species to produce triethylsilyl formate, Et$_3$SiOCHO (step $d$, Scheme 2-6). In the proposed mechanism developed for 1-Sc, this species is suggested to be 3-Sc. Adopting the same mechanism for Ti$_{III}$, this may imply the formation of the analogous titanocene formate species 3-Ti, where formate transfer to the activated hydrosilane is slower than from 3-Sc. However, the paramagnetic nature of Ti$_{III}$ hindered the direct observation of 3-Ti.
From the sigmoidal nature of the two kinetic curves we can infer that both systems operate through a second pathway (Path B, Scheme 2-6), which requires the build-up of the acetal intermediate species. The increased rate of Path B compared to the Path A is due to the labilization of the formyloxyborate moiety upon coordination of the acetal to the Lewis acidic metal center, the rate determining step now proposed to be coordination of the acetal. In the kinetic plot (Figure 2-17), we can observe the operation of Path B from the increase in the rate of Et₃SiH consumption at the end of the induction period. Therefore, comparing the Et₃SiH-consumption curves of the 1-Sc and 1-Ti catalyzed reactions, we can see that Path B is slower to operate with the latter catalyst.

A hypothesis for the observed longer induction period with 2-Ti is that the smaller Ti³⁺ cation is more sterically hindered towards CH₂(OSiEt₃)₂ coordination. This steric factor has been previously seen in the coordination of two THF molecules to Cp⁺₂Sc⁺ versus only one THF molecule for Cp⁺₂Ti⁺.⁵⁸ Therefore it is plausible that the longer induction period may not necessarily be due to the slow production of CH₂(OSiEt₃)₂, but rather that a higher concentration of this intermediate is necessary to generate the acetal-separated ion-pair from 2-Ti, resulting in a more thermodynamically difficult activation of Path B. However, a comparison of the concentrations of the reduction intermediates towards the end of the induction period reveals higher concentrations of CH₂(OSiEt₃)₂ present in the 1-Sc catalyzed system at this stage of the reaction (4.4 mM CH₂(OSiEt₃)₂ for 1-Sc vs. 1.9 mM for 1-Ti), which refutes this hypothesis. Therefore the longer induction period is likely due to the slower Path A rate determining step in the 1-Ti system compared to 1-Sc.

On comparing the kinetics of the 1-V catalyzed reaction to both 1-Sc and 1-Ti, a significant difference can be observed regarding the shape of the curve. Instead of a sigmoidal curve indicative of two pathways with differing rates, an exponential decay curve is found for 1-V (Figure 2-18).
For most of the reaction (up to \( \approx 60\% \) consumption of \( \text{Et}_{3}\text{SiH} \)) a first order decay was observed

\( R^2 = 0.9969 \) for fitting a linear curve for the plot of \( \ln[\text{Et}_{3}\text{SiH}] \) vs. time), consistent with a rate law involving \([\text{Et}_{3}\text{SiH}]\) and possibly other species with constant concentration(s) throughout the reaction (e.g. catalysts). Towards lower concentrations of \( \text{Et}_{3}\text{SiH} \), it can be reasoned that lower partial pressures of \( \text{CO}_2 \) and the production of \( \text{CH}_4 \) may complicate the diffusion rates of gases in and out of the solution phase, affecting the overall rate of \( \text{Et}_{3}\text{SiH} \) consumption. At the end of the reaction when \( \text{Et}_{3}\text{SiH} \) is consumed completely, \( \text{CH}_4 \) and \( \text{CH}_2(\text{OSiEt})_2 \) were observed as the major products, while \( \text{Et}_3\text{SiOCH}_3 \) was only present in trace amounts, for all three metals studied.

However, the exact product distribution cannot be quantified due to the evolution of \( \text{CH}_4 \) into the headspace of the sealed NMR tube.

A close observation of the \( ^1\text{H} \) NMR spectra reveals that the broad \( \text{HB}(\text{C}_6\text{F}_5)_3^- \) resonance was not observed in the \( ^1\text{H} \) NMR spectra throughout the reaction, suggesting the resting state of the metallocene catalyst to be \( 2-\text{V} \) rather than \( 1-\text{V} \). These findings are consistent with the formate transfer to form triethylsilyle formate being the rate determining step in the \( 1-\text{V} \) catalyzed reaction, which agrees with the conclusions regarding the similar rate determining step of Path A (Scheme 2-6) for the \( 1-\text{Sc} \) and \( 1-\text{Ti} \) catalyzed systems.

On comparing the rates of \( \text{Et}_3\text{SiH} \) consumption with all three of the metallocene catalysts \( 1-\text{M} \), we can see that \( 1-\text{V} \) is initially the most active catalyst. However, the absence of a second, \( \text{CH}_2(\text{OSiEt})_2 \)-mediated pathway leads to slower complete consumption of \( \text{Et}_3\text{SiH} \) with \( 1-\text{V} \) under the same conditions. Between \( 1-\text{Sc} \) and \( 1-\text{Ti} \), the two systems capable of two operational mechanisms, we can see that \( 1-\text{Sc} \) shows both a shorter induction period and faster consumption of \( \text{Et}_3\text{SiH} \) than \( 1-\text{Ti} \), as discussed above. Under the conditions used for the three systems, the
maximum TOF of Et₃SiH were found to be 8.99 h⁻¹, 0.99 h⁻¹ and 0.88 h⁻¹ for 1-Sc, 1-Ti and 1-V, respectively.

**Figure 2-18** Consumption of Et₃SiH in 1-V catalyzed CO₂ hydrosilation (green: actual consumption curve, orange: the natural logarithm of the consumption curve – the equation and $R^2$ values refer to the least-squares fit of the logarithmic curve from $t = 0 – 28.39 \, h$)
2.2.4 Reactions of the permethylmetallocenium complexes with carbon monoxide

Berkefeld and Piers have shown that treatment of CO with 1-Sc results in the formation of two CO activation products (Scheme 2-9). The O-bound nature of the products suggests the initial reversible formation of a transient scandocenium isocarbonyl complex that undergoes subsequent reaction with the hydridoborate counteranion.

Figure 2-19 Comparison of Et₃SiH consumption in the CO₂ hydrosilation with 1-M catalysts
Treatment of 1-Ti with CO led to a black oil (1-TiCO) insoluble in hydrocarbon solvents but soluble in bromobenzene. The observation of sharp resonances in the expected chemical shift regions in $^{11}$B{¹H} and $^{19}$F{¹H} NMR spectroscopy suggests a non-interacting HB(C$_6$F$_5$)$_3$⁻ anion. The doublet resonance ($^1J_{B-H} = 80$ Hz) in the proton-coupled $^{11}$B NMR spectrum further supports a B–H connectivity. The $^1$H NMR Cp⁺ signal of 1-Ti at 13.3 ppm completely disappeared, and the broad hydridoborate signal at 4.46 ppm ($\nu_{1/2} \approx 285$ Hz), except from minor aliphatic impurities, is the only observed signal in the $^1$H NMR spectrum recorded from +250 ppm to -250 ppm. The absence of the diamagnetic Cp⁺¹H resonance ($\delta 1.3$-1.8 ppm) rules out the presence of diamagnetic Cp⁺ coordination environments resulting from either possible disproportionation into Ti⁴ complexes or the spin coupling from dinuclear or multinuclear Ti³ complexes.

The FT-IR spectrum of a solid sample of 1-TiCO in a KBr pellet revealed the asymmetric (2075 cm⁻¹) and symmetric (2049 cm⁻¹) C-O stretches consistent with dicarbonyl$\text{bis}(\eta^5$-pentamethylenecyclopentadienyl) complexes such as Cp⁺₂Ti(CO)$_2$, which has two strong IR carbonyl
stretching absorptions at 1940 and 1858 cm\(^{-1}\).\(^{84}\) The lower energy C≡O stretches of the latter example is presumably due to the higher degree of back-donation into the \(\pi^*_{\text{C≡O}}\) orbital(s) from the lower oxidation state Ti\(^{II}\) center.

Based on this reasoning, a realistic proposal for the structure of \(\text{1-Ti}_{\text{CO}}\) is the ionic species depicted in Scheme 2-10. Using this molecular formula, the effective magnetic moment (\(\mu_{\text{eff}}\)) of the complex formed was estimated from Evans’ method\(^{85}\) to be \(\approx 1.9\), consistent with the bulk presence of a \(d^1\) complex.

![Scheme 2-10](image)

**Scheme 2-10** Synthesis and plausible structure of \(\text{1-Ti}_{\text{CO}}\)

The reaction of a dark red solution of \(\text{1-V}\) in \(\text{C}_6\text{H}_5\text{Br}\) with CO led to the gradual formation of the dull yellow dicarbonyl\(\text{bis(}\eta^5\text{-pentamethylcyclopentadienyl)}\)vanadium(III) hyridoborate species \(\text{1-V}_{\text{CO}}\) (Scheme 2-11) over five minutes. Literature precedence has established the dicarbonyl coordination mode to V\(^{III}\) resulting in the formation of an 18-electron low-spin diamagnetic \(d^2\) species, where the cation is coordinatively saturated and no longer Lewis acidic.\(^{86}\) The \(^1\text{H}\) chemical shift of the \(\text{Cp}^* \text{CH}_3\) groups in \(\text{1-V}_{\text{CO}}\) (\(\delta \approx 1.36\) ppm) agrees with values expected for a diamagnetic species (\(cf\). \(\text{1-Sc}\) \(\delta \approx 1.58\) ppm; paramagnetic \(\text{1-V}\), \(\delta \approx 25.10\) ppm). Subjecting a
solution sample to the Evans’ method provided extra evidence to support a low-spin diamagnetic electronic configuration, since the expected downfield shift of the resonance of an internal standard (toluene) due to the paramagnetic susceptibility of \( \text{1-V}_{\text{CO}} \) in \( \text{C}_6\text{D}_5\text{Br} \) solution was not observed, and signals were shifted slightly upfield instead, presumably due to the added diamagnetic influence of \( \text{1-V}_{\text{CO}} \). The FT-IR spectrum features two intense carbonyl stretching bands at 2003 cm\(^{-1}\) and 1954 cm\(^{-1}\) (Table 2-10), comparable to other \([\text{Cp}^*\text{V(CO)}_2]^+\) complexes reported in literature.\(^{86}\)

![Scheme 2-11 Synthesis of \( \text{1-V}_{\text{CO}} \) by carbonyl coordination to \( \text{1-V} \)](image)

Single crystal XRD allowed for the structural characterization of \( \text{1-V}_{\text{CO}} \), confirming the dicarbonyl coordination mode (Figure 2-20). No short contacts were found between the V center and the counteranion, consistent with the absence of empty coordination sites. XRD data for other reported compounds of the dicarbonyl\(b\text{is}(\eta^5\text{-pentamethylcyclopentadienyl})\text{vanadium(III)}\) cation, \([\text{Cp}^*\text{V(CO)}_2]^+\), were not available for comparison. The structure of \( \text{1-V}_{\text{CO}} \) revealed the possible arene-perfluoroarene interactions seen between the \( \text{Cp}^* \) ring and a \( \text{C}_6\text{F}_5 \) ring, akin to with the similarly separated ion-pair \( \text{1-V} \). However, the greater dihedral angle (23.13° \text{ vs } \text{1-V} 10.48°) and
parallel displacement between the two intermolecular rings (as indicated by the large distance of 4.36 Å between the two centroids) may imply that this interaction is quite weak, if present at all.

Table 2-10 IR data for the carbonyl complexes 1-Tico, 1-Vco, 2-Vco (frequencies in cm\(^{-1}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(C=O)) (asym, sym)</th>
<th>(\nu(B-H))</th>
<th>(\nu(C=O)^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Tico</td>
<td>2075, 2049</td>
<td>1510, 1466</td>
<td>2371</td>
</tr>
<tr>
<td>1-Vco</td>
<td>2003, 1954</td>
<td>1509, 1463</td>
<td>2423</td>
</tr>
<tr>
<td>2-Vco</td>
<td>1999, 1947</td>
<td>1514, 1463</td>
<td>1707, 1696, 1273, 1251 (1668, 1654, 1228, 1213)(^b)</td>
</tr>
</tbody>
</table>

\(^a\) C=O stretch of the bridging formyloxy moiety. \(^b\) Isotopically-shifted peaks on \(^{13}\)C-labelling of the formyloxy carbon

Table 2-11 Selected metrical data for 1-Vco

<table>
<thead>
<tr>
<th>Distance / Angle</th>
<th>(\text{Distance} / \text{Angle})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp}^* - \text{V1})(^a)</td>
<td>1.966 / 1.960 Å</td>
</tr>
<tr>
<td>C21–O1</td>
<td>1.130(9) Å</td>
</tr>
<tr>
<td>C22–O2</td>
<td>1.148(9) Å</td>
</tr>
<tr>
<td>V1–C21</td>
<td>1.917(7) Å</td>
</tr>
<tr>
<td>V1–C22</td>
<td>1.926(7) Å</td>
</tr>
<tr>
<td>(\angle \text{Cp}^* - \text{Cp}^* (\alpha))</td>
<td>144.89°</td>
</tr>
<tr>
<td>(\angle \text{V1–C21–O1})</td>
<td>178.2(7)°</td>
</tr>
<tr>
<td>(\angle \text{V1–C22–O2})</td>
<td>177.1(7)°</td>
</tr>
<tr>
<td>(\angle \text{C21–V1–C22})</td>
<td>85.3(3)°</td>
</tr>
</tbody>
</table>

\(^a\) Distance / Angle between the metal and the two centroids of the \(\text{Cp}^*\) rings
Figure 2-20 Thermal ellipsoid diagram of the solid state structure of 1-Vco at 50% probability. All hydrogens except for the hydridoborate B-H are removed for clarity.

The unambiguous structural characterization of 1-Vco provides support for the proposed structure of 1-Tico. Relatively lower C≡O stretching frequencies of 1-Vco compared to 1-Tico (Table 2-10) are consistent with the increased electron density at the $d^2$ V$^{III}$ center for back-donation into the $\pi^*$ orbitals of the C≡O bond.

The coordination of CO to 2-V led to the formation of another diamagnetic species, presumably the separated ion-pair 2-Vco, which is formed as a straw-coloured solution very similar to 1-Vco (Scheme 2-12). The diamagnetic nature of 2-Vco allowed the observation of the formyloxy $^{13}$C{$^1$H} resonance at $\delta$ 163.6 ppm, as well as the corresponding $^1$H resonance at $\delta$ 8.53.
ppm. The product was formed cleanly when CO was introduced to 2-V. When an extra equivalent of B(C₆F₅)₃ was present, the ¹⁹F{¹H} resonances (δ -133.2, -157.3, -163.9 ppm) of the resultant species 4-Vco were consistent with the [(C₆F₅)₃BOCHOB(C₆F₅)₃]⁻ anion as reported in literature with the TMPH⁺ cation (δ -133.4, -156.7, -163.6 ppm)⁴⁰ and the acetal-coordinated permethylscandocenium cation.⁴⁶ A comparison of the NMR resonances of the carbonyl complexes is given in Table 2-12 and Figure 2-21.

Scheme 2-12 Formation of the diamagnetic complexes 2-Vco and 4-Vco
Table 2-12 NMR data for the carbonyl complexes 1-Ti\textsubscript{CO}, 1-V\textsubscript{CO}, 2-V\textsubscript{CO} and 4-V\textsubscript{CO}

<table>
<thead>
<tr>
<th>Resonance (^a)</th>
<th>1-Ti\textsubscript{CO}</th>
<th>1-V\textsubscript{CO}</th>
<th>2-V\textsubscript{CO}</th>
<th>4-V\textsubscript{CO}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1)H NMR (\text{C}_5(\text{CH}_3)_5)</td>
<td>b</td>
<td>1.36 (s)</td>
<td>1.38 (s)</td>
<td>1.31 (s)</td>
</tr>
<tr>
<td>(\text{HB}([\text{C}_6\text{F}_5])_3)</td>
<td>4.46 (br, (\nu_{1/2} \approx 285) Hz)</td>
<td>4.28 (br, (\nu_{1/2} \approx 300) Hz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HCO}_2)</td>
<td></td>
<td>8.53 (s)</td>
<td>8.40 (s)</td>
<td></td>
</tr>
<tr>
<td>(^{10})B{(^1)H} NMR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HBAr}_3)</td>
<td>- 24.61 (s, (\nu_{1/2} \approx 45) Hz)</td>
<td>- 24.85 (s, (\nu_{1/2} \approx 50) Hz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{11})B{(^1)H} NMR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HBAr}_3)</td>
<td>-24.75 (br, (\nu_{1/2} \approx 80) Hz)</td>
<td>-24.85 (br, (\nu_{1/2} \approx 80) Hz)</td>
<td>- 4.01 (br, (\nu_{1/2} \approx 200) Hz)</td>
<td></td>
</tr>
<tr>
<td>(\text{HCO}_2\text{BAr}_3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{11})B NMR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HBAr}_3)</td>
<td>-24.75 (br d, (^{1}J_{\text{B-H}} = 80) Hz)</td>
<td>-24.85 (d, (^{1}J_{\text{B-H}} = 86) Hz)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{13})C{(^1)H} NMR (\text{C}_5(\text{CH}_3)_5)</td>
<td>107.4, 10.1</td>
<td>107.4, 10.1</td>
<td>107.4, 10.1</td>
<td></td>
</tr>
<tr>
<td>(\text{HCO}_2\text{B})</td>
<td>163.6</td>
<td></td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>(^{19})F{(^1)H} NMR (\alpha-\text{C}_6\text{F}_5)</td>
<td>-131.3 (br s, (\nu_{1/2} \approx 80) Hz)</td>
<td>- 132.1 (d, (J = 20) Hz)</td>
<td>- 133.0 (d, (J = 21) Hz)</td>
<td>- 133.2 (d, (J = 22) Hz)</td>
</tr>
<tr>
<td>(\nu_{1/2} \approx 20) Hz)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(m-\text{C}_6\text{F}_5)</td>
<td>- 165.5 (br s, (\nu_{1/2} \approx 65) Hz)</td>
<td>- 166.2 (m)</td>
<td>- 165.4</td>
<td>- 163.9</td>
</tr>
<tr>
<td>(t, J = 20) Hz)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(p-\text{C}_6\text{F}_5)</td>
<td>- 163.0 (br s, (\nu_{1/2} \approx 50) Hz)</td>
<td>- 163.4</td>
<td>- 160.8</td>
<td>- 157.3</td>
</tr>
<tr>
<td>(t, J = 21) Hz)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Recorded in \text{C}_6\text{D}_5\text{Br} at room temperature. \(^b\) The resonance was not observed.
Figure 2-21 $^{19}$F NMR spectra of the carbonyl complexes (376.5 MHz, C$_6$D$_5$Br).
2.2.5 Further investigation into the mechanism of catalytic \( \text{CO}_2 \) activation

Through the synthesis and characterization of the Ti\textsuperscript{III} and V\textsuperscript{III} systems analogous to the originally developed Sc\textsuperscript{III} catalytic system, and the comparison of their catalytic activity towards \( \text{CO}_2 \) hydrosilation, we have demonstrated that the original mechanism can be applied with slight modifications towards all three systems (Scheme 2-6). However, the distinctly different system that proves to be an invaluable contrast to the above systems is the carbonyl-coordinated V\textsuperscript{III} series, consisting of 1-V\textsubscript{CO} and 2-V\textsubscript{CO}. In both complexes, we do not expect the diamagnetic, 18-electron cationic V\textsuperscript{III} center to be Lewis acidic. Therefore, the investigation of the behaviour of these complexes was carried out in an attempt to further understand the role of the Lewis acidic metallocene species in the catalytic reaction.

When recalling the catalytic \( \text{CO}_2 \) hydrosilation facilitated by 1-Sc (Scheme 2-6), we can see that the V\textsuperscript{III} carbonyl complexes (1, 2, 4)-V\textsubscript{CO} are analogous to the various anionic species invoked in the mechanism suggested for the acetal-coordinated scandium complexes,\textsuperscript{46} albeit with the coordinatively-saturated, non-Lewis acidic \([\text{Cp}^*\text{V}(\text{CO})_2]^+\) countercation. This prompted the investigation of how these complexes behave in the mechanistic steps proposed for catalytic \( \text{CO}_2 \) hydrosilation.

While 1-V activated \( \text{CO}_2 \) to form 2-V, it was found that no reaction occurs between the analogous carbonyl complex 1-V\textsubscript{CO} and \( \text{CO}_2 \), \textit{i.e.} the analogous formyloxyborate complex 2-V\textsubscript{CO} is not formed (Scheme 2-13). This implies that the Lewis acidic metal center is needed for \( \text{CO}_2 \) activation by the hydridoborate anion.
The next step in the proposed mechanism for the 1-Sc catalyzed system entails the transfer of the formyloxy moiety from 2-Sc to Et₃SiH, aided by the presence of catalytic amounts of B(C₆F₅)₃. When 2-VCO was treated with Et₃SiH in the absence of catalytic B(C₆F₅)₃, transfer of the formyloxy group was very slow, and 6% conversion to 1-VCO was observed by ¹⁹F{¹H} NMR spectroscopy over two days (Scheme 2-14a). When the experiment was repeated with 0.5 eq. B(C₆F₅)₃, Et₃SiOCHO was observed instantaneously, while methane and other incomplete reduction products were observed after standing overnight (Scheme 2-14b). In contrast, the reaction of 2-V and Et₃SiH in the absence of B(C₆F₅)₃ resulted in the formation of 1-V (18% after 1 h by ¹⁹F{¹H} NMR spectroscopy) (Scheme 2-14c). The reverse reaction, where 1-V was reacted with Et₃SiOCHO, was also found to operate, although the equilibrium constant for this reversible reaction could not be determined due to further conversion of the triethylsilyl-containing species in subsequent reduction processes.
Scheme 2-14 Investigation of the effect of CO coordination on catalytic CO$_2$ activation by 1-V

From these observations, we can conclude that not only was CO$_2$ activation by 1-V inhibited through CO coordination, the subsequent reversible transfer of the formyloxy moiety from 2-V to Et$_3$SiH is likewise inhibited through CO coordination. Addition of catalytic B(C$_6$F$_5$)$_3$ allows the latter step to be achieved (Scheme 2-14b). In Scheme 2-14c, we can see that further reduction of Et$_3$SiOCHO was observed, even in the absence of added B(C$_6$F$_5$)$_3$. This could imply that either 1-V or 2-V were able to catalyze further reduction of Et$_3$SiOCHO, or that B(C$_6$F$_5$)$_3$ was present in trace amounts through dissociation form 1-V or 2-V. Indeed, control experiments show...
that {\text{Et}_3\text{SiOCHO}} is hydrosilated rapidly by {\text{Et}_3\text{SiH}} in the presence of catalytic B(C_6\text{F}_5)_3. ^{19}\text{F} \text{ NMR spectra of 1-V and 2-V show only one set of C_6\text{F}_5 resonances corresponding to the hydridoborate and formyloxyborate species, respectively, and free B(C_6\text{F}_5)_3 was not observed (cf. 2-Sc, see Figure 2-10). Therefore, it is unlikely that a significant amount of free B(C_6\text{F}_5)_3 is generated from either 1-V or 2-V to catalyze the reduction of {\text{Et}_3\text{SiOCHO}}. A more straightforward explanation is that 1-V or 2-V is Lewis acidic and catalytically active for subsequent reduction steps, and that this Lewis acidity is absent on carbonyl coordination.

\subsection*{2.3 Conclusions}

Taking the chemistry of early metal metallocenium cations developed by Hessen,\textsuperscript{58} as well as the 1-Sc system capable of catalytic CO\textsubscript{2} hydrosilation, two analogous systems, 1-Ti and 1-V were found to be catalytically active for said transformation, albeit with different kinetic features in the reaction.

1-Sc and 1-Ti feature sigmoidal curves for the consumption of the stoichiometric {\text{Et}_3\text{SiH}} reactant, suggesting a fast secondary pathway (Path B) likely involving the partially reduced CH\textsubscript{2}(OEt\textsubscript{3})\textsubscript{2} product. 1-V does not operate via Path B, as due to electronic reasons coordination of CH\textsubscript{2}(OEt\textsubscript{3})\textsubscript{2} does not occur. Maximum turnover frequencies (TOF) were found to be 8.99 h\textsuperscript{-1} and 0.99 h\textsuperscript{-1} for 1-Sc and 1-Ti catalysts respectively, when measured at the inflection point of the sigmoidal curve. Maximum TOF of 0.88 h\textsuperscript{-1} was found for the 1-V-catalyzed reaction at the initial stages of the reaction. The major reduction products were found to be CH\textsubscript{4} and CH\textsubscript{2}(OEt\textsubscript{3})\textsubscript{2},
although the product distribution cannot be quantified due to the liberation of CH₄ in to the headspace.

1-V was found to offer additional information regarding the role of the Lewis acidic metal center, since the Cp₂V⁺ cation can be rendered non-Lewis acidic on carbonyl coordination, generating non-Lewis acidic analogues of the species implicated in the 1-Sc and 1-Ti-catalyzed reaction. The different behaviour of the three metals in their respective Lewis acidic systems can be explained through the difference in electronic configurations, and the coordination geometries observed closely follow those reported in literature.

2.4 Future work

In the future it will be interesting to study the transfer of the formyloxy moiety from 3-M and 2-M to Et₃SiH by computational chemistry, since the mechanistic details of this step are difficult to analyze using spectroscopic techniques. This will allow for further understanding of the rate determining step of Path A of the catalytic systems 1-Sc and 1-Ti, and the overall pathway for the (1-V)-catalysed reaction. In particular, since the calculated energy difference between 2-V and the dissociated pair of 3-V and Et₃SiH strongly favours 2-V (Figure 2-16), it will be interesting to investigate the possibility that the formyloxy moiety is transferred from 2-V directly to the activated hydrosilane. Since the V³⁺ catalyzed CO₂ hydrosilation has the highest initial rate (Figure 2-19), the understanding of the chemistry of the rate-determining step may be beneficial in the design of new CO₂ hydrosilation catalysts.

The systematic investigation of metals across a row can be similarly applied down a period. While M–O bond strengths were found to decrease from Sc to V (Sc–O 671 kJ mol⁻¹, Ti–O 666.5
kJ mol$^{-1}$, V–O 629.7 kJ mol$^{-1}$), which loosely correlates to a decrease in catalytic activity towards CO$_2$ hydrosilation, the increase in M–O bond strengths in group 3 descending from Sc to La (Sc–O 671 kJ mol$^{-1}$, Y–O 714.1 kJ mol$^{-1}$, La–O 798 kJ mol$^{-1}$) may allow for an interesting comparison of this chemistry. In particular, the complexes may differ from 1-Sc structurally, since the larger ionic radii of the 2$^{nd}$ and 3$^{rd}$ row transition metals (Sc$^{3+}$ 74.5 pm, Y$^{3+}$ 90.0 pm, La$^{3+}$ 103.2 pm) may allow for different coordination modes between the ion pair, as well as with CH$_2$(OSiEt$_3$)$_2$.

The reported synthesis of Cp$^*$$_2$YCl·THF and a series of -ate complexes of the lanthanide (Ln) metals of the general formula [ML$_2$]$^+$[Cp$^*$$_2$LnCl$_2$]$^-$ (M = Li, Na, K, L$_2$ = (Et$_2$O)$_2$, DME) may serve as promising routes to the respective 1-M compounds.

It will also be interesting to explore the cooperativity of the electrophilic cation and the nucleophilic anion in the activation of other substrates. For example, activation of carbodiimides by 1-M in an analogous fashion to the activation of CO$_2$ to form 2-M, may generate a B–N bond that is considerably weaker than a B–O bond (bond dissociation energies 378 kJ mol$^{-1}$ vs. 809 kJ mol$^{-1}$, respectively). This may allow for the more facile transfer of the activated group to a broader scope of substrates, leading to a variety of organic transformations.
Chapter Three: Experimental Section

3.1 General considerations

3.1.1 Laboratory equipment and apparatus

An argon-filled MBraun glove box was used for the manipulation and storage of air- and moisture-sensitive compounds. Thermally-sensitive compounds were stored in the freezer within the glove box, maintained at -35 °C. Unless otherwise stated, all reactions were performed on a double manifold high vacuum line using standard techniques.\(^90\) Residual oxygen and moisture were removed from the argon stream by passage through an OxisorBW scrubber (Matheson Gas products). All glassware was stored in an oven maintained at 135 °C for a minimum of 2 h before transfer to the glove box or assembly and evacuation on a vacuum line. A glass vessel of known volume (35.3 mL) was used for the quantitative transfer of condensable gases (e.g. CO\(_2\)). A Fischer Scientific Ultrasonic FS-20 bath was used to sonicate reaction mixtures where indicated. Gas pressures described in “atm” are relative to the atmospheric pressure in Calgary, AB, Canada, which is approximately 660 mmHg. Values were not corrected for the deviations from sea level, where 1 atm = 760 mmHg.

3.1.2 Solvents

Toluene and hexanes were dried and purified using the Grubbs/Dow purification system\(^90\) and stored over sodium-tetraglyme / benzophenone ketal. Tetrahydrofuran was dried and purified
using the Grubbs/Dow purification system\textsuperscript{90} and stored over sodium / benzophenone ketal. Benzene and pentane were dried over CaH\textsubscript{2} and vacuum transferred into 500-mL thick-walled glass vessels containing sodium-tetraglyme/benzophenone ketal. Bromobenzene, bromobenzene-\textit{d}_5 and benzene-\textit{d}_6 were dried and stored over activated 4 Å molecular sieves (8-12 Mesh Beads, EMD chemicals). Unless otherwise noted, solvents were introduced directly into reaction vessels via vacuum transfer on a vacuum line, or vacuum transferred into glass vessels sealed with PTFE stopcocks for use in the glove box.

### 3.1.3 Instrumentation and details for NMR analysis

Nuclear magnetic resonance spectroscopy experiments (\textsuperscript{1}H, \textsuperscript{11}B\{\textsuperscript{1}H\}, \textsuperscript{13}C\{\textsuperscript{1}H\} and \textsuperscript{19}F\{\textsuperscript{1}H\}) were performed on 400 MHz (Bruker, \textsuperscript{1}H 400.1 MHz, \textsuperscript{10}B 43.0 MHz, \textsuperscript{11}B 128.4 MHz, \textsuperscript{13}C 100.6 MHz, \textsuperscript{19}F 376.5 MHz) or 600 MHz (Bruker, \textsuperscript{1}H 600.2 MHz) spectrometers. All air- and moisture-sensitive NMR samples were prepared in the glove box with NMR tubes sealed with rubber septa and wrapped in Parafilm®, or J-Young NMR tubes equipped with PTFE high-vacuum stopcocks. NMR tubes were stored in a separate oven maintained at 85 °C for a minimum of 2 h before transfer to the glove box for sample preparation. Unless otherwise stated, all NMR spectra were acquired at room temperature. \textsuperscript{1}H NMR chemical shifts were referenced to residual solvent resonances and reported relative to SiMe\textsubscript{4}. Chemical shifts for \textsuperscript{11}B, \textsuperscript{13}C and \textsuperscript{19}F experiments were referenced by default on Bruker NMR spectrometers based on the \textsuperscript{1}H NMR chemical shift of the lock solvent, and reported relative to 15% BF\textsubscript{3}·Et\textsubscript{2}O in CDCl\textsubscript{3}, SiMe\textsubscript{4} and CFCl\textsubscript{3} respectively. \textsuperscript{1}H NMR spectra are presented in the following format: chemical shift (ppm), multiplicity, coupling constant (\textit{J}, in Hz), number of protons, assignment. \textsuperscript{10}B\{\textsuperscript{1}H\} NMR spectra are presented in the following format:
chemical shift (ppm), multiplicity, width at half height ($\nu_{1/2}$, in Hz). $^{11}$B NMR spectra are presented in the following format: chemical shift (ppm), multiplicity, coupling constant ($J$, in Hz). $^{11}$B{$^1$H} NMR spectra are presented in the following format: chemical shift (ppm), multiplicity, width at half height ($\nu_{1/2}$, in Hz). $^{13}$C{$^1$H} NMR spectra of diamagnetic compounds are presented in the following format: chemical shift, multiplicity, coupling constant ($J$, in Hz), assignment. $^{19}$F{$^1$H} NMR spectra are presented in the following format: chemical shift (ppm), multiplicity, coupling constant ($J$, in Hz), number of fluorines, assignment. Experiments regarding the Evans’ method for determination of magnetic susceptibility (see Section 3.2.3) were repeated on both 400 MHz and 600 MHz spectrometers whenever possible. The calculated effective magnetic moments $\mu_{\text{eff}}$ were reported along with the frequency of the NMR spectrometer and the solvent used.

3.1.4 Other instrumentation and analysis

Elemental analyses were performed on a Perkin Elmer 2400 Series II Elemental Analyzer with C, H, N capabilities by Mr. Johnson Li. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on a Enraf-Nonius APEXII CCD four circle diffractometer using graphite monochromated Mo Kα radiation by Dr. Masood Parvez or Dr. Michael Sgro; full details can be found in individual tables for each crystal structure. Infrared spectra were collected on a Nicolet Avatar FT-IR spectrophotometer and processed on GRAMS/AI™ and Spekwin32 spectroscopy software. Spectral bands were reported in wavenumbers (cm$^{-1}$), followed by an indication of the strength of the absorption in parentheses (w = weak, m = medium, s = strong, vs = very strong).
3.1.5 Starting materials

Chlorobis(pentamethylcyclopentadienyl)titanium(III) was prepared from trichlorotris(tetrahydrofuran)-titanium(III) (Strem chemicals, used as received) and 1,2,3,4,5-pentamethylcyclopentadienylmagnesium chloride–tetrahydrofuran (1/1) as reported in literature.\(^{68}\) 1,2,3,4,5-Pentamethylcyclopentadienylmagnesium chloride–tetrahydrofuran (1/1) was prepared from isopropylmagnesium chloride (2.0 M in diethyl ether, used as received) and pentamethylcyclopentadiene (TCI America, used as received) as reported in literature.\(^{91}\) Chlorobis(pentamethylcyclopentadienyl)vanadium(III)\(^{74}\) was prepared from decamethylvanadocene and benzyl chloride according to literature procedures.\(^{86}\) Benzyl chloride was purchased from Matheson, Coleman and Bell, dried with MgSO\(_4\) overnight and distilled before use. Decamethylvanadocene was prepared from trichlorotris(tetrahydrofuran)vanadium(III) and 1,2,3,4,5-pentamethylcyclopentadienyllithium according to literature procedures.\(^{86}\) 1,2,3,4,5-Pentamethylcyclopentadienyl-lithium was prepared from n-butyllithium (2.5 M in hexanes, Sigma-Aldrich, used as received) and 1,2,3,4,5-Pentamethylcyclopentadiene (TCI America, used as received) as reported in literature.\(^{92}\) Trichlorotris(tetrahydrofuran)vanadium(III) was prepared from vanadium(III) chloride (Sigma-Aldrich, used as received) in tetrahydrofuran according to literature procedures.\(^{66}\) methylbis(pentamethylcyclopentadienyl)titanium(III) was prepared from literature procedures.\(^{93}\) 1-Se\(^{62}\) and 2-Se\(^{46}\) were prepared by literature methods. Tris(pentafluorophenyl)borane was purchased from Boulder Scientific Company and sublimed twice at 80°C under high vacuum. Triethylsilane was purchased from TCI America and purified by distillation and stored over activated 4Å molecular sieves in the glove box. Triethylsilyl formate was prepared from chlorotriethylsilane (Sigma-Aldrich), 15-crown-5 (Sigma-Aldrich) and sodium...
formate by Dr. Francis LeBlanc as per literature procedures.42 “Bone dry” carbon dioxide (Praxair), $^{13}$C-labelled carbon dioxide (Cambridge Isotope Laboratories), carbon monoxide (Sigma-Aldrich) and $^{13}$C-labelled carbon monoxide ($^{13}$C 99%, < 2% $^{18}$O, Cambridge Isotope Laboratories) were used as received.

3.2 Experimental procedures

3.2.1 Synthetic procedures

Synthesis of decamethyltitanocenium(III) hydridotris(pentafluorophenyl)borate (1-Ti)

To a 20-mL glass scintillation vial in the glove box charged with chlorobis(pentamethylcyclopentadienyl)titanium(III) (396 mg, 1.12 mmol), triethylsilane (130 mg, 1.12 mmol) and tris(pentafluorophenyl)borane (572 mg, 1.12 mmol) was added benzene (1 mL), resulting in a dark green slurry. This was allowed to stand for 30 minutes, affording a dark green crystalline precipitate, which was suitable for X-ray diffraction. The liquid was decanted and the dark solids were rinsed with benzene (8 × 0.5 mL) followed by pentane (2 mL). The remaining volatiles were removed in vacuo to afford 1-Ti as a dark green crystalline solid (635 mg, 0.764 mmol, 68%). This material is stable for several days if stored at -35 °C. $^1$H NMR (400 MHz, C$_6$D$_6$) δ 3.60 (br s, ν$_{1/2}$ ≈ 500 Hz, 1H, HB), 13.30 (br s, ν$_{1/2}$ ≈ 2250 Hz, 30H, C$_5$Me$_5$). $^{10}$B{$^1$H} NMR (43 MHz, C$_6$D$_5$Br) δ -23.4 (s). $^{11}$B NMR (128 MHz, C$_6$D$_5$Br) δ -23.22 (br s, ν$_{1/2}$ ≈ 180 Hz). $^{11}$B{$^1$H} NMR (128 MHz, C$_6$D$_6$) δ -23.22 (s). $^{19}$F{$^1$H} NMR (377 MHz, C$_6$D$_6$) δ -157.29 (br s, ν$_{1/2}$
≈ 1300 Hz, 15F, C₆F₅). ¹⁹F{¹H} NMR (377 MHz, toluene-d₈, 230 K) δ -132.18 (br s, ν₁/₂ ≈ 310 Hz, 6F, o-C₆F₅), -160.93 (br s, ν₁/₂ ≈ 120 Hz, 3F, p-C₆F₅), -164.95 (br s, ν₁/₂ ≈ 145 Hz, 6F, m-C₆F₅). IR (KBr pellet) 2970 (w), 2920 (w), 2871 (w), 2387 (w), 2348 (w), 2000 (w), 1948 (w), 1642 (m), 1608 (m), 1511 (s), 1466 (vs), 1385 (m), 1277 (m), 1103 (m), 1022 (w), 970 (s), 911 (w), 758 (w), 662 (w), 568 (w). Analysis calcd./found for C₃₈H₃₁BF₁₅Ti: C, 54.90/54.63; H, 3.76/3.92. μₑffective 2.069 (400 MHz, C₆D₆), 2.072 (600 MHz, C₆D₆).

**Synthesis of decamethylvanadocenium(III) hydridotrīs(pentafluorophenyl)borate (1-V)**

A 20-mL glass scintillation vial in the glove box was charged with chlorobis(pentamethylcyclopentadienyl)vanadium(III) (224 mg, 0.628 mmol) and trīs(pentafluorophenyl)borane (330 mg, 0.645 mmol). C₆H₅Br (4 mL) was added to the mixture giving a deep blue solution. Triethylsilane (88 mg, 0.757 mmol) was added dropwise with stirring, resulting in a red-brown solution and precipitation of a dark red solid. After 30 minutes, pentane (4 mL) was added slowly with stirring, and the pale red solution was decanted. The solids were rinsed with pentane (4 × 4 mL) and dried in vacuo to yield 1-V as a dark red-brown solid (505 mg, 0.574 mmol, 91%). Crystals suitable for X-ray analysis were obtained by layering a saturated bromobenzene solution with pentane. ¹H NMR (400 MHz, C₆D₅Br) δ 4.20 (br, ν₁/₂ ≈ 250 Hz, 1H, HB), 25.1 (br s, ν₁/₂ ≈ 500 Hz, 30H, C₅Me₅). ¹⁰B{¹H} NMR (43 MHz, C₆D₅Br) δ -24.7 (s). ¹¹B NMR (128 MHz, C₆D₅Br) δ -24.64 (br s, ν₁/₂ ≈ 160 Hz). ¹¹B{¹H} NMR (128 MHz, C₆D₅Br) δ -24.64 (s, ν₁/₂ ≈ 80 Hz). ¹⁹F{¹H} NMR (377 MHz, C₆D₅Br) δ -163.18 (s, ν₁/₂ ≈ 25 Hz, 3F, p-C₆F₅), -160.03 (br s, ν₁/₂ ≈ 600 Hz, 6F, m-C₆F₅), -131.68 (br s, ν₁/₂ ≈ 130 Hz, 6F, o-C₆F₅). IR (KBr pellet)
2963 (w), 2920 (w), 2871 (w), 2380 (w), 1641 (m), 1605 (m), 1511 (s), 1470 (s), 1388 (m), 1274 (m), 1094 (m), 1072 (m), 971 (s), 966 (s), 954 (m), 912 (w), 766 (w), 755 (m), 663 (w), 636 (w), 570 (w), 564 (w). Analysis calcd./found for C_{38}H_{31}BF_{15}V: C, 54.70/54.54; H, 3.74/3.95. ð_{eff} 2.970 (400 MHz, C_{6}D_{5}Br), 2.978 (600 MHz, C_{6}D_{5}Br).

Synthesis of dicarbonylbis(pentamethylcyclopentadienyl)titanium(III) hydridotris(pentafluorophenyl)borate (1-TiCO)

A solution of 1-Ti (80 mg, 267 μmol) in C_{6}H_{5}Br (0.5 mL) was charged to a J-Young NMR tube in the glove box, sealed and connected to the vacuum line. The solution was frozen in liquid N_{2} and evacuated before introducing CO (2 atm). The tube was resealed, thawed and agitated to give a black solution. Layering the solution with hexanes (15 mL) in a 20-mL glass scintillation vial gave a black oil within hours, and a black microcrystalline precipitate was observed after a few days. The yellow-brown supernatant was decanted, and the precipitate was rinsed with hexanes (3 × 5 mL). The remaining volatiles were removed in vacuo to yield 1-TiCO as a black solid (45 mg, 51 μmol, 19%). \textsuperscript{1}H NMR (400 MHz, C_{6}D_{5}Br) \delta 4.46 (br, v_{1/2} \approx 285 Hz, 1H, HB). The Cp\textsuperscript{*} methyl resonance was not located. \textsuperscript{10}B\{\textsuperscript{1}H\} NMR (43 MHz, C_{6}D_{5}Br) \delta -24.61 (s, v_{1/2} \approx 45 Hz). \textsuperscript{11}B NMR (128 MHz, C_{6}D_{5}Br) \delta -24.75 (br d, v_{1/2} \approx 80 Hz). \textsuperscript{19}F\{\textsuperscript{1}H\} NMR (377 MHz, C_{6}D_{5}Br) \delta -65 Hz, \textsuperscript{6}F, \textsuperscript{m}-C_{6}F_{5}), -63.03 (br s, v_{1/2} \approx 50 Hz, \textsuperscript{3}F, \textsuperscript{p}-C_{6}F_{5}), -131.25 (br s, v_{1/2} \approx 80 Hz, \textsuperscript{6}F, \textsuperscript{o}-C_{6}F_{5}). IR (KBr pellet) 2982 (w), 2954 (w), 2918 (w), 2865 (w), 2371 (w), 2075 (vs), 2049 (vs), 1640 (m), 1510 (s), 1466 (vs), 1387 (m), 1272 (m), 1115 (m), 1092 (m), 1070 (m), 967 (s), 954
Synthesis of dicarbonylbis(pentamethylcyclopentadienyl)vanadium(III) hydridotris(pentafluorophenyl)borate (1-Vco)

A suspension of 1-V (223 mg, 267 μmol) in C₆H₅Br (5 mL) was charged to a 50-mL thick-walled glass vessel. The vessel was sealed and degassed using three freeze-pump-thaw cycles on the vacuum line, and backfilled with CO (1 atm). The red-brown solution turned orange-brown over the course of 5 min. After stirring for 30 min, pentane (~ 20 mL) was added to afford bright orange crystals (221 mg, 248 μmol, 93%) suitable for X-ray diffraction. The supernatant was decanted to afford 1-Vco (152 mg, 170 μmol, 64%) as an orange-brown crystalline solid. ¹H NMR (400 MHz, C₆D₅Br) δ 1.36 (s, 30H, C₅Me₅), 4.30 (br s, 1H, ν₁/₂ ≈ 230 Hz, HB). ¹⁰B{¹H} NMR (43 MHz, C₆D₅Br) δ -24.85 (s, ν₁/₂ ≈ 50 Hz). ¹¹B{¹H} NMR (128 MHz, C₆D₅Br) δ -24.85 (d, J_B-H = 86 Hz). ¹³C{¹H} NMR (101 MHz, C₆D₅Br) δ 10.09 (s, C₅Me₅), 107.40 (s, C₅Me₅), 136.61 (dm, J_C-F = 246 Hz, C₆F₅), 137.88 (dm, J_C-F = 239 Hz, C₆F₅), 148.62 (dm, J_C-F = 238 Hz, C₆F₅). The ipso-C₆F₅ resonance was not located. ¹⁹F{¹H} NMR (377 MHz, C₆D₅Br) δ -166.22 (m, 6F, m-C₆F₅), -163.39 (d, J_F-F = 20 Hz, 3F, p-C₆F₅), -132.11 (d, J_F-F = 20 Hz, 6F, o-C₆F₅). IR (KBr pellet) 2999 (w), 2966 (w), 2914 (w), 2423 (w), 2003 (vs), 1954 (vs), 1640 (m), 1509 (s), 1463 (vs), 1388 (s), 1274 (m), 1107 (m), 1095 (m), 1072 (m), 1022 (w), 967 (s), 914 (w), 767 (w), 756 (w), 662 (w), 588 (w), 535 (w), 507 (w). Analysis calcd./found for C₄₀H₃₁BF₁₅O₂V: C, 53.96/53.71; H, 3.51/3.68.
Synthesis of decamethylscandocenium(III) ($^{13}$C)formyloxytris(pentafluorophenyl)borate (2-Sc')

1-Sc (80 mg, 97 μmol) and C$_6$D$_6$ (500 μL) were charged to a J-Young NMR tube. This was attached to the vacuum line, the contents frozen at -196 °C, and the headspace evacuated. $^{13}$CO$_2$ (70 mmHg × 35.3 mL, 121 μmol) was condensed in, and the NMR tube was resealed and warmed carefully to room temperature to yield a yellow solution. The sample was brought into the glove box and the contents were charged to a 20-mL glass scintillation vial. The solution was layered with hexanes (15 mL) and placed in the freezer, resulting in yellow crystals after several hours. The crystals were decanted from the supernatant and rinsed with hexanes (3 × 5 mL). Residual hexanes was removed in vacuo. $^{11}$B{$^1$H} and $^{19}$F{$^1$H} NMR spectra are similar to that obtained for 2-Sc. The $^1$H NMR spectrum showed the splitting of the formate resonance at 8.77 ppm into a doublet ($^1J_{C-H} = 217$ Hz) as reported in literature. IR (KBr pellet) 2915 (w), 2866 (w), 1645 (m), 1597 (s), 1581 (s), 1518 (s), 1467 (vs), 1396 (w), 1384 (w), 1375 (w), 1328 (m), 1287 (s), 1103 (s), 979 (s), 972 (s), 876 (w), 783 (w), 774 (w), 682 (s), 665 (w).

Synthesis of decamethyltitanocenium(III) formyloxytris(pentafluorophenyl)borate (2-Ti)

To a 50-mL round-bottomed flask was charged a solution of 1-Ti (157 mg, 0.189 mmol) in benzene (1 mL). The flask was attached to a swivel-frit apparatus and brought out of the glove box. The reaction mixture was degassed by three freeze-pump-thaw cycles, and filled with CO$_2$ (1 atm). The dark green solution turned purple immediately. A dark purple solid precipitated on standing for 30 minutes. Filtration and subsequent pentane rinses of the isolated solid yielded
Cp^+_2Ti^+ \text{HCO}_2\text{B(C}_6\text{F}_5)_3^{-} as a dark purple crystalline solid (81 mg, 0.093 mmol, 49%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution. ^1H NMR (400 MHz, C_6D_5Br) δ 14.80 (br s, w_{1/2} = 2700 Hz, 30H, C_5Me_5). The formate resonance was not located. \text{^11B\{^1H\} NMR (128 MHz, C_6D_5Br) δ -1.95 (br s, w_{1/2} ≈ 400 Hz). ^19F NMR (376.5 MHz, C_6D_5Br) δ -163.06 (br s, w_{1/2} ≈ 50 Hz, 6F, meta-C_6F_5), -156.35 (s, 3F, para-C_6F_5), -130.36 (br s, w_{1/2} ≈ 350 Hz, 6F, ortho-C_6F_5). IR (KBr pellet) 2975 (w), 2912 (w), 2865 (w), 1644 (m), 1618 (s), 1516 (s), 1468 (vs), 1384 (w), 1377 (w), 1337 (w), 1286 (w), 1101 (s), 978 (s), 895 (w), 879 (w), 784 (w), 774 (w), 683 (w), 665 (w). Analysis calcd./found for C_{39}H_{31}BF_{15}O_2Ti: C, 53.51/53.93; H, 3.57/3.84. μ_{eff} 2.019 (400 MHz, C_6D_6), 2.039 (600 MHz, C_6D_6).

Synthesis of decamethyltitanocenium(III) (^13C)formyloxytris(pentafluorophenyl)borate (2-Ti')

1-Ti (60 mg, 72 μmol) and C_6D_6 (500 μL) were charged to a J-Young NMR tube. This was attached to the vacuum line, the contents frozen at -196 °C, and the headspace evacuated. ^13CO_2 (55 mmHg × 35.3 mL, 95 μmol) was condensed in, and the NMR tube was resealed and warmed carefully to room temperature, resulting in an instant purple solution. A red-purple precipitate was observed on standing for several minutes. \text{^1H, ^11B\{^1H\} and ^19F\{^1H\} NMR spectra are similar to that obtained for 2-Ti. This was brought into the glove box and the contents were charged to a 20-mL scintillation vial. The solution was layered with hexanes (10 mL) and placed in the freezer, resulting in dark purple crystals after several hours. The supernatant was decanted, and the crystals were rinsed with hexanes (3 × 5 mL). Residual hexanes was removed in vacuo. IR (KBr pellet)
Synthesis of decamethylvanadocenium(III) formyloxytris(pentafluorophenyl)borate (2-V)

To a 50-mL round-bottomed flask was charged a suspension of 1-V (133 mg, 0.159 mmol) in 1 mL C₆H₅Br. This was attached to a swivel-frit apparatus, brought out of the glove box and attached to a double manifold vacuum line. The reaction mixture was degassed by three freeze-pump-thaw cycles, and filled with CO₂ (1 atm). The dark red solution turned dark blue immediately, affording dark blue crystals on standing. To the pale blue solution was added pentane (10 mL) to afford more solid, and the mother liquor was decanted. The crystals were rinsed with pentane (3 × 5 mL) and dried to afford Cp*₂V⁺ HCO₂B(C₆F₅)⁻ (82 mg, 93 μmol, 58%) as a dark blue solid. Crystals suitable for X-ray diffraction were taken directly from the reaction mixture.

¹H NMR (400 MHz, C₆D₅Br) δ 10.40 (br s, 30H, C₅Me₅). The formate resonance was not located. ¹¹B{¹H} NMR (128 MHz, C₆D₅Br) δ -0.19 (br s, 50 Hz, 30H, C₅Me₅). ¹⁹F NMR (376.5 MHz, C₆D₅Br) δ -163.18 (br s, 6F, meta-C₆F₅), -156.59 (br s, 6F, para-C₆F₅), -128.34 (br s, 6F, ortho-C₆F₅). IR (KBr pellet) 2908 (w), 2860 (w), 1635 (s), 1517 (s), 1467 (vs), 1383 (w), 1365 (w), 1321 (s), 1285 (m), 1102 (s), 980 (s), 972 (s), 877 (w), 774 (w), 743 (w), 684 (w). Satisfactory elemental analysis results could not be obtained for this compound - Analysis calcd./found for C₃⁹H₃₁BF₁₅O₂V: C, 53.33/52.17; H, 3.56/3.64 (Average of 6 measurements). μeff 2.839 (400 MHz, C₆D₅Br), 2.699 (600 MHz, C₆D₅Br).
Synthesis of dicarbonyl\textit{bis}(pentamethylenecyclopentadienyl)\textit{vanadium}(III) (\textsuperscript{13}\textit{C})formyloxy\textit{tris}-(pentafluorophenyl)borate (2-V')

\textbf{1-V} (72 mg, 86 \textmu mol) and C\textsubscript{6}D\textsubscript{5}Br (500 \textmu L) were charged to a J-Young NMR tube. This was attached to the vacuum line, the contents frozen at -196 °C, and the headspace evacuated. \textsuperscript{13}\textit{CO}\textsubscript{2} (55 mmHg \times 35.3 mL, 104 \textmu mol) was condensed in, and the NMR tube was resealed and warmed carefully to room temperature, resulting instantly in a blue solution. \textsuperscript{1}\textit{H}, \textsuperscript{11}\textit{B}\{\textsuperscript{1}\textit{H}\} and \textsuperscript{19}\textit{F}\{\textsuperscript{1}\textit{H}\} NMR spectra are similar to that obtained for 2-V. The tube was brought into the glove box and the contents were transferred to a 20-mL glass scintillation vial. The solution was layered with hexanes (10 mL) and placed in the freezer, resulting in blue crystals after several hours. The supernatant was decanted and the crystals were rinsed with hexanes (3 \times 5 mL). Residual hexanes was removed \textit{in vacuo}. IR (KBr pellet) 2916 (w), 2862 (w), 1644 (m), 1591 (vs), 1517 (s), 1466 (s), 1383 (w), 1375 (w), 1306 (m), 1285 (m), 1102 (s), 980 (s), 971 (s), 874 (w), 781 (w), 773 (w), 684 (w).

Synthesis of dicarbonyl\textit{bis}(pentamethylenecyclopentadienyl)\textit{vanadium}(III) formyloxy\textit{tris}-(pentafluorophenyl)borate (2-V\textsubscript{CO})

A suspension of \textbf{1-V} (80 mg, 96 \textmu mol) in C\textsubscript{6}H\textsubscript{5}Br (1 mL) was charged to a J-Young NMR tube, and attached to the vacuum line. The contents were frozen at -196 °C and the headspace was evacuated. CO\textsubscript{2} (165 mmHg \times 35.3 mL, 313.5 \textmu mol) was condensed in, and the NMR tube was resealed and warmed carefully to room temperature, resulting instantly in a blue solution (2-V). The tube was repeatedly inverted for 10 minutes, and residual CO\textsubscript{2} was removed by three freeze-
pump-thaw cycles at -78 °C. The temperature was lowered to -196 °C, and CO (2 atm) was added. The NMR tube was warmed carefully to room temperature, and repeatedly inverted, resulting in a gradual colour change to an orange-brown solution over the course of five minutes. This was brought into the glove box, the contents charged to a 20-mL glass scintillation vial and layered with hexanes, resulting in an orange oil. Further trituration with hexanes eventually results in an analytically pure amorphous brown solid (75 mg, 80 μmol, 84%). $^1$H NMR (400 MHz, C$_6$D$_5$Br) δ 1.38 (s, 30H, C$_5$Me$_5$), 8.53 (s, 1H, HCO$_2$B). $^{11}$B{$^1$H} NMR (128 MHz, C$_6$D$_5$Br) δ -4.01 (br s, $v_{1/2}$ ≈ 200 Hz). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_5$Br) δ 10.15 (s, C$_5$Me$_5$), 107.47 (s, C$_5$Me$_5$), 136.75 (dm, $^1J_{C-F}=245$ Hz, C$_6$F$_5$), 138.91 (dm, $^1J_{C-F}=243$ Hz, C$_6$F$_5$), 148.34 (dm, $^1J_{C-F}=241$ Hz, C$_6$F$_5$). The ipso-$C_6F_5$ and HCO$_2$B resonances were not located. $^{19}$F{$^1$H} NMR (377 MHz, C$_6$D$_5$Br) δ -165.43 (t, $^2J_{F-F}=20$ Hz, 6F, m-$C_6F_3$), -160.80 (t, $^2J_{F-F}=21$ Hz, 3F, p-$C_6F_3$), -132.95 (d, $^3J_{F-F}=21$ Hz, 6F, o-$C_6F_3$). IR (KBr pellet) 2997 (w), 2974 (w), 2925 (w), 2874 (m), 2747 (w), 1999 (vs), 1947 (vs), 1919 (w), 1726 (w), 1707 (s), 1696 (s), 1642 (s), 1514 (vs), 1463 (vs), 1388 (s), 1273 (s), 1251 (s), 1090 (s), 979 (s), 926 (w), 904 (m), 809 (m), 802 (m), 771 (m), 758 (m), 735 (w), 695 (w), 678 (m), 664 (m), 620 (w), 589 (w), 576 (w), 547 (w), 536 (m), 508 (m). Analysis calcd./found for C$_{41}$H$_{31}$BF$_{15}$O$_4$V: C, 52.70/52.70; H, 3.34/3.52.

**Synthesis of dicarbonylbis(pentamethylcyclopentadienyl)vanadium(III) (13C)formyloxytris(pentafluorophenyl)borate (2-VCO)**

1-V (78 mg, 93 μmol) and C$_6$D$_5$Br (500 μL) were charged to a J-Young NMR tube, and attached to the vacuum line. The contents were frozen at -196 °C and the headspace was evacuated. $^{13}$CO$_2$ (55 mmHg × 35.3 mL, 104 μmol) was condensed in, and the NMR tube was resealed and
the contents warmed carefully to room temperature, resulting in a blue solution. After repeated inversion of the NMR tube for 10 minutes, the contents were frozen at -78 °C and the headspace evacuated to remove excess $^{13}$CO$_2$. The temperature was lowered to -196 °C, and CO (2 atm) was added, the tube resealed and carefully returned to room temperature. Repeated inversion of the NMR tube gave a brown solution after several minutes. $^{11}$B{$^1$H} and $^{19}$F{$^1$H} NMR spectra are very similar to that of 2-V$_{CO}$. The $^{13}$C{$^1$H} NMR spectrum was also similar to that of 2-V$_{CO}$, except that the isotopically-enriched HCO$_2$B resonance was observed at $\delta$ 163.6 ppm. $^1$H NMR (400 MHz, C$_6$D$_5$Br) $\delta$ 1.38 (s, 30H, C$_5$Me$_5$), 8.53 (d, $J_{C-H}$ = 207 Hz, 1H, $H^{13}$CO$_2$B). Layering the brown solution with hexanes (15 mL) in a 20-mL scintillation vial resulted in an orange-brown oil, which solidified to a brown amorphous solid on trituration with hexanes. Decanting the supernatant and removal of solvents in vacuo afforded 2-V$_{CO}^\ast$ (30 mg, 32 μmol, 34% yield). IR (KBr pellet) 2999 (w), 2925 (w), 2864 (w), 2741 (w), 1999 (vs), 1947 (vs), 1668 (m), 1654 (m), 1643 (m), 1514 (s), 1465 (vs), 1388 (m), 1275 (m), 1228 (m), 1213 (m), 1089 (s), 1024 (w), 979 (s), 904 (w), 809 (w), 798 (w), 771 (w), 758 (w), 677 (m), 664 (w), 508 (w).

**Synthesis of dicarbonyl $\text{bis(pentamethylenecyclopentadienyl)vanadium(III) tris(pentafluorophenyl)}$borane–formate (2/1) (4-V$_{CO}$)**

To a J-Young NMR tube was charge 1-V (21 mg, 25 μmol), B(C$_6$F$_5$)$_3$ (13 mg, 25 μmol) and C$_6$D$_5$Br (550 μL) yielding a dark red-brown solution. The tube was attached to the vacuum line, the contents frozen and the headspace evacuated. CO$_2$ (14 mmHg \times 35.3 mL, 27 μmol) was condensed into the tube at -196 °C. The tube was carefully warmed to room temperature, resulting in a blue solution. This was repeatedly inverted for 15 minutes to ensure mixing. The $^{19}$F{$^1$H}
NMR spectrum of this mixture shows two sets of unperturbed C$_6$F$_5$ resonances corresponding to 2-V and B(C$_6$F$_5$)$_3$. The NMR tube was reattached to the vacuum line. Excess CO$_2$ was removed by evacuating the headspace at -78 °C. The contents were warmed to room temperature, and CO (1 atm) was added. The tube was resealed, and repeatedly inverted for 2 h to ensure mixing. $^1$H NMR (400 MHz, C$_6$D$_5$Br) $\delta$ 1.31 (s, 30H, C$_5$Me$_5$), 8.40 (s, 1H, HCO$_2$). $^{13}$C{$^1$H} NMR (101 MHz, C$_6$D$_5$Br) $\delta$ 10.1 (C$_5$Me$_5$), 107.4 (C$_5$Me$_3$). The HCO$_2$ and C$_6$F$_5$ resonances were not located. $^{19}$F{$^1$H} NMR (377 MHz, C$_6$D$_5$Br) $\delta$ -163.87 (t, $^3$J$_{F-F} = 20$ Hz, 6F, m-C$_6$F$_5$), -157.31 (t, $^3$J$_{F-F} = 21$ Hz, 3F, p-C$_6$F$_5$), -133.24 (d, $^3$J$_{F-F} = 22$ Hz, 6F, o-C$_6$F$_5$).

**Synthesis of permethyltitanocene formate (3-M)**

Methylbis(pentamethylcyclopentadienyl)titanium(III) (100 mg, 300 μmol) was charged to a 50-mL round-bottomed flask attached to an adapter with a PTFE stopcock. The apparatus was sealed, brought out of the glovebox and attached to the vacuum line. Benzene (5 mL) was added through vacuum transfer, and the setup was warmed to room temperature, giving a dark green solution. H$_2$ (1 atm) was added, resulting in an instant color change to a dark red solution (Cp$_2^{\ast}$TiH). The reaction was stirred for 15 minutes, after which the gases were removed at -78°C. The reaction was warmed to room temperature, and CO$_2$ (1 atm) was added, resulting in an instant color change to a dark blue solution. The reaction was let stir for another 15 min, after which all volatiles were removed in vacuo, yielding 3-M as a blue powder (78 mg, 220 μmol, 72% yield). The IR spectrum was comparable to literature.$^{68}$
3.2.2 Other experimental procedures

Investigation of the CO\textsubscript{2} activation ability of 1-V\textsubscript{CO}

1-V (19 mg, 23 μmol) and C\textsubscript{6}D\textsubscript{5}Br (500 μL) were charged to a J-Young NMR tube. This was attached to the vacuum line, the contents frozen at -78 °C and the headspace evacuated. CO (1.5 atm) was added at -78°C, and the tube was resealed. The contents were warmed carefully to room temperature, and the tube was repeatedly inverted for 10 min, resulting in a dull brown solution, \textsuperscript{1}H, \textsuperscript{11}B{\textsuperscript{1}H}, \textsuperscript{13}C{\textsuperscript{1}H} and \textsuperscript{19}F{\textsuperscript{1}H} NMR spectra matching that of pure 1-V\textsubscript{CO}. The NMR tube was frozen at -78 °C, and excess CO was removed in vacuo, and the contents were warmed to room temperature. \textsuperscript{13}CO\textsubscript{2} (1 atm, \approx 140 μmol) was added. The NMR tube was repeatedly inverted. NMR spectra taken after 5 h showed no observable reaction between 1-V\textsubscript{CO} and \textsuperscript{13}CO\textsubscript{2}.

Reaction between 2-V\textsubscript{CO} and Et\textsubscript{3}SiH (the forward reaction in Scheme 2-14a)

1-V (44 mg, 53 μmol) and C\textsubscript{6}D\textsubscript{5}Br (550 μL) were charged to a J-Young NMR tube. The tube was attached to the vacuum line, the contents frozen at -196 °C and the headspace evacuated. \textsuperscript{13}CO\textsubscript{2} (30 mmHg \times 35.3 mL, 57 μmol) was added, the contents warmed carefully to room temperature, resulting in a blue solution. The tube was repeatedly inverted for 30 min, resulting in a dark blue solution with a blue crystalline precipitate (2-V‘). The tube was reattached to the vacuum line, the headspace evacuated at -78 °C, and the contents returned to room temperature. CO (1 atm) was added, resulting in a yellow-brown solution on agitating for 5 minutes. \textsuperscript{1}H, \textsuperscript{11}B{\textsuperscript{1}H}, \textsuperscript{13}C{\textsuperscript{1}H} and \textsuperscript{19}F{\textsuperscript{1}H} NMR spectra confirm the presence of pure 2-V\textsubscript{CO’}. The headspace
was evacuated at -78 °C to remove excess CO, and the NMR tube was returned to the glove box, where Et$_3$SiH (8.4 μL, 53 μmol) was added, resulting in no observable change. The tube was inverted repeatedly for two days. 1-V$_{CO}$ was observed as a minor species (6%) in the $^{19}$F{$^{1}$H} NMR spectrum.

**Reaction between 1-V$_{CO}$ and Et$_3$SiOCHO (the reverse reaction in Scheme 2-14a)**

1-V$_{CO}$ (20 mg, 22 μmol), Et$_3$SiOCHO (4 μL, 22 μmol) and C$_6$D$_5$Br (550 μL) were added to a J-Young NMR tube. The tube was sealed and repeatedly inverted to mix. $^1$H, $^{11}$B{$^{1}$H} and $^{19}$F{$^{1}$H} NMR spectra were taken 15 minutes and 24 hours later. No reaction was observed, and the spectra corresponded to the superimposition of 1-V$_{CO}$ and Et$_3$SiOCHO when compared to the spectra of the respective reagents.

**Reaction between 2-V$_{CO}$ and Et$_3$SiH in the presence of B(C$_6$F$_5$)$_3$ (Scheme 2-14b)**

1-V (30 mg, 36 μmol) and C$_6$D$_5$Br (550 μL) were added to a J-Young NMR tube. The tube was attached to the vacuum line, contents frozen at -196 °C and the headspace evacuated. $^{13}$CO$_2$ (25 mmHg $\times$ 35.3 mL, 47 μmol) was condensed in, the tube sealed and the contents warmed carefully to room temperature. The tube was repeatedly inverted for 5 min, resulting in a blue solution (2-V$'$). The tube was reattached to the vacuum line, the contents frozen at -78 °C and the headspace evacuated. The contents were warmed to room temperature, and CO (1 atm) was added. The tube was repeatedly inverted for 15 minutes, resulting in a dull yellow-brown solution. $^1$H, $^{11}$B{$^{1}$H} and $^{19}$F{$^{1}$H} NMR spectra confirms the sample to be pure 2-V$_{CO}$ with a $^{13}$C-labelled
formyloxy group. Et₃SiH (23 μL, 144 μmol, 4 eq) and B(C₆F₅)₃ (9 mg, 18 μmol, 0.5 eq) were added to the NMR tube in the glove box, and the contents were agitated. ¹H and ¹³C{¹H} NMR spectra taken 35 minutes later show the presence of Et₃SiO⁻⁻CHO. On standing overnight, new resonances corresponding to the reduction products were observed in the ¹H and ¹³C{¹H} NMR spectra: ¹³CH₄: ¹H NMR (400 MHz, C₆D₅Br) δ 0.09 (d, ¹J_C-H = 126 Hz). ¹³C{¹H} NMR (101 MHz, C₆D₅Br) δ -4.0 (s). (Et₃SiO)₂¹³CH₂: ¹H NMR (400 MHz, C₆D₅Br) δ 4.99 (d, ¹J_C-H = 161 Hz, (Et₃SiO)₂CH₂), –CH₂CH₃ and –CH₂CH₃ resonances overlap with other Et₃Si- species at δ 0.90 ppm (t, ³J_H-H = 8.0 Hz) and 0.47 ppm (q, ³J_H-H = 8.0 Hz) respectively. ¹³C{¹H} NMR (101 MHz, C₆D₅Br) δ 84.2 (s, (Et₃SiO)₂CH₂). The non-enriched –CH₂CH₃ and –CH₂CH₃ resonances were not observed. Et₃SiO³⁻⁻CHO: ¹H NMR (400 MHz, C₆D₅Br) δ 8.39 (d, ¹J_C=H = 220 Hz, O⁻⁻CHO), –CH₂CH₃ and –CH₂CH₃ resonances overlap with other Et₃Si- species at δ 0.90 ppm (t, ³J_H-H = 8.0 Hz) and 0.47 ppm (q, ³J_H-H = 8.0 Hz) respectively. ¹³C{¹H} NMR (101 MHz, C₆D₅Br) δ 173.9 (s, OCHO). The non-enriched –CH₂CH₃ and –CH₂CH₃ resonances were not observed. (Et₃Si)₂O: δ 0.47 (q, ³J_H-H = 8.0 Hz, CH₂CH₃), 0.90 (t, ³J_H-H = 8.0 Hz, CH₂CH₃). ¹³C{¹H} NMR (101 MHz, C₆D₅Br) δ 6.6 (s, CH₂CH₃), 7.0 (s, CH₂CH₃).

Investigation of the forward reaction in Scheme 2-14c

1⁻⁻V (15 mg, 18 μmol) and Et₃SiOCHO (8.0 μL, 45 μmol, 2.5 eq) were dissolved in C₆D₅Br (600 μL) in an NMR tube sealed with a rubber septum and wrapped with Parafilm®, resulting in the instant dissolution of 1⁻⁻V giving a blue solution (reminiscent of 2⁻⁻V). The ¹⁹F NMR spectrum taken after 1 h show two sets of C₆F₅ resonances corresponding to 1⁻⁻V and 2⁻⁻V in the ratio 1:6.5. A ¹H NMR spectrum taken after the reaction was allowed to stand overnight shows the presence
of CH$_2$(OSiEt)$_2$, Et$_3$SiOCH$_3$ ($\delta$ 3.36, s, CH$_3$) and CH$_4$ in the ratio 17.6:1.68:1 in solution (not accounting for CH$_4$ in the headspace), and 85% consumption of Et$_3$SiOCHO (based on integrations of total Et$_3$Si and the OCHO singlet at $\delta$ 7.95 ppm).

**Reaction between 2-V and Et$_3$SiH (the forward reaction in Scheme 2-14c)**

2-V (40 mg, 46 μmol) and Et$_3$SiH (7.3 μL, 46 μmol) and C$_6$D$_5$Br (550 μL) were charged to an NMR tube. The tube was then sealed with a rubber septum and wrapped in Parafilm®. The blue crystals of 2-V dissolved after 30 min of sonication. After standing for an additional 30 min, the $^{19}$F NMR spectrum showed 1-V and 2-V in a 1:4 ratio.

**3.2.3 Representative procedure for determination of paramagnetic susceptibility**

Paramagnetic susceptibility was determined using the Evans’ method$^{94,85,95}$ – a solution of the paramagnetic compound (15 – 20 mg, carefully weighed out) in C$_6$D$_6$ or toluene-$d_8$ was diluted to 1.0 mL in a volumetric flask. A sample of this solution was charged to a capillary tube. The capillary tube was placed in an NMR tube containing C$_6$D$_6$ or toluene-$d_8$ respectively, and the $^1$H NMR spectrum was recorded on 400 MHz and 600 MHz spectrometers with rotation (20 Hz) of the NMR tube. Differing chemical shifts of the residual solvent resonances in different environments were observed, and the chemical shift difference $\Delta\delta$ (Hz) was recorded.

For C$_6$D$_5$Br samples, the solution of the paramagnetic compound was made in C$_6$D$_5$Br containing a known concentration of toluene (as the reference standard). The capillary tube containing this sample was placed in an NMR tube containing C$_6$D$_5$Br with the same concentration.
of toluene. The $^1$H NMR spectrum was recorded on 400 MHz and 600 MHz spectrometers. The differing chemical shifts of the toluene methyl resonance in different environments were recorded.

The resulting chemical shift difference allowed the determination of the mass paramagnetic susceptibility ($\chi_i$) of the compound, as depicted in Eq 3.1:

$$ \chi_i = -\frac{3}{4\pi m} \left( \frac{\Delta\delta}{v_0} \right) + \chi_0 $$

(3.1)

where $m$ (g mL$^{-1}$) is the concentration of the paramagnetic substance, $\Delta\delta$ (Hz) is the chemical shift difference of the reference peak, $v_0$ is the spectrometer frequency, and $\chi_0$ is the mass susceptibility of the solvent. Values of $\chi_0$ (cm$^3$ mol$^{-1}$) were converted from literature reported values of the mass diamagnetic susceptibility $\chi$ (cm$^3$ g$^{-1}$) of the solvents by Eq. 3.2:

$$ \chi_0 = \frac{\chi}{MW_{\text{solvent}}} $$

(3.2)

The sample susceptibility is then converted from mass units ($\chi_i$) to molar units, yielding the molar sample paramagnetic susceptibility $\chi_m$, as depicted in Eq. 3.3:

$$ \chi_m = MW_{\text{sample}} \times \chi_i $$

(3.3)

The effective magnetic moment ($\mu_{\text{eff}}$) of the compound can then be calculated:

$$ \mu_{\text{eff}} = 2.828 \sqrt{\chi_m T} $$

(3.4)

where $T$ is the temperature of the NMR probe at which the spectrum was recorded. For the first-row transition metals studied here, the spin-only approximation (Eq. 3.5) allows the correlation to the number of unpaired electrons $n$:

$$ \mu_{\text{eff}} = \sqrt{n(n+2)} $$

(3.5)
3.2.4 Representative procedure for catalytic CO$_2$ hydrosilation

In a glove box, a J-Young NMR tube was charged with C$_6$D$_5$Br solutions of Cp$^*$$_2$M$^+$/HB(C$_6$F$_5$)$_2$ (M = Sc, Ti, V) (213 μL, 18.8 mM, 4.00 μmol), Et$_3$SiH (50.0 μL, 2.4 M, 120 μmol), B(C$_6$F$_5$)$_3$ (37.5 μL, 106 mM, 4 μmol) and toluene (50.0 μL, 0.80 M, 40 μmol) and diluted with 200 μL C$_6$DsBr to a total volume of 550 μL. The tube was sealed, the contents were thoroughly mixed. The tube was attached to the vacuum line and degassed by three freeze-pump-thaw cycles. The contents were frozen, and CO$_2$ (165 mmHg × 35.3 mL, 313 μmol) was condensed quantitatively at -196 °C. The tube was kept at -196 °C, and was only thawed and thoroughly agitated immediately before NMR spectra were acquired. For M = Ti, V, the reaction was monitored by regularly acquiring $^1$H NMR spectra (600 MHz, $T = 298$ K, 3-second relaxation delay; 16 scans) at 375 s intervals. For M = Sc, to ensure complete relaxation of Et$_3$SiH, the reaction was monitored by regularly acquiring $^1$H (600 MHz, $T = 298$ K) NMR spectra (40-second relaxation delay; 8 scans) at 2 s intervals. Peak areas in the $^1$H NMR spectrum corresponding to the Et$_3$SiH resonance (3.890 - 3.440 ppm) were integrated and normalized to that of the toluene- $h_8$ internal standard (2.260 - 1.890 ppm).

3.2.5 Theoretical calculations

Energy profiles for the CO$_2$ activation by 1-M resulting in 2-M were calculated by Dr. Ludovic Castro and Prof. Laurent Maron at the University of Toulouse. Calculations were performed at the DFT level using the hybrid function B3PW91.$^{98-100}$ The Sc, Ti and V atoms were treated with the small core Stuttgart-Dresden ECP, associated with its adapted basis set.$^{101}$ H, C,
B, and O atoms were described with the all-electrons 6-31G(d,p) basis set. F atoms were treated with the Stuttgart-Dresden ECP, associated with its adapted basis set and completed with a set of d polarisation functions. Gibbs free energies were obtained at $T = 298.15$ K and $P = 1$ atm (760 mmHg).
### Appendix I: Crystallographic Data

**Table A-1** Data collection and structural refinement details for 1-Ti.

<table>
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<th>Parameter</th>
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**Table A-3** Bond lengths [Å] for 1-Ti

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C2 - C7 1.487(4)  C39 - C40 1.348(5)
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C21 - C26 1.378(3)  C40 - H40 0.9500
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**Table A-4** Bond angles [°] for 1-Ti

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C15 - C20 - H20A 109.5  C21 - B1 - C33 107.6(2)
C15 - C20 - H20B 109.5  C21 - B1 - H1 111.5(14)
C15 - C20 - H20C 109.5  C22 - C21 - B1 124.1(2)
C15 - Ti1 - C1 128.13(9)  C22 - C23 - C24 119.7(2)
C15 - Ti1 - C5 144.75(9)  C23 - C22 - C21 124.4(2)
C16 - C11 - Ti1 125.84(18)  C23 - C24 - C25 118.8(2)
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C2 - C3 - C8 126.5(3)  C27 - B1 - H1 103.4(14)
C2 - C3 - Ti1 72.62(14)  C28 - C27 - B1 127.9(2)
C2 - C7 - H7A 109.5  C29 - C28 - C27 124.0(2)
C2 - C7 - H7B 109.5  C29 - C30 - C31 118.9(2)
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Table A-5 Data collection and structural refinement details for 1-V

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Table A-6  Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for 1-V

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**Table A-7** Bond lengths [Å] for 1-V

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C17 - H17B  0.9800  C30 - C31  1.363(5)
C17 - H17C  0.9800  C31 - C32  1.366(5)
C18 - H18A  0.9800  C33 - B1  1.640(5)
C18 - H18B  0.9800  C33 - C34  1.384(4)
C18 - H18C  0.9800  C33 - C38  1.375(4)
C19 - H19A  0.9800  C34 - C35  1.370(5)
C19 - H19B  0.9800  C35 - C36  1.367(5)
C19 - H19C  0.9800  C36 - C37  1.366(5)
C2 - C3  1.417(5)  C37 - C38  1.380(4)
C2 - C7  1.496(5)  C4 - C5  1.403(5)
C20 - H20A  0.9800  C4 - C9  1.502(6)
C20 - H20B  0.9800  C5 - C10  1.492(5)
C20 - H20C  0.9800  C6 - H6A  0.9800
C21 - B1  1.632(5)  C6 - H6B  0.9800
C21 - C22  1.378(5)  C6 - H6C  0.9800
C21 - C26  1.378(4)  C7 - H7A  0.9800
C22 - C23  1.372(5)  C7 - H7B  0.9800
C23 - C24  1.360(5)  C7 - H7C  0.9800
C24 - C25  1.368(5)  C8 - H8A  0.99(13)
C25 - C26  1.380(4)  C8 - H8B  0.93(7)
C27 - B1  1.625(5)  C8 - H8C  0.87(7)
C27 - C28  1.379(4)  C9 - H9A  0.9800
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C28 - C29  1.375(5)  C9 - H9C  0.9800
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C3 - C4  1.413(5)  F10 - C32  1.345(4)
F11 - C34 1.348(4) F9 - C31 1.343(4)
F12 - C35 1.340(4) V1 - C1 2.286(4)
F13 - C36 1.340(4) V1 - C11 2.188(4)
F14 - C37 1.338(4) V1 - C12 2.234(4)
F15 - C38 1.344(3) V1 - C13 2.294(4)
F2 - C23 1.342(4) V1 - C14 2.261(3)
F3 - C24 1.340(4) V1 - C15 2.212(4)
F4 - C25 1.333(4) V1 - C2 2.201(3)
F5 - C26 1.347(4) V1 - C3 2.143(4)
F6 - C28 1.341(4) V1 - C4 2.214(4)
F7 - C29 1.342(4) V1 - C5 2.294(3)
F8 - C30 1.339(4)

Table A-8 Bond angles [°] for 1-V

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<th>Angle [°]</th>
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\[ \rho_{\text{calc}}, \text{ g cm}^{-3} \quad 1.567 \]
\[ F(000) \quad 900 \]
\[ \mu, \text{ mm}^{-1} \quad 0.373 \]
\[ \text{crystal size, mm}^3 \quad 0.16 \times 0.12 \times 0.10 \]
\[ \text{transmission factors} \quad 0.7456 - 0.6736 \]
\[ \theta \text{ range, deg} \quad 2.37 - 27.42 \]
\[ \text{data / restraints / param} \quad 8295/1/546 \]
\[ \text{GoF} \quad 1.178 \]
\[ R_1 (I > 2\sigma(I)) \quad 0.0832 \]
\[ wR_2 (\text{all data}) \quad 0.1793 \]
\[ \text{residual density, e/Å}^3 \quad 0.509 \text{ and } -0.265 \]

Table A-10 Atomic coordinates (\( \times 10^{-4} \)) and equivalent isotropic displacement parameters (\( \text{Å}^2 \times 10^3 \)) for 1-Vco

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Table A-13 Data collection and structural refinement details for 2-V

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\( \gamma, \text{ deg} \) & 90.00 \\
\( V, \text{ Å}^3 \) & 7842.2(4) \\
\( Z \) & 8 \\
\( T, \text{ K} \) & 173(2) \\
\( \lambda, \text{ Å} \) & 0.71073 \\
\( \rho_{\text{calc}}, \text{ g cm}^{-3} \) & 1.554 \\
\( F(000) \) & 3704 \\
\( \mu, \text{ mm}^{-1} \) & 0.615 \\
crystal size, \( \text{mm}^3 \) & 0.26 \times 0.16 \times 0.10 \\
transmission factors & 0.9410 – 0.8564 \\
\( \theta \) range, deg & 1.00 – 26.02 \\
data / restraints / param & 7703/0/499 \\
GoF & 1.166 \\
\( R_1 (I > 2\sigma(I)) \) & 0.0946 \\
w\( R_2 \) (all data) & 0.2339 \\
residual density, e/Å\(^3\) & 1.054 and -1.052 \\

**Table A-14** Atomic coordinates (\( \times 10^{-4} \)) and equivalent isotropic displacement parameters (Å\(^2 \times 10^3 \)) for 2-V

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**Table A-16 Bond angles [°] for 2-V**

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C13' - C14' - C19'  126.0  C14' - C15' - V1  67.54(18)
C13' - C14' - V1  70.72(17)  C14' - C19' - H19D  109.5
C13' - C18' - H18D  109.5  C14' - C19' - H19E  109.5
C13' - C18' - H18E  109.5  C14' - C19' - H19F  109.5
C13' - C18' - H18F  109.5  C14' - V1 - C1  130.90(19)
C13' - V1 - C1  161.96(19)  C14' - V1 - C11  55.73(18)
C13' - V1 - C11  49.09(17)  C14' - V1 - C11'  62.06(14)
C13' - V1 - C11'  62.05(12)  C14' - V1 - C12'  63.02(12)
C13' - V1 - C12'  37.63(8)  C14' - V1 - C13'  38.58(9)
C13' - V1 - C15'  63.02(14)  C14' - V1 - C15'  37.64(10)
C13' - V1 - C2  133.24(19)  C14' - V1 - C2  136.36(19)
C13' - V1 - C3  120.47(18)  C14' - V1 - C3  154.35(18)
C13' - V1 - C4  131.88(18)  C14' - V1 - C4  160.07(19)
C13' - V1 - C5  160.20(18)  C14' - V1 - C5  141.89(18)
C14 - C13 - C18  126.0  C15 - C11 - C16  126.0
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C14 - C15 - V1  75.25(17)  C15 - C20 - H20A  109.5
C14 - C19 - H19A  109.5  C15 - C20 - H20B  109.5
C14 - C19 - H19B  109.5  C15 - C20 - H20C  109.5
C14 - C19 - H19C  109.5  C15' - C11' - C16'  126.0
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C15' - C20' - H20E  109.5  C2' - V1 - C5  63.16(12)
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C16' - C11' - V1  126.32(16)  C2' - C7' - H7'1  109.5
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C17' - C12' - V1  124.04(17)  C2' - C7' - H7'3  109.5
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C18' - C13' - V1  120.26(19)  C20' - C15' - V1  124.01(15)
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C19' - C14' - V1  120.24(15)  C21 - O2 - B1  128.1(4)
C2 - C1 - C5  108.0  C22 - B1 - C34  111.0(4)
C2 - C1 - C6  126.0  C22 - C23 - C24  124.6(4)
C2 - C1 - V1  70.36(16)  C22 - C27 - C26  123.7(5)
C2 - C3 - C4  108.0  C23 - C22 - B1  120.5(4)
C2 - C3 - C8  126.0  C23 - C22 - C27  114.1(4)
C2 - C3 - V1  71.69(17)  C25 - C24 - C23  119.4(5)
C2 - C7 - H7A  109.5  C25 - C26 - C27  119.5(5)
C2 - C7 - H7B  109.5  C26 - C25 - C24  118.8(5)
C2 - C7 - H7C  109.5  C27 - C22 - B1  125.4(4)
C2 - V1 - C1  37.71(8)  C28 - B1 - C22  114.3(4)
C2 - V1 - C11  88.58(17)  C28 - B1 - C34  112.6(4)
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C2 - V1 - C12'  95.61(18)  C28 - C33 - C32  124.1(6)
C28 - C33 - F10  119.5(9)  C30 - C29 - F6'  118.7(6)
C29 - C28 - B1  121.2(4)  C31 - C30 - C29  119.8(6)
C29 - C30 - F7'  111.4(8)  C31 - C30 - F7'  127.6(7)
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C3 - V1 - C15'  129.46(19)  C37 - C38 - C39  120.0(5)
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C3 - V1 - C4  38.16(8)  C39 - C34 - B1  122.8(4)
C3 - V1 - C5  63.46(12)  C39 - C34 - C35  113.0(4)
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C4 - V1 - C12'  121.92(18)  C5' - C10' - H10D  109.5
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C5 - C10 - H10A  109.5  F1 - C23 - C24  115.4(4)
C5 - C10 - H10B  109.5  F10' - C33 - C28  120.6(10)
C5 - C10 - H10C  109.5  F10' - C33 - C32  113.8(10)
C5 - C4 - C3  108.0  F11 - C35 - C34  120.8(4)
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C5 - C4 - V1  72.00(16)  F12 - C36 - C35  119.6(5)
C5 - V1 - C1  37.59(8)  F12 - C36 - C37  120.5(5)
C5 - V1 - C11  150.44(17)  F13 - C37 - C36  121.2(5)
C5 - V1 - C11'  137.71(18)  F13 - C37 - C38  120.2(5)
C5 - V1 - C12'  154.69(17)  F14 - C38 - C37  120.2(5)
C5 - V1 - C15'  131.71(19)  F14 - C38 - C39  119.8(6)
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