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### Citation for published version:

Arnold, PL, Marr, IA, Zlatogorsky, S, Bellabarba, R & Tooze, RP 2014, 'Activation of carbon dioxide and carbon disulfide by a scandium N-heterocyclic carbene complex', *Dalton Transactions*, vol. 43, no. 1, pp. 34-37. <https://doi.org/10.1039/c3dt52762j>

### Digital Object Identifier (DOI):

[10.1039/c3dt52762j](https://doi.org/10.1039/c3dt52762j)

### Link:

[Link to publication record in Edinburgh Research Explorer](#)

### Document Version:

Peer reviewed version

### Published In:

Dalton Transactions

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Published article available at: <http://dx.doi.org/10.1039/C3DT52762J>

Cite as:

Arnold, P. L., Marr, I. A., Zlatogorsky, S., Bellabarba, R., & Tooze, R. P. (2014). Activation of carbon dioxide and carbon disulfide by a scandium N-heterocyclic carbene complex. *Dalton Transactions*, 43(1), 34-37.

Manuscript received: 03/10/2013; Accepted: 11/10/2013; Article published: 28/10/2013

## Activation of Carbon Dioxide and Carbon Disulfide by a Scandium N-Heterocyclic Carbene Complex\*\*†

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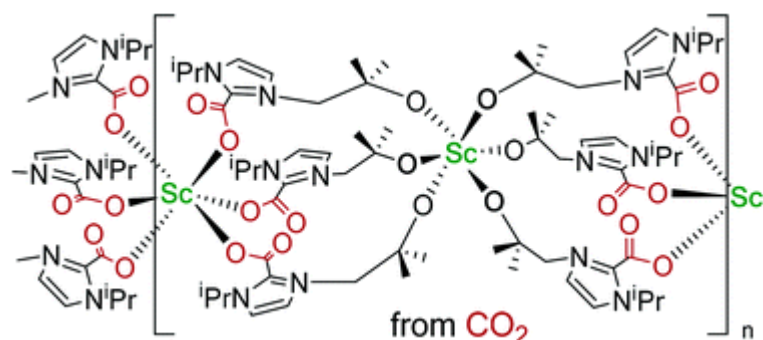
<sup>[\*\*]</sup>We are grateful to Prof S.E. Ashbrook and Mr D. Dawson for collection and interpretation of the solid state NMR spectroscopic data. Supplementary data: full experimental and crystallographic (CCDC 954361-954364) data.

<sup>[†]</sup>Celebrating 300 years of Chemistry at Edinburgh.

### Supporting information:

Electronic supplementary information (ESI) available: Full experimental and crystallographic data. CCDC 954361–954364. For ESI and crystallographic data in CIF or other electronic format see <http://dx.doi.org/10.1039/C3DT52762J>

### Graphical abstract:

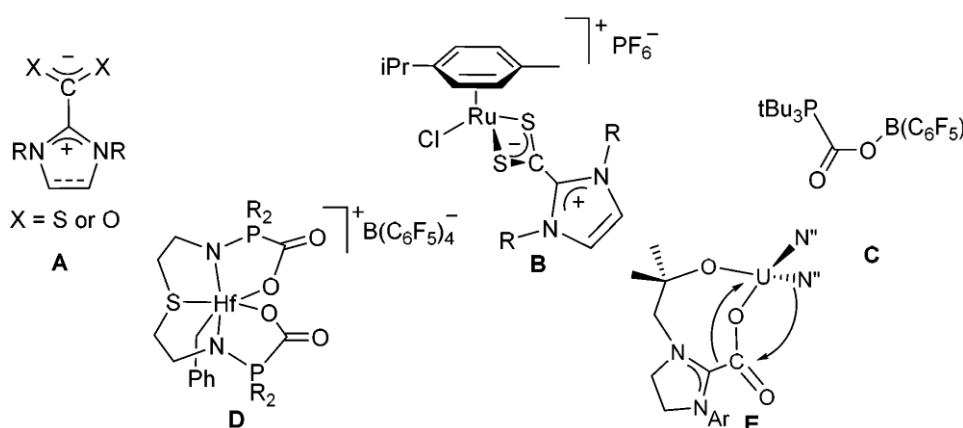


## Abstract

A Sc NHC complex readily activates three equivalents of CO<sub>2</sub> showing ‘Frustrated Lewis Pair’ type reactivity with each metal-carbene bond, but whilst CS<sub>2</sub> is also activated by the labile carbenes, no metal involvement is observed.

## Main text

Carbon dioxide (CO<sub>2</sub>) is an inexpensive and abundant natural resource and an attractive C<sub>1</sub> building block for the synthesis of more valuable molecules;<sup>1,2</sup> thus catalytic reactions using CO<sub>2</sub> as a feedstock are currently of great interest.<sup>3,4</sup> Carbon disulfide (CS<sub>2</sub>) is isoelectronic with CO<sub>2</sub> and has a more electrophilic carbon centre due to the weaker  $\pi$ -donor ability of the softer S, and is often studied as a comparator for CO<sub>2</sub>.

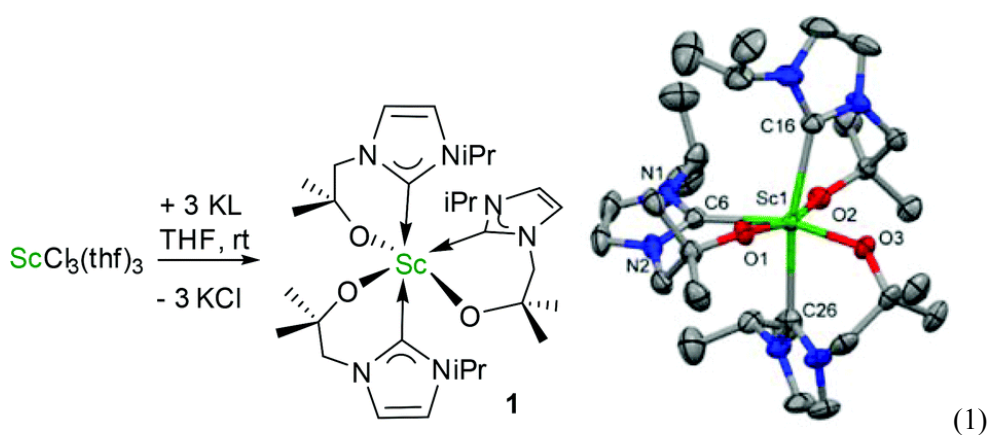


**Chart 1.**

Neutral N-heterocyclic carbenes (NHCs) are highly nucleophilic and are known to react with both CO<sub>2</sub> and CS<sub>2</sub> to form zwitterionic imidazolium carboxylates (NHC.CO<sub>2</sub>) and dithiocarboxylates (NHC.CS<sub>2</sub>) respectively (A in Chart 1).<sup>5</sup> Imidazolium carboxylates have been shown to successfully catalyse reactions such as the coupling of epoxides and carbon dioxide to produce cyclic carbamates.<sup>6</sup> The more Lewis basic nature of imidazolium dithiocarboxylates has allowed them to be used successfully as catalysts for the cyanosilylation of aldehydes,<sup>7</sup> and in the Staudinger reaction to prepare  $\beta$ -lactams.<sup>8</sup>

Delade demonstrated that the NHC.CS<sub>2</sub> can also be used as ligand and coordinates as a  $\kappa^2$ ,S,S' chelate to the Ru<sup>II</sup> centre in the first examples of transition-metal complexes with such ligands (B in Chart 1). His experiments also demonstrated the greater stability of the NHC.CS<sub>2</sub> than NHC.CO<sub>2</sub> betaines towards CE<sub>2</sub> loss.<sup>9</sup>

Frustrated Lewis pair (FLPs) systems are combinations of Lewis acids and Lewis bases that are prevented from reacting together by steric congestion. These have been used to activate CO<sub>2</sub>, for example, Stephan used B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and PtBu<sub>3</sub> to trap CO<sub>2</sub> (C in Chart 1).<sup>10</sup> Such activation of CO<sub>2</sub> using FLPs has allowed subsequent reduction to methanol and methane.<sup>11, 12</sup> There are few, but an increasing number, of transition metal FLP type systems which can activate CO<sub>2</sub> in the same way as main group FLPs. Wass used [Cp<sub>2</sub>Zr(OC<sub>6</sub>H<sub>4</sub>P<sup>t</sup>Bu<sub>2</sub>)] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] to trap CO<sub>2</sub><sup>13</sup> and Stephan used a cationic hafnium complex [S(CH<sub>2</sub>CH<sub>2</sub>NPR<sub>2</sub>)<sub>2</sub>Hf(CH<sub>2</sub>Ph)<sub>2</sub>] (R = Ph or <sup>i</sup>Pr) to activate two equivalents of CO<sub>2</sub> in a FLP type manner (D in Chart 1).<sup>14</sup> We and others have studied the NHC as the Lewis base centre in metal-FLP chemistry using complexes in which the M-NHC bond is very weak.<sup>15-19</sup> For example, U(L<sup>R</sup>)N''<sub>2</sub> (L = OCM<sub>2</sub>CH<sub>2</sub>(1-C{NCH<sub>2</sub>CH<sub>2</sub>NR}), R = 2,6-<sup>i</sup>Pr-C<sub>6</sub>H<sub>3</sub> or 2,4,6-Me-C<sub>6</sub>H<sub>2</sub>, N'' = N(SiMe<sub>3</sub>)<sub>2</sub>) reacts with CO<sub>2</sub> to form [U(L<sup>R</sup>)N''(OSiMe<sub>3</sub>)(O=C=NSiMe<sub>3</sub>)<sub>n</sub>]<sup>20</sup> presumed to proceed *via* E in chart 1. Herein, we report the synthesis of a homoleptic scandium-alkoxy-NHC complex and its reactivity with both CO<sub>2</sub> and CS<sub>2</sub>.



Treatment of ScCl<sub>3</sub>(thf)<sub>3</sub> with three equivalents of KL (L = [OCMe<sub>2</sub>CH<sub>2</sub>(1-C{NCHCHN<sup>i</sup>Pr})]) affords Sc(L)<sub>3</sub> **1** in a 67 % yield, eq 1. The <sup>1</sup>H NMR spectrum of **1** at room temperature shows one set of broad ligand resonances which would indicate either C<sub>3</sub> symmetry in solution or that a fluxional process between free and bound carbenes is occurring on the NMR timescale. A variable temperature <sup>1</sup>H NMR study (20 °C to -70 °C) of a d<sub>8</sub>-toluene solution of **1** was undertaken (see SI for spectra). Upon cooling, decoalescence features begin to be observed at 263 K, presumably the point at which the labile carbene dissociates readily from the metal. At 233 K two sets of broadened ligand resonances can be made out, with the isopropyl septet the most obvious feature (a septet which resonates at 5.85 ppm at 298 K, split to 6.73 and 5.49 ppm at 233 K in a 1:2 ratio). At lower temperatures still, further splitting of the ligand resonances is observed. Again, observing the isopropyl CH, the lower frequency resonance splits into two resonances (split from 5.49 to 5.46 and 5.50 ppm at 203 K). At 203 K three sets of ligand resonances are clearly present showing all three ligands to be in

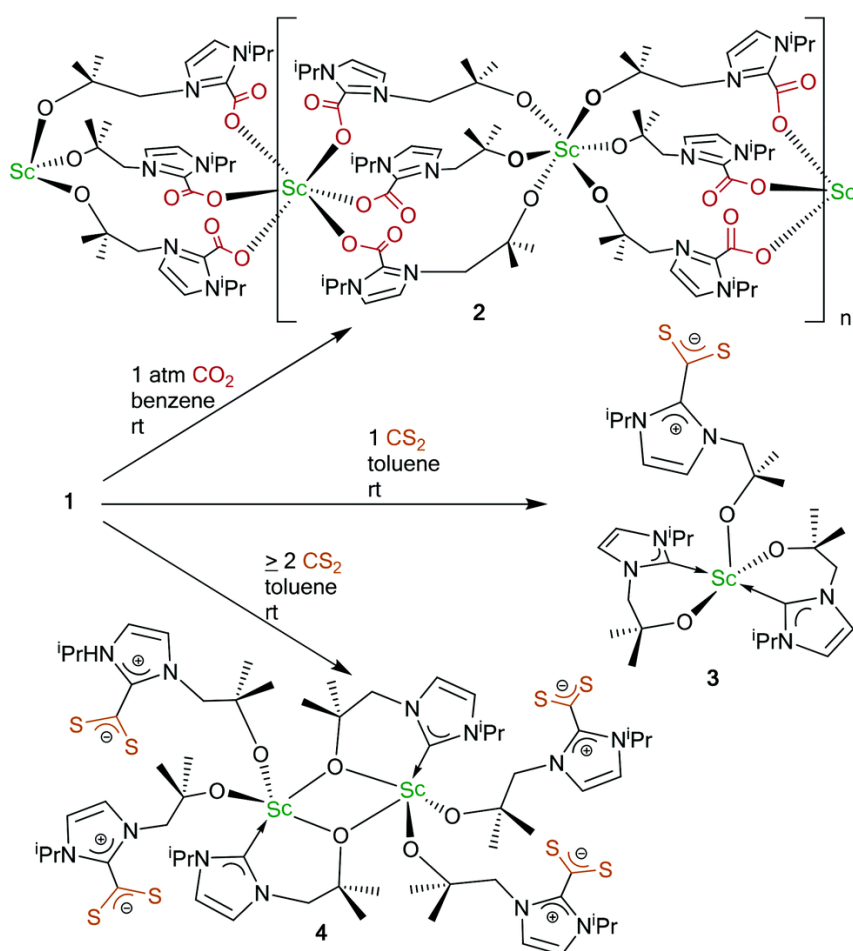
inequivalent environments to one another, indicating *meridionally*-aligned ligands. It can be observed from the spectrum at this temperature that all methyl groups and CH<sub>2</sub> protons in the molecule are diastereotopic.

X-ray quality single crystals of **1** were grown by slow diffusion of hexane into a concentrated benzene solution at 298 K over five days. The molecular structure of the  $\Lambda$ -*mer* enantiomer of **1** is shown alongside equation 1 (the asymmetric unit contains both  $\Delta$ -*mer* and  $\Lambda$ -*mer* enantiomers). The molecule is isostructural with Ti(L)<sub>3</sub> and Y(L)<sub>3</sub>, previously reported by our group.<sup>21, 22</sup> The Sc centre lies in a pseudo - octahedral environment, coordinated by three bidentate ligands in a *mer*-conformation. The mean Sc-C<sub>carbene</sub> bond distance is 2.436 Å, range 2.411(3) Å to 2.495(3) Å. The bond between the metal and the NHC *trans* to the alkoxide group is notably longer than the other two Sc-C<sub>carbene</sub> bond distances (2.452(3) c.f. 2.411(3) and 2.402(3) Å in the  $\Delta$ -*mer* isomer). Conversely, the distance between the scandium centre and alkoxide *trans* to the NHC is the shortest of the three Sc-O bonds in both molecules (1.989(2) c.f. 2.036(2) and 2.046(2) Å). The structure exhibits similar long *trans* NHC-M distances to those in Y(L)<sub>3</sub> and Ti(L)<sub>3</sub>.<sup>21, 22</sup> The mean Sc - C<sub>carbene</sub> bond length (2.422 Å) in **1** is comparable with other Sc-NHC complexes. For example, the distances in [Sc(L<sup>D</sup>)<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)] (L<sup>D</sup> = ({C(NDippCH<sub>2</sub>CH<sub>2</sub>N)}CH<sub>2</sub>CMe<sub>2</sub>O)) and [Sc(Ind(CH<sub>2</sub>CH<sub>2</sub>(1-C{NCHCHNMe<sub>3</sub>})))(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (Ind = indole) are 2.442 (mean) and 2.350(3) Å respectively.<sup>18, 23</sup> However, the M-C bond of 2.495(3) Å for the carbene *trans* to the alkoxide in **1** is the longest Sc-NHC distance yet reported, suggesting lability.<sup>18, 24, 25</sup>

To investigate the potential for the Sc-NHC combination to engage in FLP-type behaviour, reactions of **1** with CO<sub>2</sub> and CS<sub>2</sub> were investigated. A solution of **1** in benzene was exposed to an atmosphere of CO<sub>2</sub> upon which a colourless precipitate, **2**, immediately formed, Scheme 1. The isolated precipitate is insoluble in solvents with which it does not react, and assigned as the product of insertion of 3 equivalents of CO<sub>2</sub> into the Sc-C bonds, Sc(OCMe<sub>2</sub>CH<sub>2</sub>(1-O<sub>2</sub>CC{NCHCHN<sup>Pr</sup>}))<sub>3</sub> **2** (abbreviated as Sc(L<sup>CO<sub>2</sub></sup>)<sub>3</sub>) from elemental analysis, FTIR, and solid state NMR spectroscopies. Infrared spectroscopy (nujol mull) shows one set of distinct carbonyl stretching frequencies to be present, indicating high symmetry. The band at 1672 cm<sup>-1</sup> is assigned as the COO<sup>-</sup> asymmetric stretch for the imidazolium carboxylate, which typically range from ca. 1630 to 1690 cm<sup>-1</sup> depending on the *N*-substituents.<sup>26, 27</sup>

The <sup>13</sup>C MAS NMR spectrum of **2** shows a single set of resonances assignable to the ligand resonances. Most notably, two resonances at 156.1 and 145.0 ppm are assigned to the carbons of the NHC-coordinated CO<sub>2</sub> and the azolium C<sub>2</sub> respectively.<sup>27</sup> The resonances are slightly broader than expected, which combined with the insolubility, suggest a polymeric structure, formed through ligand bridging. Finally, the observation of two resonances in the <sup>45</sup>Sc MAS NMR spectrum of **2**, at 128 ppm and 45 ppm, has led us to propose the polymeric structure of **2** as shown in Scheme 1. The two chemical shifts are both indicative of a [ScO<sub>6</sub>], six-coordinate Sc centre ligated exclusively by oxygen atoms, with the broader resonance at 45 ppm (fwhm = 12 KHz) arising from a less symmetric environment at Sc.<sup>28, 29</sup>

For comparison, reactions with one, two, and an excess of equivalents of CS<sub>2</sub> were studied. Treatment of **1** with one equivalent of CS<sub>2</sub> in toluene affords the microcrystalline red solid [Sc(OCMe<sub>2</sub>CH<sub>2</sub>(1-S<sub>2</sub>CC{NCHCHN<sup>i</sup>Pr}))<sub>2</sub>(L)<sub>2</sub>], **3** (Sc(L<sup>CS<sub>2</sub>)(L)<sub>2</sub>), which was shown by a single crystal X-ray study to contain a single dithiocarboxylated imidazolium group, coordinated to Sc through the alkoxide. The <sup>1</sup>H NMR spectrum of **3** shows two sets of ligand resonances in a 2:1 ratio and the <sup>13</sup>C NMR spectrum is in agreement, with the resonance at 226.7 ppm attributed to the dithiocarboxylate group and a resonance at 150.6 ppm attributed to the C<sub>2</sub> imidazolium carbon through which CS<sub>2</sub> is bound. In previously reported imidazolium-2-dithiocarboxylates the CS<sub>2</sub> carbon resonance is usually observed in the range 220 - 226 ppm, and the C<sub>2</sub> in the unsaturated imidazolium ring around 149 ppm.<sup>30, 31</sup> In a separate reaction, we also isolated the CS<sub>2</sub> adduct of the proligand, HL.CS<sub>2</sub>; full characterisation including a single crystal X-ray structure, is in the SI.</sup>

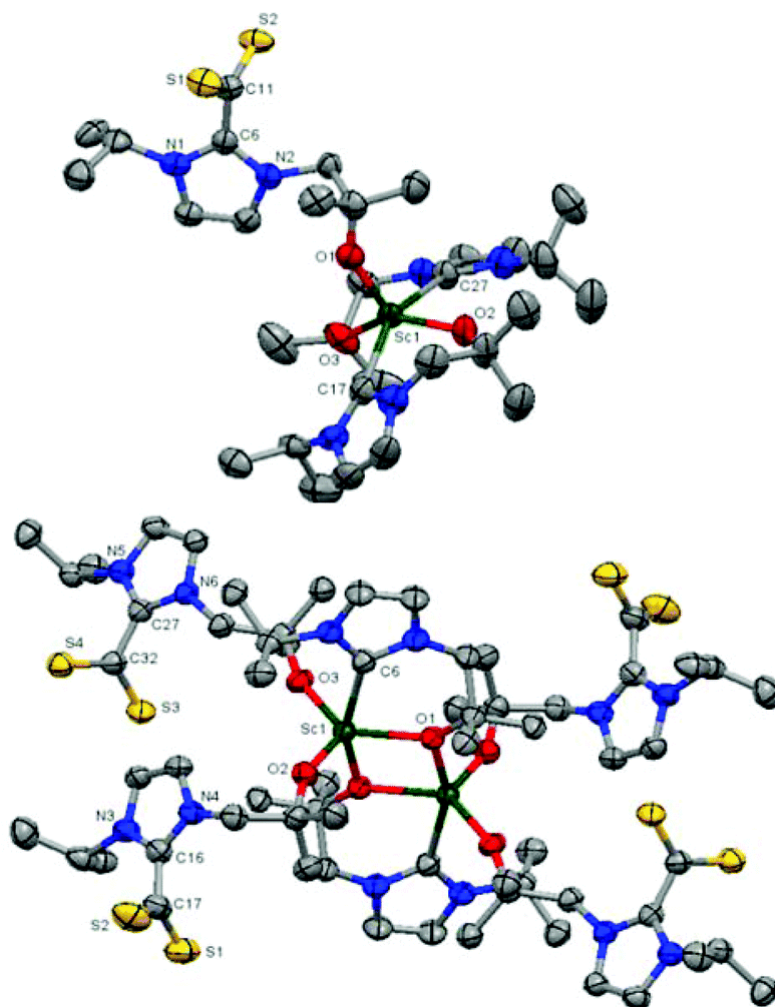


**Scheme 1.** Reactions of **1** with CO<sub>2</sub> and CS<sub>2</sub>.

Treatment of **1** with two equivalents of CS<sub>2</sub> in toluene leads to immediate formation of **3**, followed by the slow formation of [Sc(OCMe<sub>2</sub>CH<sub>2</sub>(1-S<sub>2</sub>CC{NCHCHN<sup>i</sup>Pr}))<sub>2</sub>(L)], **4** abbreviated as Sc(L<sup>CS<sub>2</sub>)(L)<sub>2</sub>, as a red oil,</sup>

evidenced by monitoring the reaction by  $^1\text{H}$  NMR. The addition of further equivalents of  $\text{CS}_2$  does not lead to the formation of  $\text{Sc}(\text{L}^{\text{CS}_2})_3$  but instead accelerates the rate at which **4** is formed. Notably, in a reaction where  $\text{CS}_2$  was used as both solvent and reagent, diffraction quality crystals of **4** were grown from the reaction mixture.\* Bright red X-ray quality single crystals of **3** were grown by slow diffusion of hexane into a concentrated benzene solution of **3** over a period of one week.

The molecular structures of **3** and **4** are shown in Figure 1. In the solid state **3** is monomeric with five coordinate –scandium positioned in a distorted square planar pyramidal environment.



**Figure 1.** Displacement ellipsoid plot of the molecular structures of **3** and **4** (50 % probability ellipsoids). H atoms omitted for clarity.

\* Crystals of **4** were also grown by adding a few drops of thf, then three equivalents of  $\text{CS}_2$  to a toluene solution of **1** at room temperature.

Whilst it can be ascertained that the two bound alkoxy tethered carbenes form the square base whilst the fifth coordination site is occupied by the alkoxy-bound pendant imidazolium-dithiocarboxylate group, which points away from the metal centre, the data are not of high quality. There are two independent molecules of **3** present in the asymmetric unit which are enantiomers.

Complex **4** is dimeric in the solid state with an alkoxy bridged  $\text{Sc}_2\text{O}_2$  core. Each metal centre is five-coordinate, distorted trigonal bipyramidal geometry, and the  $\text{CS}_2$  plane is always orthogonal to the imidazolium plane. Salient bond distances are similar in compounds **3** and **4** (but see caveat above). The mean  $\text{Sc-C}_{\text{carbene}}$  bond distance in **3** is 2.411 Å and in **4** 2.391(4) Å, the latter is significantly shorter than in **1** (mean distance 2.436 Å). The mean C-C bond distance between the  $\text{N}_2\text{C}^+$  unit and the  $\text{CS}_2^-$  unit in **4** is 1.481 Å.<sup>5, 31, 32</sup> Most surprising in both **3** and **4** is the absence of interaction between the scandium centre and the  $\text{CS}_2$  group, despite its formal negative charge.<sup>9</sup>

To conclude,  $\text{Sc(L)}_3$  readily incorporates three equivalents of  $\text{CO}_2$  showing 'Frustrated Lewis Pair' type reactivity, but it has not been possible to incorporate fewer equivalents.  $\text{CS}_2$  is coordinated through the same general M-NHC insertion process, but the  $\text{CS}_2$  part of the zwitterion formed does not compete with the NHC group for the Sc centre. Despite the proven lability of the NHC group, only up to two can be displaced by  $\text{CS}_2$  incorporation. Work is in progress to identify further reactions that allow these  $\text{CE}_2$  groups to be transferred into other organic substrates.



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