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Self-Assembly Fabrication of Hollow Mesoporous Silica@Co–Al Layered Double Hydroxide@Graphene and Application in Toxic Effluents Elimination

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Jiang, Shu-Dong, Song, Lei, Zeng, Wen-Ru, Huang, Zheng-Qi, Zhan, Jing, Stec, Anna A, Hull, T Richard, Hu, Yuan and Hu, Wei-Zhao (2015) Self-Assembly Fabrication of Hollow Mesoporous Silica@Co–Al Layered Double Hydroxide@Graphene and Application in Toxic Effluents Elimination. ACS Applied Materials & Interfaces, 7 (16). pp. 8506-8514. ISSN 1944-8244

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<http://dx.doi.org/10.1021/acsami.5b00176>

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Activation of carbon dioxide and carbon disulfide
by a scandium N-heterocyclic carbene complex†‡Cite this: *Dalton Trans.*, 2014, **43**, 34Received 3rd October 2013,
Accepted 11th October 2013

DOI: 10.1039/c3dt52762j

www.rsc.org/dalton

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A Sc NHC complex readily activates three equivalents of CO₂ showing 'Frustrated Lewis Pair' type reactivity with each metal-carbene bond, but whilst CS₂ is also activated by the labile carbenes, no metal involvement is observed.

Carbon dioxide (CO₂) is an inexpensive and abundant natural resource and an attractive C₁ building block for the synthesis of more valuable molecules;^{1,2} thus catalytic reactions using CO₂ as a feedstock are currently of great interest.^{3,4} Carbon disulfide (CS₂) is isoelectronic with CO₂ and has a more electrophilic carbon centre due to the weaker π-donor ability of the softer S, and is often studied as a comparator for CO₂.

Neutral N-heterocyclic carbenes (NHCs) are highly nucleophilic and are known to react with both CO₂ and CS₂ to form zwitterionic imidazolium carboxylates (NHC·CO₂) and dithiocarboxylates (NHC·CS₂) respectively (A in Chart 1).⁵ Imidazolium carboxylates have been shown to successfully catalyse reactions such as the coupling of epoxides and carbon dioxide to produce cyclic carbamates.⁶ The more Lewis basic nature of

imidazolium dithiocarboxylates has allowed them to be used successfully as catalysts for the cyanosilylation of aldehydes,⁷ and in the Staudinger reaction to prepare β-lactams.⁸

Delaude demonstrated that the NHC-CS₂ can also be used as ligand and coordinates as a κ²,S,S' chelate to the Ru^{II} 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-CS₂ than NHC·CO₂ betaines towards CE₂ loss.⁹

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 CO₂, for example, Stephan used B(C₆F₅)₃ and PtBu₃ to trap CO₂ (C in Chart 1).¹⁰ Such activation of CO₂ using FLPs has allowed subsequent reduction to methanol and methane.^{11,12} There are few, but an increasing number, of transition metal FLP type systems which can activate CO₂ in the same way as main group FLPs. Wass used [Cp₂Zr(OC₆H₄P^tBu)₂][B(C₆F₅)₄] to trap CO₂¹³ and Stephan used a cationic hafnium complex [S(CH₂CH₂NPR₂)₂Hf(CH₂Ph)₂] (R = Ph or ^tPr) to activate two equivalents of CO₂ in a FLP type manner (D in Chart 1).¹⁴ 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.^{15–19} For example, U(L^R)N''₂ (L = OCMe₂CH₂(1-C{NCH₂CH₂NR}), R = 2,6-ⁱPr-C₆H₃ or 2,4,6-Me-C₆H₂, N'' = N(SiMe₃)₂) reacts with CO₂ to form [U(L^R)N''-(OSiMe₃)(O=C=NSiMe₃)_n]²⁰ 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 CO₂ and CS₂.

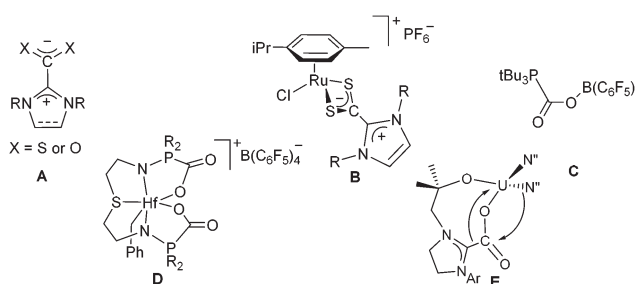


Chart 1

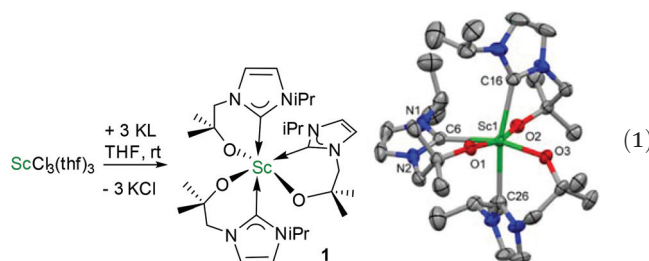
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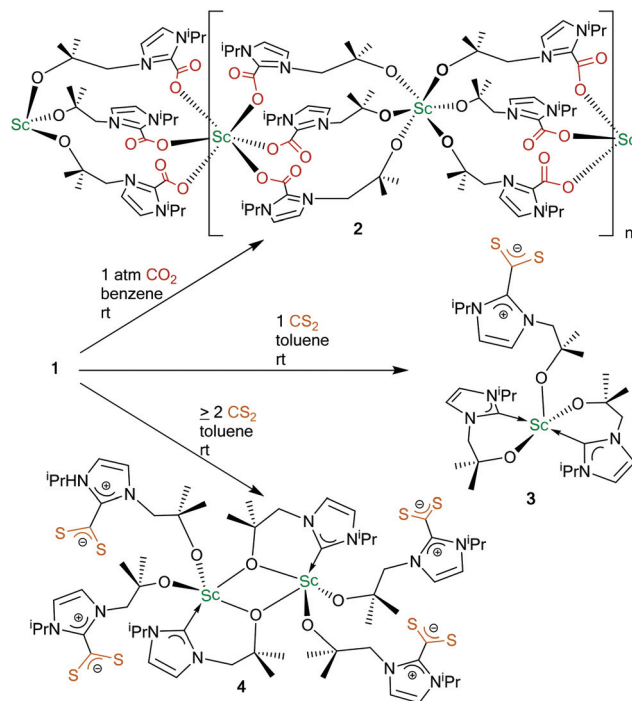
‡ Electronic supplementary information (ESI) available: Full experimental and crystallographic data. CCDC 954361–954364. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52762j



Treatment of $\text{ScCl}_3(\text{thf})_3$ with three equivalents of KL ($\text{L} = [\text{OCMe}_2\text{CH}_2(1\text{-C}\{\text{NCHCHN}^i\text{Pr}\})]$) affords $\text{Sc}(\text{L})_3$ **1** in a 67% yield, eqn (1). The ^1H NMR spectrum of **1** at room temperature shows one set of broad ligand resonances which would indicate either C_3 symmetry in solution or that a fluxional process between free and bound carbenes is occurring on the NMR timescale. A variable temperature ^1H NMR study (20 °C to -70 °C) of a d_8 -toluene solution of **1** was undertaken (see ESI† 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_2 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 Λ -*mer* enantiomer of **1** is shown alongside eqn (1) (the asymmetric unit contains both Δ -*mer* and Λ -*mer* enantiomers). The molecule is isostructural with $\text{Ti}(\text{L})_3$ and $\text{Y}(\text{L})_3$, previously reported by our group.^{21,22} The Sc centre lies in a pseudo-octahedral environment, coordinated by three bidentate ligands in a *mer*-conformation. The mean $\text{Sc}-\text{C}_{\text{carbene}}$ 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 $\text{Sc}-\text{C}_{\text{carbene}}$ bond distances (2.452(3) *cf.* 2.411(3) and 2.402(3) Å in the Δ -*mer* isomer). Conversely, the distance between the scandium centre and alkoxide *trans* to the NHC is the shortest of the three $\text{Sc}-\text{O}$ bonds in both molecules (1.989(2) *cf.* 2.036(2) and 2.046(2) Å). The structure exhibits similar long *trans* NHC–M distances to those in $\text{Y}(\text{L})_3$ and $\text{Ti}(\text{L})_3$.^{21,22} The mean $\text{Sc}-\text{C}_{\text{carbene}}$ bond length (2.422 Å) in **1** is comparable with other Sc–NHC complexes. For example, the distances in $[\text{Sc}(\text{L}^{\text{D}})_2(\text{CH}_2\text{SiMe}_3)]$ ($\text{L}^{\text{D}} = \{\{\text{C}(\text{NDippCH}_2\text{CH}_2\text{N})\}-\text{CH}_2\text{CMe}_2\text{O}\}$) and $[\text{Sc}(\text{Ind}(\text{CH}_2\text{CH}_2(1\text{-C}\{\text{NCHCHNMe}_3\})))-(\text{CH}_2\text{SiMe}_3)_2]$ (Ind = indole) are 2.442 (mean) and 2.350(3) Å respectively.^{18,23} 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.^{18,24,25}

To investigate the potential for the Sc–NHC combination to engage in FLP-type behaviour, reactions of **1** with CO_2 and CS_2 were investigated. A solution of **1** in benzene was exposed to an atmosphere of CO_2 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_2



Scheme 1 Reactions of **1** with CO_2 and CS_2 .

into the Sc–C bonds, $\text{Sc}(\text{OCMe}_2\text{CH}_2(1\text{-O}_2\text{CC}\{\text{NCHCHN}^i\text{Pr}\}))_3$ **2** (abbreviated as $\text{Sc}(\text{L}^{\text{CO}_2})_3$) 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^{-1} is assigned as the COO^- asymmetric stretch for the imidazolium carboxylate, which typically range from *ca.* 1630 to 1690 cm^{-1} depending on the *N*-substituents.^{26,27}

The ^{13}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_2 and the azolium C_2 respectively.²⁷ 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 ^{45}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 $[\text{ScO}_6]$, 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.^{28,29}

For comparison, reactions with one, two, and an excess of equivalents of CS_2 were studied. Treatment of **1** with one equivalent of CS_2 in toluene affords the microcrystalline red solid $[\text{Sc}(\text{OCMe}_2\text{CH}_2(1\text{-S}_2\text{CC}\{\text{NCHCHN}^i\text{Pr}\}))(\text{L})_2]$, **3** ($\text{Sc}(\text{L}^{\text{CS}_2})(\text{L})_2$), which was shown by a single crystal X-ray study to contain a single dithiocarbonylated imidazolium group, coordinated to Sc through the alkoxide. The ^1H NMR spectrum of **3** shows two sets of ligand resonances in a 2 : 1 ratio and the ^{13}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 C₂ imidazolium carbon through which CS₂ is bound. In previously reported imidazolium-2-dithiocarboxylates the CS₂ carbon resonance is usually observed in the range 220–226 ppm, and the C₂ in the unsaturated imidazolium ring around 149 ppm.^{30,31} In a separate reaction, we also isolated the CS₂ adduct of the proligand, HL-CS₂; full characterisation including a single crystal X-ray structure, is in the ESI.†

Treatment of **1** with two equivalents of CS₂ in toluene leads to immediate formation of **3**, followed by the slow formation of [Sc(OCMe₂CH₂(1-S₂CC{NCHCHN⁺Pr})₂(L))₂(L)], **4** abbreviated as Sc(L^{CS₂})₂(L), as a red oil, evidenced by monitoring the reaction by ¹H NMR. The addition of further equivalents of CS₂ does not lead to the formation of Sc(L^{CS₂})₃ but instead accelerates the rate at which **4** is formed. Notably, in a reaction where CS₂ 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 Fig. 1. In the solid state **3** is monomeric with five coordinate-scandium positioned in a distorted square planar pyramidal environment. 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.

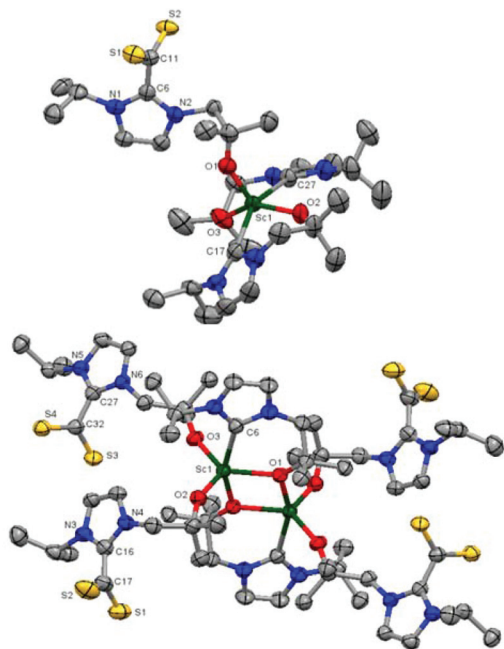


Fig. 1 Displacement ellipsoid plot of the molecular structures of **3** and **4** (50% probability ellipsoids). H atoms omitted for clarity.

Complex **4** is dimeric in the solid state with an alkoxy bridged Sc₂O₂ core. Each metal centre is five-coordinate, distorted trigonal bipyramidal geometry, and the CS₂ plane is always orthogonal to the imidazolium plane. Salient bond distances are similar in compounds **3** and **4** (but see caveat above). The mean Sc–C_{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 N₂C⁺ unit and the CS₂[−] unit in **4** is 1.481 Å.^{5,31,32} Most surprising in both **3** and **4** is the absence of interaction between the scandium centre and the CS₂ group, despite its formal negative charge.⁹

To conclude, Sc(L)₃ readily incorporates three equivalents of CO₂ showing ‘Frustrated Lewis Pair’ type reactivity, but it has not been possible to incorporate fewer equivalents. CS₂ is coordinated through the same general M–NHC insertion process, but the CS₂ 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 CS₂ incorporation. Work is in progress to identify further reactions that allow these CE₂ groups to be transferred into other organic substrates.

We are grateful to Prof. S.E. Ashbrook and Mr D. Dawson for collection and interpretation of the solid state NMR spectroscopic data.

Notes and references

‡ Crystals of **4** were also grown by adding a few drops of thf, then three equivalents of CS₂ to a toluene solution of **1** at room temperature.

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