Carbon–Silicon and Carbon–Carbon Bond Formation by Elimination Reactions at Metal N-Heterocyclic Carbene Complexes**

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Supporting information: Full experimental details and X-ray crystallographic data (CIFs deposited with the CCDC, codes 824248-824254 and 824414). This material is available free of charge via the Internet at www.ccdc.cam.ac.uk

Graphical abstract:
Abstract

Two functional groups can be delivered at once to organo-rare earth complexes (L)MR₂ and (L)₂MR (M = Sc, Y; L = {1-C(NDippCH₂CH₂N)}CH₂CMe₂O), Dipp = 2,6-iPr₂-C₆H₃; R = CH₂SiMe₃, CH₂CMe₂), via the addition of E-X across the metal-carbene bond to form a zwitterionic imidazolinium metal complex (Lₖ)MR₂X, where Lₖ = {1-EC(NDippCH₂CH₂N)}CH₂CMe₂O, E is a p-block functional group such as SiR₃, PR₂, SnR₃ and X is a halide. The 'ate' complex (L₄Li)ScR₃ is readily accessible, and is best described as a Li carbene adduct, {1-Li(thf)C(NDippCH₂CH₂N)}CH₂CMe₂O)Sc(CH₂SiMe₃), since structural characterization shows the alkoide ligand bridging the two metals and the carbene Li-bound with the shortest yet recorded Li-C bond distance. This can be converted via lithium halide-eliminating salt metathesis reactions to alkylated or silylated imidazolinium derivatives (Lₖ)ScR₃, E = SiMe₃ or CPh₃. All the E-functionalized imidazolinium complexes spontaneously eliminate functionalized hydrocarbyl compounds upon warming to room temperature or slightly above, forming new organic products ER, i.e. forming C-Si, C-P, and C-Sn bonds, and reforming the inorganic metal carbene (L)MR(X) or (L)₂MX complex respectively. Warming the tris(alkyl) complexes (L₄)MR₃ forms organic products arising from C-C or C-Si bond formation, and appear to proceed via the same elimination route. Treatment of (L)₂Sc(CH₂SiMe₃) with iodopentafluorobenzene results in the 'reverse sense' addition, which upon thermolysis forms the metal aryl complex (L)₂Sc(C₆F₅) and releases the iodoalkane Me₃SiCH₂I, again facilitated by the reversible functionalisation of the NHC group in these tethered systems.

Introduction

Carbon-element bond formation reactions are important for a wide range of synthetic and catalytic transformations; their formation can be controlled and catalysed by many metal complexes from across the periodic table, via various reaction types. In homogeneous catalysis the lanthanides and actinides are characterized by their facile bond activation reactions that proceed through a four-centered σ-bond metathesis mechanism rather than a conventional two-electron oxidative addition-reductive elimination pathway. For example, the first example of methane activation was observed in the reaction between Cp*₂YCH₃ (Cp* = C₅Me₅) and ¹³CH₄ which results in the interchange of labeled Y₁³CH₃ and unlabelled Y¹²CH₃ groups. The methane interconversion reactions in these systems are non-productive because the H atom always resides in the β position in the four-centre σ-bond metathesis transition state. However, Tilley’s group has demonstrated that silicon can take this β position, and used this to generate complexes capable of catalytic carbon-silicon bond formation: the reaction of CH₄ with Ph₃SiH₂ in the presence of catalytic (10 %) amounts of Cp*₂ScCH₃ affords
Ph₂MeSiH and H₂(Cp* = C₅Me₅). The reductive elimination of C-element bonds is a fundamental step in organic chemistry and homogeneous catalysis, and is generally seen for platinum group metal–based catalysts; the formation of C-C and C-Si bond is somewhat more fundamental and more difficult. While other Cp*₂LnR alkyl complexes exhibit interesting hydrocarbon chemistry such as β-carbon elimination from Cp*₂Sm(CH₂CMMe₂) to form the bridging planar trimethylenemethane dianion in [(Cp*)₂Sm]₂(µ-η²:η¹-C(CH₃)₃), the formation of C-element bonds using early d- and f-block metal catalysts is best represented by a variety of hydroelementation reactions, in which an organolanthanide complex catalyses the controlled addition of H and a main group element functional group (amine, phosphine, thiol, alcohol) across an unsaturated C-C bond, i.e. catalysts for the hydroamination, phosphination, alkoxylation, and silylation of alkenes. These too rely on σ-bond metathesis mechanisms to exchange the substrate and product at the end of each turnover. A range of asymmetric Michael addition reactions are probably the most well-known carbon-carbon bond forming reactions currently known for rare-earth alkoxide complexes in which the metal coordinates and activates a substrate prior to attack by a carbanion; basic lanthanum BINOL-ate derivatives were the first asymmetric catalysts for nitroaldol reactions. Carbon-element bond forming reactions that take place at a σ-bound rare-earth alkyl group however are rare. Early transition metal complexes often react with N-heterocycles to lead to ortho-metallated complexes and Teuben's group reported that (Cp*)₂Y(η²-C,N-NC₅H₄) is formed from the hydride [(Cp*)₂YH]₂ by the selective metallation of pyridine. The hydride also metallates other arenes. The addition of a further equivalent of pyridine forms the adduct (Cp*)₂Y(η¹-2-N₅C₄H₄)(NC₅H₄NC₅H₄) which on heating first forms the non-aromatic C-C coupled product (Cp*)₂Y[κ¹-2,2'-NC₅H₃(2-NC₅H₄)] by insertion, then eliminates hydrogen, allowing 2,2'-bipyridine to be eliminated upon quenching of the complex, or 2-alkylated pyridines to be formed if alkenes were incorporated into the mixture. Recently, Diaconescu reported similar scandium(III) chemistry in which two pyridine ligands were C-C coupled to form a ligated dearomatized bipyridine, in a mechanism also proposed to occur via σ-bond metathesis chemistry since other oxidation states are not generally accessible for group 3 metals.

We recently demonstrated that two functional groups can be delivered to an f-block metal at once by the use of a bound N-heterocyclic carbene as a reactive donor ligand. A polar reagent such as a halosilane can be added across the metal carbene bond, quaternizing the imidazolinium fragment, driven by the formation of the metal-halide bond. This functions as a substitute to an oxidative addition reaction at a metal with an accessible Mn²/Mn⁴ redox pair. The elimination reaction that completes the formal addition/elimination pair could be achieved by heating the complex to regenerate the metal carbene bond, releasing the carbene-bound electrophile now bound to an anion formerly coordinated to the metal. Scheme 1 shows a generic scheme for the addition of E-X (E = SiR₃, BR₂, PR₂, SnR₂; X = Cl, N₃) to (L)MN"₂ (M = Y, Ce; L = {C(NDippCH₂CH₂N)}CH₂CMMe₂O) to
afford \((L^E)MN''_2X\) \((L^E = \{1-EC(NDippCH_2CH_2N)\}CH_2CMe_2O)MN''_2X\), then thermally induced elimination of \(E-N''\), and a final salt metathesis step to regenerate \((L)MN''_2\).

**Scheme 1.** Addition-elimination cycles of reactivity for \(d^0\) metal carbene complexes with \(E-X\).

A small but increasing number of examples of non-innocent behaviour of the imidazolinium NHC unit are being reported, and these instances include reactions of early transition metal and f-block N-heterocyclic carbene complexes that are being explored for an increasing array of catalytic chemistry.\(^{12,13}\) In a most recent case, a \(Zr^{IV}\) complex of a dianionic bis(aryloxide) carbene complex \((L)Zr(CH_2Ph)(Cl)\) \((L = CN(3,5-tBu-C_6H_2O)CH_2CH_2(3,5-tBu-C_6H_2O))\) has been shown to be isolable, but additional donor coordination (a thf molecule) promotes benzyl migration from the metal to the carbene carbon, representing classical Fischer-type carbene behaviour and converting the carbene \(C\) to an \(sp^3\)-hybridized carbanion, and allowing additional donation from the two NHC nitrogen atoms to the metal.\(^{14}\) Mid- to high-oxidation state group 10 alkyl carbene complexes are known to suffer from decomposition via the reductive elimination of a monodentate NHC and alkyl group to form a \(C1\)-alkylated imidazolinium salt, with concomitant release of the two electron reduced metal complex. In certain cases, this can be used for productive heterocycle functionalization.\(^{15}\) In related chemistry, a \(Ni^{II}\) hydrocarbyl complex \(NiClPh(PPh_3)_2\) reacted with a bidentate saturated imidazolium NHC ligand to ring open the NHC group via insertion into one \(N-C\) bond, the product presumably resulting from the intramolecular attack by the \(Ni\)-bound alkyl on the empty carbene \(p\) orbital followed by the reductive elimination of the 2-alkylimidazolinium salt.\(^{16}\) Possibly the most interesting \(C-N\) bond
reactivity observed recently in nitrogen heterocycles relates to the C-C coupling, ring size reduction and dearomatization of imidazole- and NHC-supported Re-bound pyridines when treated with protons or methyl triflate.13

Aware of the absence of two-electron redox reactivity for the rare earth metals, the clean and reversible amido-functionalization chemistry elucidated in Scheme 1, and the potentially useful hydrocarbon reactivity that low-coordinate f-block complexes show, we have sought to extend the addition-elimination reactivity to alkyl-lanthanide complexes. Herein, we show how this strategy can be used to effect carbon-silicon and carbon-carbon bond forming reactions at organo-rare earth carbene complexes, as well as the derivatization of f-block alkyls with heteroatom functional groups such as stannanes or phosphines. We also demonstrate a new route to perfluoroaryl-rare earth complexes that avoids the use of mercury reagents.

Results

Syntheses of mono and bis(carbene) metal alkyl complexes

Complexes containing the σ-alkyl ligands neosilyl (CH₂SiMe₃) and neopentyl (Np = CH₂CMe₃) were chosen as targets with which to study the NHC-labilization chemistry; both mono and bis(ligand)
compounds of the rare earth Y\textsuperscript{III} and Sc\textsuperscript{III} cations are accessible using these anions. The mono(carbene) alkyl complexes \([(L)MR\textsubscript{2}]\textsubscript{2} (M = Sc or Y, R = CH\textsubscript{2}SiMe\textsubscript{3}) can be made readily from the thermally sensitive tris(alkyl) complexes by a protonolysis reaction between MR\textsubscript{3}(thf)\textsubscript{2} and HL in hexanes or hexanes/thf at 0 °C, and isolated in 62 % (Sc) and 51 % (Y) yield. The preparation of the same complexes from an \textit{in situ} reaction of MCl\textsubscript{3}(thf)\textsubscript{n} (n = 3 Sc, n = 3.5 Y) and three equivalents of LiR is less clean since the 'ate' complex \((L\textsuperscript{Li})MR\textsubscript{3}\) forms more readily than the neutral complex, so extra purification steps are required.\textsuperscript{17} The 'ate' complex can be made specifically from treatment of MCl\textsubscript{3}(thf)\textsubscript{n} with four equivalents of LiR and one equivalent of HL, Scheme 2. The alkyl complexes \([(L)MR\textsubscript{2}]\textsubscript{2} are dimeric at least in the solid state show much lower air- and thermal stability than the heterobimetallic 'ate' complexes, and the Sc complexes are much more readily isolated than the yttrium complexes, presumably due to the greater degree of steric protection afforded by the ligands to Sc. The three complexes \([(L)ScR\textsubscript{2}]\textsubscript{2}, [(L)YR\textsubscript{2}]\textsubscript{2}, and \((L\textsuperscript{Li})MR\textsubscript{3}\) have all been structurally characterized by single crystal X-ray diffraction techniques. The structures are discussed below.

The bis(carbene) alkyls \((L)\textsubscript{2}MR (M = Sc or Y, R = CH\textsubscript{2}SiMe\textsubscript{3}) can also be made from the tris(alkyl) complexes MR\textsubscript{3}(thf)\textsubscript{2} by treatment with two equivalents of the proligand HL in hexanes (Sc) or toluene (Y) at 0 °C. All reaction mixtures were stirred at room temperature before the volatiles were removed \textit{in vacuo} to yield the final products in 33 % \((L)\textsubscript{2}YR\) and 81 % \((L)\textsubscript{2}ScR\) yield, Scheme 1. These complexes are significantly more thermally stable than the mono(L) complexes, and have thus been used for the majority of reactivity studies described below. The complex \((L)\textsubscript{2}ScR\) can be heated to 80 °C in C\textsubscript{6}D\textsubscript{6} without noticeable signs of decomposition. The \textsuperscript{1}H NMR spectra of all of the bis(ligand) alkyl compounds were indicative of a rigid molecular structure in solution at room temperature. For example, in \((L)\textsubscript{2}ScR\) four doublets define the CH\textsubscript{Me\textsubscript{2}} protons of the Dipp groups and two singlets for the CMe\textsubscript{2} alkoxy arm protons. The CH\textsubscript{2}SiMe\textsubscript{3} alkyl resonances show geminal coupling (\(\textsuperscript{2}J\textsubscript{HH} = 11 \text{ Hz}\)) and appear as two doublets, implying the restricted rotation of the scandium alkyl Sc-CH\textsubscript{2}SiMe\textsubscript{3} bond. In the analogous \((L)\textsubscript{2}YR\), a doublet of doublets represents the CH\textsubscript{2}SiMe\textsubscript{3} protons due to the coupling to yttrium (\(\textsuperscript{1}J\textsubscript{YH} = 3 \text{ Hz}\)) in addition to the geminal coupling of the protons (\(\textsuperscript{2}J\textsubscript{HH} = 11 \text{ Hz}\)). The synthesis and characterization of the neopentyl complex \((L)\textsubscript{2}ScR (R = CH\textsubscript{2}CMe\textsubscript{3})\) has also been carried out successfully in 47 % yield; details are included in the supplementary information.

\textit{Addition/elimination reactions of metal carbene alkyl complexes to form carbon-silicon and carbon-carbon bonds}\n
The reactions of these alkyl complexes with reagents that can add across the metal carbene bond allows for the formation of carbon-heteroatom bonds, and for the study of C-C and C-Si bond
formation from an organolanthanide complex. The reaction chemistry of the bis(ligand) scandium complex has been studied in greatest detail due to the superior thermal stability of the complex, but additional NMR tube-scale reactions of the yttrium analogue, and mono(carbene) analogues have been carried out in a number of cases to ensure the generality of the procedures; these are included in the SI.

Reactions of \((L)_2Sc(CH_2SiMe_3)\) and \((L)_2Sc(CH_2CMe_3)\) with halosilanes and haloalkanes: C-Si bond formation

![Scheme 3. Formation of C-Si bonds from addition of halosilanes to \(d^0\) metal carbene complexes](image)

Treatment of the bis(ligand) Sc neosilyl or neopentyl complex \((L)_2ScR\) with one equivalent of trimethylsilyl chloride or iodide in benzene results in the formation of a clear, colorless solution which slowly (over five days for \(R = CH_2SiMe_3\) and ten days for \(R = CH_2CMe_3\)) at room temperature react to form a clean mixture of \((L)_2ScCl\) and the product of C-Si bond formation, \(Me_3SiCH_2SiMe_3\) or \(Me_3SiCH_2CMe_3\) respectively, in each case, Scheme 3. Here, and in the following cases, the organic product has been identified by NMR spectroscopies and/or mass spectrometry, and by comparison with spectra of genuine samples of the organic product. At the end of the five day reaction period, an unstirred reaction between \((L)_2ScR\) \((R = CH_2SiMe_3)\) and \(Me_3SiCl\) had deposited single crystals of the Sc product \((L)_2ScCl\) which were suitable for a single crystal structural analysis; details are given below.
In an effort to extend C-Si bond formation to C-C bond formation, we carried out the reactions of (L)2MR (M = Sc or Y, R = CH2SiMe3 or CH2CMe3) with a number of alkyl halides (MeI, iPrCl, iPrI, tBuI, Ph3CCl, CH2CHCH2Cl, BnBr, Me3SiCH2Cl) and aryl halides (PhCl, PhI, C6F5I). In a typical reaction, an equimolar quantity of each reagent was combined in a J-Young Teflon valve NMR tube in C6D6 (0.5 mL). The 1H NMR spectrum was recorded immediately and then after the reaction mixture had been heated to 80 ºC for 16 h. In all but the tube containing (L)2Sc(CH2SiMe3) and MeI or C6F5I (see below), no reaction had occurred. In the reaction with MeI no reaction was observed until the mixture was heated; after two hours at 80 ºC the scandium iodide, inorganic product (L)2ScI was isolated in 35 % yield, but no C-C bonded organic product H3C-CH2SiMe3 was observed, suggesting decomposition of the CH3I has occurred. The same outcome was observed in the presence or absence of daylight (where MeI is known to liberate free I2) and MeI is thermally stable up to 270 ºC. When the reaction was carried out with an excess of MeI, the solution became red-brown in color due to the formation of I2. No haloalkane Me3SiCH2I was observed in the reaction mixture, a byproduct which might be expected from a reaction with I2. X-ray quality single crystals of (L)2ScI were grown from a toluene solution of this reaction mixture at room temperature, confirming its structure, see below and the SI for further details of the molecular structure. This observation supports the assignment of a general addition/elimination mechanism for the reactions. In the reaction with C6F5I, a formally reverse sense addition across the M-C carbone bond and subsequent C-I bond formation has occurred, i.e. (L)2Sc(C6F5) and Me3SiCH2I are the products; this is discussed below.

Reaction of [(L)Sc(CH2SiMe3)2]2 with halosilanes and haloalkanes: C-Si and C-C bond formation

\[
\frac{1}{2} [(L)ScR2]2 + Me3SiCl \rightarrow [(LSiMe3)ScR2(Cl)] \\
(L)ScR(Cl) + Me3SiCH2SiMe3
\]

The mono(ligand) neosilyl complex [(L)ScR2]2 (R = CH2SiMe3) reacts much more quickly than the bis(ligand) complex with one equivalent of trimethylsilyl chloride in benzene to form a clear, colorless solution (over 3 h at 25 ºC) which contains the product of C-Si bond formation Me3SiCH2SiMe3, eq. 1. As before, the most reasonable mechanism for this reactivity involves the initial addition across the M-Carbone bond to form the quaternized NHC complex (LSiMe3)ScR2(Cl), which decomposes at room temperature cleanly eliminating Me3SiCH2SiMe3. If this mechanism is occurring then the scandium-containing byproduct should be (L)ScR(Cl), but it is not observed in the
byproducts. In the analogous amide chemistry the product (L)MN"Cl was usually observed to redistribute ligands to form equimolar (L)MN" and (L)MCl. Here, neither (L)ScR(Cl) nor [(L)ScR₂]₂ is found in solution, suggesting that the sterically unsaturated (L)ScR(Cl) product could be formed but has decomposed.

**Scheme 4.** Formation of C-Si and C-C bonds from the addition of group 14 halides to [(L)MR₂]₂.

The heterobimetallic ScLi compound (L¹)ScR₃ allows another route to the introduction of a functional group via metathetical displacement of the lithium cation. Thus treatment with either trimethylsilyl chloride or triphenylmethyl chloride at room temperature affords a colorless precipitate of lithium chloride and the 2-silylated or 2-alkylated imidazolinium scandium complex (L⁺SiMe₃)ScR₃ and (L⁺CPh₃)ScR₃ respectively after one or two hours, Scheme 4. If the mixture is kept at 0 °C, the silylated imidazolinium complex (L⁺SiMe₃)ScR₃ is isolable as a colorless powder in 78 % yield, and has been fully characterized. This reaction effectively generates the intermediate in the addition-elimination reactivity scheme which could not be isolated when the mono(ligand) alkyl complexes were treated with Me₃SiCl. The increased stability may arise from the greater steric protection of the scandium centre by the presence of three CH₂SiMe₃ ligands rather than two nosilyl and one chloride ligand, which has a lesser steric demand. Upon warming to room temperature the isolated powder of (L⁺SiMe₃)ScR₃ decomposes in the solid state, but if redissolved in toluene, it cleanly undergoes elimination chemistry: by integration of the ¹H NMR spectrum, approximately 0.9 equivalents of the
anticipated (L)ScR₂ was formed. A small amount of (L)₂ScR (~0.1 equivalents) was also observed, presumably as a result of ligand redistribution to this more stable product. Heating a toluene solution of (L⁻[CPh₃])ScR₃ results similarly in the straightforward spontaneous thermal elimination of Ph₃C-CH₂SiMe₃ to regenerate (L)ScR₂. This represents a new way to achieve carbon-carbon bond formation from a rare earth complex. From the reaction mixture that formed (L)ScR₂ and Ph₃C-CH₂SiMe₃, single crystals of the Sc alkyl complex were grown of sufficient quality for a single crystal X-ray structural determination. The structure is discussed below.

The C-Cl bond strength in trityl chloride Ph₃C-Cl is very weak, estimated as 280 kJmol⁻¹,¹⁹ rendering it an easy substrate with which to demonstrate the C-C bond formation reaction. No evidence for the formation of Gomberg's hydrocarbon dimer was found by spectroscopy, confirming the absence of any competing homolytic Ph₃C-X cleavage chemistry. This observation again supports the assignment of a general addition/elimination mechanism for the reactions. No reaction was observed between (L⁻[Li])ScR₃ and simpler alkyl or aryl halides such as ¹PrCl, ¹PrI, ¹BuI, PhCH₂Br, PhCl or PhI.

Addition/elimination reactions of metal carbene alkyl complexes to form other carbon-heteroatom bonds

We also previously communicated reactions of the amido complexes with halophosphines, boranes and stannanes, which resulted in the formation of new N-element bonds. It is now possible to extend these reactions to the formation of carbon-heteroatom bonds.

Halophosphines and stannanes: C-P and C-Sn bond formation

Scheme 5. Formation of C-heteroatom bonds from the addition of halogenated p-block reagents to (L)₂ScR (R = CH₂SiMe₃).
The reaction of (L)ScR₂ (R = CH₂SiMe₃) at room temperature in C₆D₆ with one equivalent of tBu₃SnCl, Ph₃SnCl or Ph₂PCl resulted in C-Sn and C-P bond formation to yield tBu₃SnCH₂SiMe₃, Ph₃SnCH₂SiMe₃ and Ph₂PCH₂SiMe₃ respectively with the generation of (L)₂ScCl. Scheme 5 shows the general reaction sequence to make tin and phosphorus alkyls alongside the conversion of (L)₂ScR into (L)₂ScCl. Again no intermediate imidazolinium complexes are observed by NMR spectroscopy, despite the reaction to form the P-C bond proceeding over the course of five days, suggesting the addition across the metal-carbene bond is the rate limiting step. A surprising difference in the reaction time was observed in the tin chemistry; the formation of tBu₃SnCH₂SiMe₃ proceeds quantitatively over 17 hours, but the formation of Ph₃SnCH₂SiMe₃ take up to five days to reach completion. The tBu₃SnCH₂SiMe₃ product was identified by both EI-MS (m/z = 363.1 [M-Me]) and ¹H and ¹³C{¹H} NMR spectroscopy. In the ¹³C{¹H} NMR spectrum, the resonance for the methylene tBu carbons of tBu₃SnCH₂SiMe₃ occurs at 10.7 ppm and coupling to the NMR active ¹¹⁹Sn and ¹¹⁷Sn isotopes was visible as tin satellites (²J_{¹¹⁹SnC} = 162 Hz, ²J_{¹¹⁷SnC} = 155 Hz).

Perfluoroaryl iodides: C-I bond formation

In contrast to the addition of group 14 and 15 halides, and as mentioned above, the reaction of [(L)ScR₂]₂ (R = CH₂SiMe₃) with C₆F₅I proceeds instantly to afford the product arising from the
addition in the reverse sense, \textit{i.e.} the carbene forms the 2-iodoimidazolinium salt and a metal aryl bond is formed. The two products isolated from the reaction are the alkyl halide Me$_3$SiCH$_2$I and (L)Sc(R)(C$_6$F$_5$) which crystallizes as an alkoxide bridged dimer, eq. 2. The analogous reaction between (L)$_2$ScR and C$_6$F$_5$I was found to proceed equally cleanly, with both (L)$_2$Sc(C$_6$F$_5$) (isolated in 86 % yield) and Me$_3$SiCH$_2$I identified as the products. X-ray quality single crystals of [(L)Sc(R)(C$_6$F$_5$)]$_2$ and (L)$_2$Sc(C$_6$F$_5$) were grown from toluene solution of the reaction mixtures at -20 °C and at room temperature respectively. The molecular structure of [(L)Sc(R)(C$_6$F$_5$)]$_2$ is described in the SI, while that of monomeric (L)$_2$Sc(C$_6$F$_5$) is shown in Figure 1e).

\section*{Discussion}

It is proposed that as before (Scheme 1), the mechanism which leads to the elimination of organic products with new carbon-element bonds arises from the initial addition of the E-X reagent across the M-Carbene bond in a heterolytic fashion to form a quaternized imidazolinium complex. For example, (L)$_2$ScR reacts with Me$_3$SiCl to form (L$^\text{SiMe}_3$)(L)ScR(Cl), {1-Me$_3$SiC(NDippCH$_2$CH$_2$N)})CH$_2$CMe$_2$O)(C(NDippCH$_2$CH$_2$N)})CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)Cl initially. The addition reaction appears to be driven by the formation of a strong M-X bond (Sc-Cl: 464 kJmol\(^{-1}\) in ScCl$_3$; 331 kJmol\(^{-1}\) for the diatomic ScCl, Y-Cl: 523 ± 84 kJmol\(^{-1}\) for diatomic YCl) and the use of a polar substrate. Upon warming to room temperature this 'ate'-like complex cleanly eliminates Me$_3$SiCH$_2$SiMe$_3$, reforming a metal carbene complex; in this example (L)$_2$ScCl.\(^{11}\) In the bis(ligand) complex reactions no inorganic products other than (L)$_2$ScX are isolated and we assume that only one of the two NHC groups is functionalized by the addition reaction, since the functionalization of two would place a large negative change on the Sc centre which seems unlikely. The bis(ligand) complex (L)$_2$ScCl is readily reconverted back to the alkyl (L)$_2$ScR starting materials, but the mono(ligand) chemistry is insufficiently stable to allow the metal complex to be recycled in this manner. This parallels the increased thermal stability of (L)$_2$ScR with respect to [(L)ScR$_2$]$_2$. The tris(alkyl) complex (L$^\text{CPh}_3$)ScR$_3$ is however sufficiently thermally stable that it can be isolated at low temperature in the solid state, but if redissolved in toluene, it cleanly undergoes elimination chemistry to form Me$_3$Si-CH$_2$SiMe$_3$ as anticipated, and [(L)ScR$_2$]$_2$. The isolation of both of these mono(ligand) products suggests that steric congestion is the main factor allowing their isolation. The straightforward spontaneous thermal elimination of Ph$_3$C-CH$_2$SiMe$_3$ from (L$^\text{CPh}_3$)ScR$_3$ to regenerate [(L)ScR$_2$]$_2$ is a new way to achieve carbon-carbon bond formation from a rare earth complex. This reactivity may be likened to that of 'frustrated Lewis pairs', in which a Lewis acid and Lewis base too bulky to react with each other, \textit{e.g.} a bulky phosphine PR$_3$ in combination with strongly electrophilic B(R)(C$_6$F$_5$)$_2$ can react to cleave H$_2$ (or other small molecules) in a heterolytic manner affording [HPR$_3$][HB(R)$_3$].\(^{20}\) In contrast to the amido chemistry, in the Ln-alkyl systems the intermediates are not
sufficiently stable to allow the isolation of single crystals which would provide structural confirmation of the intermediates. Another related possibility for the mechanism is suggested by consideration of the unusual stabilizing capabilities of the N-heterocyclic carbene. It is known that the coordination of small molecules to an NHC can reduce the strength of the adjacent bonds by a surprisingly large amount; the B-H BDE of an NHC-coordinated BH$_3$ molecule H$_3$B-C(NDippCH)$_2$ is lowered by approximately 125 kJmol$^{-1}$ compared with the BH$_3$ B-H bond.$^{21}$ Thus NHC-borane complexes are an emerging class of reagents for a variety of reduction reactions.$^{22}$ We have shown before that neutral Lewis acids such as boranes can compete with rare-earth metal centers for the NHC group in these bidentate ligands,$^{23}$ and it seems reasonable that a labilized NHC group in a mono- or bis(ligand) complex might have a similar effect on one of these substrates.

The formation of an organic product with a new C-Si bond is observed for scandium silylalkyl and scandium alkyl complexes, and also in the reaction of (L)$_2$YR with Me$_3$SiCl, showing the generality of the reaction. However, the addition of a range of alkyl halides, even those with very weak carbon-halogen bonds (such as Ph$_3$CCl), in an attempt to form carbon-carbon bonded products was not successful in this respect. Low yields of the iodide (L)$_2$ScI are formed from reactions of (L)$_2$ScR with methyl iodide, but only under conditions at which the MeI reagent can decompose, suggesting a simple radical attack, and no reaction is observed between (L)$_2$ScR and PhI. The C-I bond strength in Me-I is 239 kJmol$^{-1}$, that in Ph-I is 281 kJmol$^{-1}$.$^{24,25}$ Alkyl halides such as tert-butyl chloride have previously been shown to act as a single electron oxidant towards Ln$^{II}$ organometallics to form a Ln$^{III}$ halide, but there is no reason that any direct Ln$^{III}$-alkyl halide reactivity might be anticipated.$^{26}$

In the case of the mono(ligand) product, the instability of the metal product formed from the elimination step hampers the development of this system. We previously observed in the (L)MN$^{n^+}$ systems that the mono(ligand) products formed after elimination of the organic amine, i.e. (L)LnN$^{+}$Cl, were susceptible to ligand redistribution reactions, forming a 50:50 mixture of (L)MN$^{n^+}$ and (L)MX$_2$.

If this was the case here, one would anticipate [(L)ScR$_2$]$^2$ and (L)ScCl$_2$ although maybe only the former is isolable. It appears here that the mono(alkyl) complex (L)ScR(Cl) is insufficiently unstable.
to undergo any ligand distribution process before it decomposes, eq. 3, with the result that we have focused further C-heteroatom bond forming reactivity studies on the bis(ligand) complexes.

The heterobimetallic alkyl complex (L\textsuperscript{Li})ScR\textsubscript{3} in which the carbene binds to the lithium cation allows a straightforward carbene-C-alkylation to be carried out, and the quaternized intermediate, (L\textsuperscript{CPt})ScR\textsubscript{3} with no coordinated halide allows the formation of a C-C bonded organic product to be formed smoothly, without any decomposition of the final inorganic product since the dialkyl scandium complex (L)ScR\textsubscript{2} is also thermally stable. This represents a new type of C-C bond forming reaction, and one of particular potential use to a metal complex with no access to two-electron reductive elimination chemistry.

The robust bis(ligand)Sc framework has allowed the study of the formation of C-heteroatom bonds from the addition of p-block halides to the rare earth alkyl (L\textsubscript{2})ScR, and the polarity of the main group halide bond makes these reactions straightforward and high yielding for the formation of C-P and C-Sn bonds. The Sn-Cl bond strength is relatively high at 425 ± 17 kJmol\textsuperscript{-1} in Me\textsubscript{3}Sn–Cl\textsuperscript{27} but the polarity and formation of the strong Sc-Cl bond presumably drives the reaction. The use of two different tin reagents with very different sizes provides further information since the quantitative formation of nBu\textsubscript{3}SnCH\textsubscript{2}SiMe\textsubscript{3} takes 17 hours, but that of Ph\textsubscript{3}SnCH\textsubscript{2}SiMe\textsubscript{3} take up to five days. This must primarily be due to the differences in steric congestion that results in a slow addition of the triphenyl tin reagent. The Sn-Cl bond strength is high (for example, 425 ± 17 kJmol\textsuperscript{-1} in Me\textsubscript{3}SnCl, 439 kJmol\textsuperscript{-1} in nBu\textsubscript{3}SnCl and 350 ± 8 kJmol\textsuperscript{-1} for the diatomic Sn-Cl)\textsuperscript{28} but the polarity of the bond and the formation of a strong Sc-Cl bond (464 kJmol\textsuperscript{-1} in ScCl\textsubscript{3} and 331 kJmol\textsuperscript{-1} for the diatomic Sc-Cl)\textsuperscript{28,29} is presumed to facilitate the reaction.

Precedent for the reverse addition of C\textsubscript{6}F\textsubscript{5}I to form the iodoimidazolinium intermediate (which is not directly observed) has been previously set. The free carbene IAd (IAd = C{N(Ad)CHCHN(Ad)}, Ad = 1-adamantyl) reacts in thf with C\textsubscript{6}F\textsubscript{5}I to give the reverse ylid, 2-C\textsubscript{6}F\textsubscript{5}I-C{N(Ad)CHCHN(Ad)}, i.e. a halonium methylene ylid, a zwitterion where a positive charge is formally centered on the N-heterocyclic ring and a negative charge is on the iodine atom, which exists in an equilibrium in solution with the free carbene and C\textsubscript{6}F\textsubscript{5}I. The adduct reportedly underwent some decomposition in solution at room temperature over several hours, suggesting that C-I bond cleavage may occur. The complex is stable in the solid state, although the solutions were reported to decompose over a period of hours to release pentafluorobenzene and the 2-iodoimidazolium ion, suggesting that either carbon-iodine bond can be cleaved.\textsuperscript{30} It is interesting to compare the C-I BDE value\textsuperscript{24} of 277 kJmol\textsuperscript{-1} for C\textsubscript{6}F\textsubscript{5}I with that for C\textsubscript{6}H\textsubscript{5}I (281 kJmol\textsuperscript{-1}) which was not reactive for this chemistry. The simple 2-iodoimidazolium salt [2-I-C(NAdCH)\textsubscript{2}][I] can also be prepared by treatment of the free carbene IAd with I\textsubscript{2},\textsuperscript{30} and [1-I-C(NEtCH)\textsubscript{2}][I] was reported to be formed from the reaction of molybdenum or chromium carbonyl complexes [M(1-C(NEtCH)\textsubscript{2})(CO)\textsubscript{5}] (M = Mo or Cr) in chloroform with iodine.\textsuperscript{31}
Stack has also the first example of reductive elimination of C-carbene-halogen bonds from IPrCu\(^{III}\) halide complexes (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) to form the 1,3-bis(2,6-diisopropylphenyl)-2-chloroimidazolium cation.\(^{32}\) The formation of the iodoalkane Me\(_3\)SiCH\(_2\)I associated with the formation of the ScC\(_6\)F\(_5\) containing complexes by elimination from the Sc-R and imidazolium-I fragments mirrors the reductive elimination of MeI from Pt\(^{IV}\) complexes which has been previously reported.\(^{33}\)

Complexes containing a rare earth metal-C\(_6\)F\(_5\) group have previously been made via a few distinct reactions. The reaction of elemental Yb or Eu with HgPhC\(_6\)F\(_5\),\(^{34,35}\) affords the Ln\(^{II}\)-C\(_6\)F\(_5\) unit. An unusual \(\sigma\)-bond metathesis reaction involving either C-F or C-Si bond cleavage occurs with bis(cyclopentadienyl) cerium and samarium hydrides: The former reacts with C\(_6\)F\(_5\) to afford Cp\(_t\)\(_2\)Ce(C\(_6\)F\(_5\)) (Cp\(_t\) = C\(_5\)tBu\(_3\)H);\(^{36}\) the latter reacts with C\(_6\)F\(_5\)SiH\(_3\) to afford \([\text{Cp}^*\text{Sm}(\text{C}_6\text{F}_5)]\)\(^2\) (Cp* = C\(_5\)Me\(_5\)).\(^{37}\) The decomposition (via C\(_6\)F\(_5\) transfer to the metal) of a sterically unencumbered cationic scandium \(\beta\)-diketimato complex \([\text{Sc}(\text{Me})\{\text{(Ar)NC(Me)CHC(Me)N(Ar)}\}][\text{MeB}(\text{C}_6\text{F}_5)]\) affords \([\text{Sc}(\text{C}_6\text{F}_5)\{\text{(Ar)NC(Me)CHC(Me)N(Ar)}\}][\text{MeB}(\text{C}_6\text{F}_5)]\) (Ar = 2,6-\(i\)-Pr-C\(_6\)H\(_3\)).\(^{38}\) Finally, the protonolysis reaction of the chiral metallacycle Ce(\{1,2,4-\(t\)-Bu\}_3C\(_5\)H\(_2\))\(_2\)(\{1,2-\(t\)-Bu-4-CMe\(_2\)CH\(_2\)\}_3C\(_5\)H) with C\(_6\)F\(_5\)H forms Ce(\{1,2,4-\(t\)-Bu\}_3C\(_5\)H\(_2\))\(_2\)(\{1,2,4-\(t\)-Bu\}_3C\(_5\)H\(_2\)).\(^{36}\) There are also a limited number of transition metal NHC-containing complexes with a M-C\(_6\)F\(_5\) bond that have been formed by oxidative addition of C\(_6\)F\(_5\)X (X = F, CF\(_3\), C\(_6\)F\(_5\)),\(^{39,40}\) as in the case of trans-(L)\(_2\)Ni(F)(C\(_6\)F\(_5\)) (L = 1-C(MeNCH\(_2\)))\(^{39}\) or by simple substitution reactions, as for (L)Au(C\(_6\)F\(_5\)) (L = 1-C(MeNCH\(_2\))).\(^{41}\) Thus the iodoarene addition across the M-NHC bond straightforward reaction offers a new atom economic, and non-toxic method to introduce a fluoroaryl group.

**X-ray structures of the complexes**

From the reactions described above, single crystals of, [(L)YR\(_2\)\(_2\)], (L\(^{14}\))ScR\(_3\), (L\(_2\))ScR\(_2\), (L\(_2\))ScCl\(_2\), (L\(_2\))ScI\(_2\), (L\(_2\))Sc(C\(_6\)F\(_5\)) and [(L)Sc(R)(C\(_6\)F\(_5\))]\(_2\) were grown and the molecular structure determined by X-ray diffraction. The structures of [(L)ScR\(_2\)\(_2\)], (L\(^{14}\))ScR\(_3\), (L\(_2\))ScR\(_2\), (L\(_2\))ScCl\(_2\), and (L\(_2\))Sc(C\(_6\)F\(_5\)) are shown below in Figure 1, a) – e) respectively, with selected metrical data collected in Table 1. The structures of [(L)YR\(_2\)\(_2\)], (L\(_2\))ScI\(_2\) and [(L)Sc(R)(C\(_6\)F\(_5\))]\(_2\) are discussed in the supplementary information.
Figure 1. Thermal displacement drawings (50% probability ellipsoids) of the molecular structures of a) [(L)ScR$_2$]$_2$, b) (L$_2$ScR$_3$, c) (L)$_2$ScR, d) (L)$_2$ScCl, and e) (L)$_2$Sc(C$_6$F$_5$). Methyl groups, H atoms and lattice solvent molecules omitted for clarity.
Table 1. Selected bond lengths (Å) and angles (°) of a) [(L)ScR₂]₂, b) (L¹)ScR₃, c) (L)₂ScR, d) (L)₂ScCl, and e) (L)₂Sc(C₆F₅).

<table>
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<th>Bond Type</th>
<th>[(L)ScR₂]₂</th>
<th>(L¹)ScR₃</th>
<th>(L)₂ScR</th>
<th>(L)₂ScCl</th>
<th>(L)₂Sc(C₆F₅)</th>
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<tr>
<td>M-C_Carbene</td>
<td>2.4572(16)</td>
<td>2.114(5) (M = Li)</td>
<td>2.442 (av.)</td>
<td>2.416 (av.)</td>
<td>2.422</td>
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<tr>
<td>Sc₁-C_Carbene</td>
<td>2.247 (av.)</td>
<td>2.245 (av.)</td>
<td>2.282 (av.)</td>
<td>-</td>
<td>2.417(6)</td>
</tr>
<tr>
<td>Sc₁-C_Altl</td>
<td>2.0821(11)</td>
<td>1.904(5) (M = Li)</td>
<td>1.945 (av.)</td>
<td>1.879(3)</td>
<td>1.918(4)</td>
</tr>
<tr>
<td>C₁-Sc₁-C₁</td>
<td>-</td>
<td>-</td>
<td>166.4 (av.)</td>
<td>174.48(16)</td>
<td>177.2(2)</td>
</tr>
<tr>
<td>O₁-Sc₁-O₂</td>
<td>-</td>
<td>-</td>
<td>131.8 (av.)</td>
<td>127.9(2)</td>
<td>120.96(19)</td>
</tr>
</tbody>
</table>

Single crystals of [(L)M R₂]₂ (M = Sc or Y, R = CH₂SiMe₃) were grown from toluene solutions at -20°C. The displacement ellipsoid plot when M = Sc is shown in Figure 1a). The molecular structure of [(L)MR₂]₂ (M = Sc or Y) is dimeric in the solid state with the alkoxy groups bridging the metal centers to form an M₂O₂ core which is centered over a crystallographic inversion centre. Each metal centre is five-coordinate, in a distorted trigonal bipyramidal geometry where the silylalkyl groups and one alkoxy bridging group define the equatorial plane. The L ligand is not parallel with the C₂O₂ plane but pitched away from the plane defined by the C₂O₂ core by approximately 28°. The Sc-C_Carbene distance is 2.4572(16) Å and Sc-C_Altl average is 2.247 Å bond lengths are comparable to those previously reported complexes: Sc-C_Carbene = 2.350(3) Å and Sc-C_Altl average = 2.209 Å in (L)ScR₂ (L = IndCH₂CH₂(1-C₆NCHCHNMe)), Sc-C_Carbene = 2.343(4) Å and Sc-C_Altl average = 2.201 Å in (L)ScR₂ (L = FluCH₂CH₂(1-C₆NCHCHNMe)).

Crystals of (L¹)ScR₃ were grown from a toluene solution at -20 °C. The displacement ellipsoid plot is shown in Figure 1b). Lithium NHC complexes remain rare. The molecular structure of (L¹)ScR₃ contains the shortest reported Li-C_Carbene distance (2.114(5) Å) reported to date. Existing examples range from 2.124(4) Å in [Li(L)₃] (L = 'BuNCH₂CH₂(1-C₆NCHCHNMe)) to 2.237(3) Å in [Li(L)(C≡C'Bu)]₄ (L = (1-C₆NMeCMMe)₂). The Li-C_Carbene-centroid_NHC angle is approaching linearity (166.5°) and so there is no severe distortion. The Li-C_Carbene distance is far shorter than the Sc-C_Carbene distance in [(L)ScR₂]₂ (2.4572(16) Å) and much shorter than expected based on the differences in ionic radii (Li⁺, 6C.N. = 0.76 Å, Sc³⁺, 6C.N. = 0.745 Å).

The coordination geometry at the scandium centre is distorted tetrahedral, with the Sc-C_Altl average bond length (2.245 Å) very similar to that in [(L)ScR₂]₂ (2.247 Å). The Li⁺ ion forms part of a six-membered metallacyclic ring where five of the atoms (O₁-Li₁-C₁-N₁-C₈) are, unusually, virtually co-planar and Li₁ is in a distorted trigonal coordination environment, sitting 0.471 Å above the plane defined by O₁-O₂-C₁.
Crystals of \((\text{L})_2\text{ScR}\) were grown from a toluene solution at -30 °C. The displacement ellipsoid plot is shown in Figure 1c). \((\text{L})_2\text{ScR}\) crystallized with four molecules in each asymmetric unit of the unit cell. It is noted that one molecule (labeled C) was largely disordered. Comparable to all of the \((\text{L})_2\text{ScX}\) molecular structures discussed here, the scandium cation is in a distorted trigonal bipyramidal environment with the alkoxide and chloride groups defining the equatorial plane. The bond lengths and angles are comparable to those previously reported scandium alkyl complexes.

Crystals of \((\text{L})_2\text{ScCl}\) were grown from \(\text{C}_6\text{D}_6\) at room temperature from the reaction mixture of \((\text{L})_2\text{ScR}\) and \(\text{Me}_3\text{SiCl}\). The displacement ellipsoid plot is shown in Figure 1d). The scandium centre is in a distorted trigonal bipyramidal coordination environment (C1-Sc1-C11 = 174.48(16)°, C1-Sc1-Cl1 = 90.23(11)°, O1-Sc1-Cl1 = 115.12(15)°) with the alkoxide and chloride groups defining the equatorial plane. There is a significant asymmetry to the coordination of the N-heterocyclic ring to the metal ion (N1-Sc1-C1 = 115.1(3)°, N2-Cl-Sc1 = 136.6(3)°), with the N-Dipp groups being forced backwards in order to minimize unfavorable interactions. A \(C_2\) axis is present through the Sc1-Cl1 bond.

Crystals of \((\text{L})_2\text{Sc(C}_6\text{F}_5)\) were grown from a saturated toluene solution at -20 °C, but the quality of the data is not very good. The displacement ellipsoid plot is shown in Figure 1e). \((\text{L})_2\text{Sc(C}_6\text{F}_5)\) crystallized with two molecules in each asymmetric unit of the unit cell and, since both have very similar metrical parameters, only one is discussed here. The metal ion has a trigonal bipyramidal coordination geometry with the carbene donors as axial groups (O1-Sc1-O2 = 120.96(19)° and C1-Sc-C11 = 177.8(2)°), the N-heterocyclic rings being near co-planar (interplane angle defined by N1-C1-N2 and N3-C11-N4 = 8.73 Å) and the bulky N-Dipp groups opposite to each other in order to minimize unfavorable interactions. The Sc-C\text{carbene} bond length (2.412(5) Å) is comparable to that in \((\text{L})_2\text{Sc(1)}\) (2.431(2) Å). The Sc-C\text{aryl} bond length in \((\text{L})_2\text{Sc(C}_6\text{F}_5)\) (2.412(5) Å) is long. Comparison with \((\text{L})\text{Y(C}_6\text{F}_5)\text{thf}\) (L = 1-NPh-2-CNPh-C\text{6H}4) (2.492(3) Å) confirms this even when taking into account with 0.155 Å difference in ionic radii of Sc\text{III} and Y\text{III}. The Sc···F\text{average} bond distance of 3.53 Å is also long (outside the combined van der Waals’ radii of 3.47 Å) and there is no significant asymmetry in the coordination of the \(\text{C}_6\text{F}_5\) group to the scandium centre (C48-C47-Sc1 = 125.04(4) Å and C52-C47-Sc1 = 123.89(4) Å) to indicate the presence of any stabilizing Sc···F interactions (see SI for discussion of Sc···F interactions in \([\text{L}]{\text{Sc(R)(C}_6\text{F}_5})\text{]_2}\)).

Conclusions

The addition of E-X, where E is a functional group such as silyl, phosphinyl or stannyl and X is a halide, across the metal-carbene bond in scandium and yttrium alkyl complexes with tethered, bidentate NHC ligands results in the formation of unstable metal 'ate' complexes. The displaced NHC
group binds E the heteroatom functional group, and the halide X binds to the metal. The addition reaction appears to be driven by the formation of a strong M-X bond and the use of a polar substrate. Subsequent thermolysis is facile for these organolanthanide complexes, and in each case allows the formation of the heteroatom-functionalized hydrocarbon. The remaining lanthanide halide metal product can be recycled back to the alkyl complex by standard salt elimination routes. This chemistry is particularly straightforward for the bis(ligand) complexes presumably due to an increased level of steric protection afforded to the metal complexes.

The combination of Lewis acidic metal cation and nucleophilic carbene is strong enough to cleave the C-I bond in iodofluoroarenes offering a clean route to metallofluorobenzenes. The combination is not sufficiently reactive to cleave even the weakest carbon halogen bonds by addition across the metal-carbene bond, but the lithium carbene 'ate' complexes are reactive enough to allow a new means for the formation of carbon-carbon bonds at a redox-innocent organometallic such as found in Group 3 and lanthanide chemistry. This new type of C-element bond forming reaction might be of particular use to a metal complex with no access to two-electron redox chemistry.

The analogy between this Lewis-acid/NHC reactivity to frustrated Lewis pairs, and also catalytic reactions that combine NHCs with Lewis acidic metal catalysts suggests that tuning of these systems may allow for a variety of other small molecules to be activated and incorporated into organo-rare earth metal chemistry. The successful formation of C-heteroatom bonds suggests that asymmetric versions of the ligand, readily available from chiral epoxides and primary amines, might allow asymmetric carbon-element bonds to be formed. Work is in progress to develop asymmetric routes to silanes and phosphines, and to develop the potential for a relevant catalytic cycle for the formation of carbon-carbon and carbon-heteroatom bonds.

**Experimental Details**

1. **General Details**

All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of dinitrogen. Protio solvents were degassed by sparging with dinitrogen, dried by passing through a column of activated sieves and stored over potassium mirrors (hexanes, toluene, benzene) or activated 4 Å molecular sieves (thf). Deuterated solvents were dried over potassium (d$_6$-benzene, d$_8$-thf), distilled under reduced pressure, freeze-pump-thaw degassed three times prior to use.

$^1$H NMR spectra were recorded at 298 K, unless otherwise stated, on Bruker AVA 400, AVA 500 or AVA 600 spectrometers and $^{13}$C{$^1$H} or $^{13}$C spectra on the same spectrometers at operating frequencies of 100, 125 and 150 MHz respectively. Two dimensional $^1$H-$^1$H and $^{13}$C-$^1$H correlation
experiments were used, when necessary, to confirm $^1$H and $^{13}$C assignments. All NMR spectra were referenced internally to residual protio solvent ($^1$H) or solvent ($^{13}$C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). Chemical shifts are quoted in $\delta$ (ppm) and coupling constants in Hertz. Mass spectra were recorded by the mass spectrometry service of the University of Edinburgh’s School of Chemistry. Elemental analyses were carried out at London Metropolitan University.

2. Synthetic Details

$\text{ScCl}_3(\text{thf})_3$, $\text{YCl}_3(\text{thf})_{3.5}$, $\text{Sc(CH}_2\text{SiMe}_3)_3(\text{thf})_2$, $\text{Y(CH}_2\text{SiMe}_3)_3(\text{thf})_2$, $\text{Sc(CH}_2\text{CMe}_3)_3(\text{thf})_1.5$, $\text{Y}\{\text{CH(SiMe}_3\text{)}_2\}_3(\text{thf})_2$ and $\text{HL}_5$ were prepared with reference to published methods. Ph$_3$CCl was recrystallized from toluene and washed with hexanes, TMSCl was distilled under reduced pressure, TMSI was distilled under reduced pressure and stored in the absence of light, BnBr was dried over activated alumina and distilled under reduced pressure and then stored in the dark, Ph$_3$SnCl was sublimed (10$^{-4}$ Torr, 90 ºC) and Ph$_2$PCl was distilled under reduced pressure (10$^{-1}$ Torr, 120 ºC) prior to use. All other reagents were purchased and used without further purification.

2.1. Synthesis of mono(L) complexes

2.1.1. Synthesis of (L)Sc(CH$_2$SiMe$_3$)$_2$

a. At 0 ºC, to a slurry of Sc(CH$_2$SiMe$_3$)$_3$(thf)$_2$ (1.1 g, 2.4 mmol) in hexanes (15 mL) was added a solution of HL (0.72 g, 2.4 mmol) in hexanes (10 mL). The reaction mixture was stirred for 3 h during which time a white precipitate formed. The precipitate was collected by filtration and dried in vacuo to afford (L)Sc(CH$_2$SiMe$_3$)$_2$ as a white powder. Storage at room temperature in the solid state or in solution led to decomposition over a period of 24 h. Yield: 0.77 g (62 %). Diffraction quality crystals were grown from a toluene solution at -20 ºC. $^1$H NMR (C$_6$D$_6$, 500 MHz): 7.26 (1 H, t, $^3$J$_{HH}$ = 8 Hz, 4-C$_6$H$_3$), 7.16 (2 H, d, $^3$J$_{HH}$ = 8 Hz, 3,5-C$_6$H$_3$), 3.33 – 3.20 (2 H, br m, H$_2$CMe$_2$), 3.25 and 2.92 (2 H each, t, $^3$J$_{HH}$ = 11 Hz, NCH$_2$CH$_2$N), 2.17 (2 H, s, OCMe$_2$CH$_2$), 1.61 (6 H, s, CMe$_2$), 1.53 and 1.14 (6 H each, d, $^3$J$_{HH}$ = 7 Hz, HCN), 2.17 (2 H, s, OCMe$_2$CH$_2$), 1.61 (6 H, s, CMe$_2$), 1.53 and 1.14 (6 H each, d, $^3$J$_{HH}$ = 7 Hz, HCN), 0.21 (9 H, s, SiMe), -0.21 (2 H, br. s, CH$_2$SiMe$_3$) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 125 MHz): 147.0 (1-C$_6$H$_3$), 137.3 (2,6-C$_6$H$_3$), 129.5 (4-C$_6$H$_3$), 125.2 (3,5-C$_6$H$_3$), 75.9 (CMe$_2$), 54.3 and 52.0 (NCH$_2$CH$_2$N), 28.3 (HCMe$_2$), 26.4 and 24.1 (HCMe$_2$), 4.6 (SiMe) ppm. The NCN, CMe$_2$ and CH$_2$SiMe$_3$ resonances could not be located. Anal. Found (calcd for C$_{27}$H$_{51}$N$_2$OScSi$_2$): C, 62.18 (62.26); H, 8.77 (8.97); N, 5.48 (5.38).

b. in situ preparation from ScCl$_3$(thf)$_3$: At -78 ºC, to a slurry of ScCl$_3$(thf)$_3$ (0.28 g, 0.77 mmol) in hexanes/thf (15 mL/20 mL) was added dropwise a solution of LiCH$_2$SiMe$_3$ (0.29 g, 3.1 mmol) in hexanes (20 mL) to afford a clear, colorless solution. The reaction mixture was stirred at 0 ºC for 2 h
and then a slurry of $[\text{H}_2\text{L}]\text{Cl}$ (0.26 g, 0.77 mmol) in thf (20 mL) was added in one portion to afford a clear, colorless solution. The reaction mixture was stirred for 2 h and then the volatiles were removed \textit{in vacuo} to give a white solid. Extraction into cold (0 ºC) toluene (2 x 10 mL) afforded a clear, pale yellow solution. The volatiles were removed \textit{in vacuo} to afford a white solid. The synthesis of (L)Sc(CH$_2$SiMe$_3$)$_2$ was confirmed by $^1$H NMR spectroscopy. This route was not as clean as the simple protonolysis reaction and required recrystallisation for purification.

2.1.2. Synthesis of (L)Y(CH$_2$SiMe$_3$)$_2$

At 0 ºC, to a solution of Y(CH$_2$SiMe$_3$)$_3$(thf)$_2$ (0.55 g, 1.1 mmol) in hexanes (15 mL) was added dropwise a solution of HL (0.34, 1.1 mmol) in hexanes (10 mL) to afford a clear, pale yellow solution. The reaction mixture was stirred for 1 h to yield a white precipitate which was collected by filtration, washed with hexanes (3 x 5 mL) and dried \textit{in vacuo} to afford (L)Y(CH$_2$SiMe$_3$)$_2$ as a white powder.

Storage at room temperature, both in the solid state and in solution led to decomposition over the course of 24 h. Yield: 0.32 g (51 %). Diffraction quality crystals were grown from a saturated toluene solution at -20 ºC.

$^1$H NMR (C$_6$D$_6$, 500 MHz): 7.27 - 7.02 (3 H, overlapping m, 4-C$_6$H$_3$ and 3,5-C$_6$H$_3$), 3.20 (2 H, t, $^3$J$_{HH}$ = 11 Hz, NCH$_2$CH$_2$N), 3.14 (2 H, sept, $^3$J$_{HH}$ = 7 Hz, HCHMe$_2$), 2.89 (2 H, t, $^3$J$_{HH}$ = 11 Hz, NCH$_2$CH$_2$N), 2.11 (2 H, s, OCMc$_2$C$\text{H}_2$), 1.56 (6 H, s, CMe$_2$), 1.50 and 1.15 (6 H each, d, $^3$J$_{HH}$ = 7, H$_2$Me$_2$), 0.26 (18 H, s, SiMe), -0.65 - 0.96 (2 H, br. m, C$_2$H$_2$SiMe$_3$) ppm.

$^{13}$C{$_{^1}$H} NMR (C$_6$D$_6$, 125 MHz): 215.4 (d, $^1$J$_{YC}$ = 30 Hz, NCN), 146.7 (1-C$_6$H$_3$), 136.8 (2,6-C$_6$H$_3$), 129.7 (4-C$_6$H$_3$) 125.0 (3,5-C$_6$H$_3$), 74.5 (CMe$_2$), 60.8 (OCMe$_2$C$\text{H}_2$), 54.0 and 52.4 (NCH$_2$CH$_2$N), 37.6 ($^1$J$_{YC}$ = 38 Hz, CH$_2$SiMe$_3$), 30.5 (CMe$_2$), 28.4 (HCHMe$_2$), 25.8 and 24.8 (HCHMe$_2$), 4.8 (SiMe). Anal. Found (calcd for C$_{27}$H$_{51}$N$_2$OSi$_2$Y): C, 57.35 (57.42); H, 8.98 (9.10); N 5.03 (4.96).

2.2. Synthesis of mono(L) ate complexes

2.2.1. Synthesis of {1-Li(thf)C(N DippcCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$

To a slurry of ScCl$_3$(thf)$_3$ (1.0 g, 2.8 mmol) in thf (40 mL) at -78 ºC was added dropwise a solution of LiCH$_2$SiMe$_3$ (1.1 g, 1.1 mmol). The reaction mixture was allowed to warm to 0 ºC and stirred for 2 h. To the reaction mixture was added a solution of HL (0.85 g, 2.8 mmol) and it was then stirred for a further 2 h. The volatiles were removed \textit{in vacuo} to yield a white powder. Extraction into toluene (3 x 15 mL) and removal of the volatiles under reduced pressure gave a white powder which was washed with hexanes (3 x 15 mL) and dried once more to afford {1-Li(thf)C(N DippcCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$ as a white solid. Yield: 1.45 g (75 %). $^1$H NMR (C$_6$D$_6$, 600 MHz): 7.08 (1 H, t, $^3$J$_{HH}$ = 8 Hz, 4-C$_6$H$_3$), 6.96 (2 H, d, $^3$J$_{HH}$ = 8 Hz, 3,5-C$_6$H$_3$), 3.13
Synthesis of bis(L) complexes

2.3.1. Synthesis of (L)₂Sc(CH₂SiMe₃)

a. From Sc(CH₂SiMe₃)₃(thf): At 0 °C, to a clear, colorless solution of Sc(CH₂SiMe₃)₃(thf)₂ (0.86 g, 1.9 mmol) in hexanes (20 mL) was added a solution of HL (1.2 g, 3.8 mmol) in hexanes (10 mL). The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 1.9 mmol) in hexanes (20 mL) was added a solution of HL (1.2 g, 3.8 mmol) in hexanes (10 mL). The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 1.5 h. To this reaction mixture was added a solution of Me₂SiCl (0.51 mmol) in toluene (5 mL). The volatiles were removed in vacuo to afford {1-Me₃SiC(NDippCH₂CH₂N)_2}CH₂CM₂O)Sc(CH₂SiMe₃)_3 as a colorless powder. Storage at room temperature in solution resulted in further elimination reactivity or decomposition in the solid state. Yield: 0.27 g (78 %). ¹H NMR (CD₂Cl₂, 500 MHz): 6.99 (1 H, t, ⁴J_HH = 8 Hz, 4-C₆H₄), 6.75 (2 H, d, ⁴J_HH = 8 Hz, 3,5-C₆H₄), 4.58 and 3.35 (2 H each, t, ⁴J_HH = 12 Hz, NCH₂CH₂N), 2.46 (2 H, sept, ⁴J_HH = 7 Hz, HCM₂O), 3.30 (2 H, s, OCM₂CH₂), 1.52 (6 H, s, CMe₂), 0.93 (12 H, d, ⁴J_HH = 7 Hz, HCM₂O), 0.58 (27 H, s, CH₂SiMe₃), 0.16 (6 H, br. s, CH₃SiMe₂), -0.43 (9 H, s, CSiMe₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz): ppm. 174.8 (NCN), 146.3(1-C₆H₄), 132.4 (2,6-C₆H₄), 131.3(4-C₆H₄), 125.2 (3,5-C₆H₄), 73.02 (CM₂O), 64.2 (OCM₂CH₂), 54.7 and 51.5 (NCH₂CH₂N), 31.5 (CM₂O), 28.5 (HCM₂O), 25.6 and 23.3 (HCM₂O), 4.91 (CH₂SiMe₃, and CH₂SiMe₃), 1.48 (CSiMe₃) ppm. Anal. Found (calcld for C₃₅H₇₅N₉O₇ScSi₃): C, 59.89 (59.94); H, 10.41 (10.50); N, 4.14 (4.11).
crystals were grown from a hexanes solution at -20 °C. ¹H NMR (C₆D₆, 500 MHz): 7.27 (2 H, t, 3J_HH = 8 Hz, 4-C₆H₄), 7.26 (4 H, d, 1J_HH = 8 Hz, 3,5-C₆H₄), 3.74 (2 H, d, 3J_HH = 13 Hz, OCMe₂CH₂), 3.32 (2 H, m, HCH₂), 3.25 – 2.28 (10 H, overlapping m, NCH₂CH₂N and HCH₂), 2.56 (2 H, d, 3J_HH = 13 Hz, OCMe₂CH₂), 1.58 1.51 1.21 and 1.16 (6 H each, d, 1J_HH = 7 Hz, HCH₂), 0.87 and 0.60 (6 H each, s, CMe₂), 0.37 (9 H, s, CH₃), -0.33 and -0.72 (1 H each, d, 2J_HH = 11 Hz, CH₃SiMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 125 MHz): 147.8 and 147.1 (2,6-C₆H₄), 138.4 (1-C₆H₄), 128.4 (4-C₆H₄), 124.02 (3,5-C₆H₄), 72.7 (CMe₂) 62.41 (OCMe₂CH₂), 53.3 and 52.7 (HCMe₂ and NCH₂CH₂N), 30.2 (CMe₂), 28.7 (CH₃SiMe₃), 28.3 (CMe₂), 27.6 25.9 25.3 and 25.1 (HCMe₂), 4.7 (SiMe) ppm. The NCN resonance could not be located. Anal. Found (calcd for C₄₂H₆₀N₄O₄ScSi): C, 68.50 (68.63); H, 9.26 (9.46); N, 7.74 (7.62).

b. From (L)₂ScCl: (L)₂ScCl (0.014 g, 0.020 mmol) and LiCH₃SiMe₃ (0.0019 g, 0.020 mmol) were combined in C₆D₆ in a J-Young teflon valve NMR tube. The reaction mixture was heated to 80 °C for 12 h. The formation of (L)₂Sc(CH₃SiMe₃) was confirmed by ¹H NMR spectroscopy.

### 2.3.2. Synthesis of (L)₂Sc(CH₃CMe₂)

At 0 °C, to a clear, colorless solution of Sc(CH₃CMe₂)₃(thf)₀.₆₅ (0.10 g, 0.34 mmol) in hexanes (5 mL) was added a solution of HL (0.15 g, 0.51 mmol) in hexanes (5 mL). The reaction mixture was allowed to warm to room temperature and was stirred at room temperature for 1.5 h at room temperature to afford a clear, colorless solution. The volatiles were removed under reduced pressure to afford (L)₂Sc(CH₃CMe₂) as a white solid. Yield: 0.11 g (47 %). Diffraction quality crystals were grown from a hexanes solution at -20 °C. ¹H NMR (C₆D₆, 500 MHz): 7.30 (2 H, t, 3J_HH = 8 Hz, 4-C₆H₄), 7.18 (4 H, m, 2,6-C₆H₄), 3.92 (2 H, d, 1J_HH = 13 Hz, OCMe₂CH₂), 3.46 (2 H, sept, 1J_HH = 7 Hz, HCH₂), 3.27 (2 H, m, NCH₂CH₂N), 3.11 – 2.87 (6 H, overlapping m, HCH₂ and NCH₂CH₂N), 2.64 (2 H, d, 3J_HH = 13 Hz, OCMe₂CH₂), 1.62 and 1.52 (6 H each, d, 3J_HH = 7 Hz, HCH₂), 1.41 (9 H, s, CMe₃), 1.22 and 1.16 (6 H each, d, 3J_HH = 7 Hz, HCH₂), 0.91 and 0.67 (6 H each, s, CMe₂), 0.50 and 0.37 (1 H each, d, 1J_HH = 12 Hz, CH₃CMe₃) ppm. ¹³C{¹H} NMR (C₆D₆, 500 MHz): 147.9 and 147.1 (2,6-C₆H₄), 138.6 (1-C₆H₄), 124.0 (3,5-C₆H₄), 72.5 (CMe₂), 62.3 (OCMe₂CH₂), 53.3 ad 52.8 (NCH₂CH₂N), 36.9 (Bu), 31.6 (CMe₂), 28.7 and 28.2 (HCH₂), 27.8 (CMe₂), 26.0 25.8 25.5 and 25.1 (HCMe₂) ppm. The resonance for the 4-C₆H₄ C was obscured by the C₆D₆ resonance and the NCN and CH₃CMe₃ resonances could not be located. Anal. Found (calcd for C₄₃H₆₀N₄O₄Sc): C, 71.74 (71.83); H, 9.75 (9.67); N, 7.61 (7.79).

### 2.3.3. Synthesis of (L)₂Y(CH₃SiMe₃)

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To a clear, colorless solution of Y(CH₂SiMe₃)₃(thf)₂ (0.27 g, 0.55 mmol) in hexanes (10 mL) was added a solution of HL (0.33 g, 1.11 mmol) in hexanes (5 mL) to afford a pale yellow solution. The reaction mixture was stirred for 12 h at room temperature and then the volatiles were removed under reduced pressure to yield a pale yellow solid which was washed with hexanes (3 x 5 mL) and dried under reduced pressure to afford (L)₂Y(CH₂SiMe₃) as a white solid. Yield: 0.14 g (33 %). ¹H NMR (C₆D₆, 600 MHz): 7.29 (2 H, t, ³J_HH = 8 Hz, 4-C₆H₃), 7.17 (4 H, m, 3,5-C₆H₃), 3.63 (2 H, d, ³J_HH = 14 Hz, OCMe₂CH₂), 3.38 – 2.85 (12 H, overlapping m, NCH₂CH₂N and HCMε₂), 2.67 (2 H, d, ¹J_HH = 14 Hz, OCMe₂CH₂), 1.57 1.49 and 1.19 (6 H each, d, ¹J_HH = 7 Hz, HCMε₂), 0.87 and 0.79 (6 H each, s, CMe₂), 0.41 (9 H, s, SiMe), -0.48 and -1.04 (1 H each, dd, ¹J_HH = 11 Hz, ¹J_VV = 3 Hz, CH₂SiMe₃) ppm. ¹³C [¹H] NMR (C₆D₆, 125 MHz): 217.9 (d, ¹J_YC = 33 Hz, NCN), 147.6 and 147.2 (2,6-C₆H₃), 137.7 (1-C₆H₃), 128.6 (4-C₆H₃), 124.1 and 124.0 (2,6-C₆H₃), 67.9 and 63.2 (OCMe₂CH₂), 53.2 and 53.0 (NCH₂CH₂N), 31.2 and 28.7 (CMe₂), 28.3 and 28.0 (HCMε₂), 25.9 25.6 25.1 and 25.0 (HCMε₂) 5.0 (SiMe) ppm. The CH₂SiMe₃ resonance could not be located. Satisfactory elemental analysis was not obtained from powdered single crystals and the compound decomposes readily at room temperature.

2.4. Addition/Elimination reactions of bis(L) complexes to form carbon-silicon bonds

2.4.1. Reaction of (L)₂Sc(CH₂SiMe₃) with E-X to form C-Si bonded products

2.4.1.1. Reaction of (L)₂Sc(CH₂SiMe₃) with Me₃Si-Cl to form a C-Si bond and (L)₂ScCl

a. Preparative scale: (L)₂Sc(CH₂SiMe₃) (0.17 g, 0.23 mmol) and Me₃SiCl (29 µL, 0.23 mmol) were combined in C₆D₆ (1 mL) in a J-Young teflon valve NMR tube to afford a clear, colorless solution. After 5 days, colorless crystals had formed and these were isolated by filtration, washed with hexanes (3 x 2 mL) and dried in vacuo to afford (L)₂ScCl as a colorless solid. Yield: 0.071 g (45 %).

Diffraction quality crystals were grown from a saturated C₆D₆ solution. ¹H NMR (C₆D₆, 500 MHz): 7.25 (2 H, t, ³J_HH = 8 Hz, 4-C₆H₃), 7.19 and 7.14 (2 H each, dd, ³J_HH = 8 Hz, ³J_HH = 1 Hz, 3,5-C₆H₃), 3.69 (2 H, d, ³J_HH = 13 Hz, OCMe₂CH₂), 3.59 (2 H, sept, ³J_HH = 7 Hz, HCMε₂), 3.25 – 3.19 (2 H, m, NCH₂CH₂N), 3.11 – 3.03 (4 H, overlapping m, HCMε₂ and NCH₂CH₂N), 2.92 - 2.82 (4 H, m, NCH₂CH₂N), 2.49 (2 H, d, ³J_HH = 13 Hz, OCMe₂CH₂), 1.72 1.60 1.21 and 1.21 (6 H each, d, ³J_HH = 7 Hz, HCMε₂), 0.98 and 0.50 (CMe₂) ppm. ¹³C [¹H] NMR (C₆D₆, 125 MHz): ppm. 215.2 (NCN), 147.8 147.6 and 129.3 (1,2,6-C₆H₃), 128.6 (4-C₆H₃), 124.3 and 124.1 (3,5-C₆H₃), 73.3 (CMe₂), 62.3 (OCMe₂CH₂), 52.3 and 52.6 (NCH₂NCH₂), 29.4 (CMe₂), 28.8 and 28.2 (HCMε₂), 27.2 (CMe₂), 25.8 25.4 and 25.0 (HCMε₂) ppm. Anal. Found (calcd for C₃₈H₅₉Cl₄O₂Sc): C, 67.16 (66.79); H, 8.91 (8.56); N, 7.85 (8.20).
b. NMR tube scale: To a solution of \((\text{L})_2\text{Sc(CH}_2\text{SiMe}_3)\) (0.024 g, 0.032 mmol) in \(\text{C}_6\text{D}_6\) (1 mL) in a J-Young teflon valve NMR tube was added \(\text{Me}_3\text{SiCl}\) (4.2 µL, 0.032 mmol) to afford a clear, colorless solution. Over the course of 5 days the reaction was monitored by \(^1\text{H}\) NMR spectroscopy and the formation of \((\text{L})_2\text{ScCl}\) and \(\text{Me}_3\text{SiCH}_2\text{SiMe}_3\) was observed.

2.4.1.2. Reaction of \((\text{L})_2\text{Sc(CH}_2\text{SiMe}_3)\) with E-X to form a C-Si bond and \((\text{L})_2\text{ScI}\)

NMR tube scale \(\text{Me}_3\text{SiI}\): To a solution of \((\text{L})_2\text{Sc(CH}_2\text{SiMe}_3)\) (0.066 g, 0.090 mmol) in \(\text{C}_6\text{D}_6\) (1 mL) in a J-Young teflon valve NMR tube was added \(\text{Me}_3\text{SiI}\) (12.8 µL, 0.090 mmol) to afford a clear, colorless solution. Over the course of 5 days the reaction was monitored by \(^1\text{H}\) NMR spectroscopy and the formation of \((\text{L})_2\text{ScI}\) was observed. The volatiles were distilled off and were shown to contain \(\text{Me}_3\text{SiCH}_2\text{SiMe}_3\) by \(^1\text{H}\) NMR spectroscopy.

2.4.1.3. Reaction of \((\text{L})_2\text{Sc(CH}_2\text{CMe}_3)\) with E-X to form C-Si bonded products

\(\text{Me}_3\text{SiCl}\): To a solution of \((\text{L})_2\text{Sc(CH}_2\text{CMe}_3)\) (0.012 g, 0.017 mmol) in \(\text{C}_6\text{D}_6\) (1 mL) in a J-Young teflon valve NMR tube was added \(\text{Me}_3\text{SiCl}\) (2.1 µL, 0.017 mmol) to afford a clear, colorless solution. Over the course of 10 days the reaction was monitored by \(^1\text{H}\) NMR spectroscopy and the formation of \((\text{L})_2\text{ScCl}\) and \(\text{Me}_3\text{SiCH}_2\text{CMe}_3\).

\[^1\text{H}\] NMR: \((\text{C}_6\text{D}_6, 400 \text{ MHz, } 298 \text{ K})\): 1.26 (9 H, s, \text{CMe}_3), 0.14 (9 H, s, \text{SiMe}), 0.07 (2 H, s, \text{CH}_2) \text{ ppm}.

2.4.2. Thermolytic elimination reactions of mono(L) 'ate' complexes to form carbon-silicon and carbon-carbon bonds

2.4.2.1. Reaction of \{\text{1-Li(thf)}C(\text{NDippCH}_2\text{CH}_2\text{N})\}CH_2\text{CMe}_2\text{O})\text{Sc(CH}_2\text{SiMe}_3)\text{, with E-X to give C-C bond formation}

\(\text{Ph}_3\text{CCl}\): To a solution of \{\text{1-Li(thf)}C(\text{NDippCH}_2\text{CH}_2\text{N})\}CH_2\text{CMe}_2\text{O})\text{Sc(CH}_2\text{SiMe}_3)\text{, (0.11 g, 0.16 mmol) in toluene (2 mL) was added a solution of Ph}_3\text{CCl (0.045 g 0.16 mmol) in toluene (1 mL) to immediately afford a pale orange solution. The reaction mixture was allowed to stir for 1 h during which time a white precipitate formed. No NMR evidence for any intermediate was observed. The solution was filtered off and the precipitate was washed with toluene (3 x 1 mL). The combined washings were dried in vacuo to afford an orange solid. \(^1\text{H}\) NMR spectral analysis showed this to be a combination of \((\text{L})\text{Sc(CH}_2\text{SiMe}_3)\text{, and Ph}_3\text{CCH}_2\text{SiMe}_3\). Ei-MS: \(m/z\): 330.2 \([\text{Ph}_3\text{CCH}_2\text{SiMe}_3]^+\) (25 %), 315.2 \([\text{Ph}_3\text{CCH}_2\text{SiMe}_3-\text{Me}]^+\) (6 %), 243.1 \([\text{Ph}_3\text{CCH}_2\text{SiMe}_3-\text{CH}_2\text{SiMe}_3]^-\) (100 %).
2.4.2.2. Thermolysis of \{1-Me_{2}SiC(NDippCH_{2}CH_{2}N)\}CH_{2}CMe_{2}O)Sc(\text{CH}_{2}\text{SiMe}_{3})_{3}\ to give C-Si bond formation

\{1-Me_{2}SiC(NDippCH_{2}CH_{2}N)\}CH_{2}CMe_{2}O)Sc(\text{CH}_{2}\text{SiMe}_{3})_{3}\ (0.021 \text{ g}, 0.031 \text{ mmol}) was dissolved in C_{6}D_{6} (1 \text{ mL}) in a J-Young teflon valve NMR tube. The reaction mixture was kept at room temperature for 2 h, after which time the \(^1\text{H}\) NMR spectrum contained resonances for Me_{2}SiCH_{2}SiMe_{3}, (L)Sc(\text{CH}_{2}\text{SiMe}_{3})_{2}\ (~0.9 \text{ equivalents}) and (L)_{2}Sc(\text{CH}_{2}\text{SiMe}_{3}) (~0.1 \text{ equivalents}).

2.4.3. Addition reactions of bis(L)M complexes with E-X to form other carbon-heteroatom bonded products

2.4.3.1. C-P: Reaction of (L)_{2}Sc(\text{CH}_{2}\text{SiMe}_{3}) with Ph_{3}PCl to form a C-P bond and (L)_{2}ScCl

Ph_{3}PCl: To a solution of (L)_{2}Sc(\text{CH}_{2}\text{SiMe}_{3}) (0.051 \text{ g}, 0.069 \text{ mmol}) in C_{6}D_{6} (1 \text{ mL}) in a J-Young teflon valve NMR tube was added Ph_{3}PCl (12.3 \mu \text{L}, 0.069 \text{ mmol}) to afford a clear, colorless solution. Over the course of 5 days the reaction was monitored by \(^1\text{H}\) NMR spectroscopy and the formation of (L)_{2}ScCl and Ph_{2}PCH_{2}SiMe_{3} in 95 \% yield was observed. \(^1\text{H}\) NMR (C_{6}D_{6}, 500 MHz, 298 K): 7.45 (12 \text{ H}, m, -C_{6}H_{4}), 0.36 (\text{CH}_{2}\text{SiMe}_{3}) \text{ ppm}. EI-MS: m/z: 272.1 [Ph_{2}PCH_{2}SiMe_{3}]^{+} (100 \%).

2.4.3.2. C-Sn: Reaction of (L)_{2}Sc(\text{CH}_{2}\text{SiMe}_{3}) with tris(hydrocarbyl) tin chlorides to form a C-Sn bond and (L)_{2}ScCl

a. "BuSnCl: To a solution of (L)_{2}Sc(\text{CH}_{2}\text{SiMe}_{3}) (0.037 \text{ g}, 0.051 \text{ mmol}) in C_{6}D_{6} (1 \text{ mL}) in a J-Young teflon valve NMR tube was added "BuSnCl (14 \mu \text{L}, 0.051 \text{ mmol}) to afford a clear, colorless solution. Over the course of 17 h the reaction was monitored by \(^1\text{H}\) NMR spectroscopy and the formation of 1 equivalent of (L)_{2}ScCl and 1 equivalent of "BuSnCH_{2}SiMe_{3} were observed. \(^1\text{H}\) NMR (C_{6}D_{6}, 500 MHz, 298 K): 1.67 (6 \text{ H}, m, (CH_{2})_{3}CH_{3}), 1.49 (6 \text{ H}, m, (CH_{2})_{2}CH_{3}), 1.06 - 0.94 (36 \text{ H}, overlapping m, 4-(CH_{2})_{4}CH_{3} and 1-(CH_{2})_{4}CH_{3}), 0.24 (9 \text{ H}, s, SiMe), -0.13 (2 \text{ H}, s, \text{CH}_{2}\text{SiMe}_{3}) \text{ ppm.} \(^{13}\text{C}\)\{\(^{1}\text{H}\)\} NMR (C_{6}D_{6}, 125 MHz): 29.7 ((2,3-(CH_{2})_{3}CH_{3}), 27.9 (2,3-(CH_{2})_{3}CH_{3}), 14.0 (4-(CH_{2})_{3}CH_{3}), 10.7 (1-(CH_{2})_{3}CH_{3}), \text{J}_{119\text{Sn}} = 162 \text{ Hz}, \text{J}_{117\text{Sn}} = 155 \text{ Hz}), 1.9 (\text{SiMe}), -7.1 (\text{CH}_{2}\text{SiMe}_{3}) \text{ ppm. EI-MS: m/z: 363.1 ["BuSnCH}_{2}\text{SiMe}_{3}^{+}] (5 \%), 321.1 ["BuSnCH}_{2}\text{SiMe}_{3}^{3}{\text{Bu}}^{+} (100 \%), 264.0 ["BuSnCH}_{2}\text{SiMe}_{3}^{2}{\text{Bu}}^{+} (18 \%), 207.0 ["BuSnCH}_{2}\text{SiMe}_{3}^{3}{\text{Bu}}^{+} (66 \%), 102.0 ["BuSnCH}_{2}\text{SiMe}_{3}^{2}{\text{Bu}}^{+} (18 \%)

b. Ph_{3}SnCl: (L)_{2}Sc(\text{CH}_{2}\text{SiMe}_{3}) (0.019 \text{ g}, 0.026 \text{ mmol}) and Ph_{3}SnCl (0.010 \text{ g}, 0.026 \text{ mmol}) were combined in C_{6}D_{6} (1 \text{ mL}) in a J-Young teflon valve NMR tube. Over the course of 5 days the reaction
was monitored by $^1$H NMR spectroscopy and the formation of (L)$_2$ScCl and Ph$_3$SnCH$_2$SiMe$_3$ were observed. $^1$H NMR (C$_6$D$_6$, 500 MHz, 298 K): 7.62 – 7.60 (3 H, overlapping m, C$_6$H$_3$), 7.21 – 7.13 (overlapping m, C$_6$H$_4$), 0.36 (2 H, s, CH$_2$SiMe$_3$), 0.01 (9 H, s, SiMe) ppm. Integration of the aromatic protons could not be performed accurately due to overlap with both the residual protio solvent and (L)$_2$ScCl resonances. $^{13}$C {$^1$H} NMR (C$_6$D$_6$, 125 MHz, 298 K): 137.3 and 128.7 (C$_6$H$_3$), 1.7 (CH$_2$SiMe$_3$), -5.0 (SiMe) ppm. The remaining –C$_6$H$_4$ resonances are obscured by residual protio solvent and (L)$_2$ScCl resonances. EI-MS: m/z: 423.1 [Ph$_3$SnCH$_2$SiMe$_3$-Me]$^+$ (10 %), 361.1 [Ph$_3$SnCH$_2$SiMe$_3$-Ph]$^+$ (14 %), 351.0 [Ph$_3$SnCH$_2$SiMe$_3$-CH$_2$SiMe$_3$]$^+$ (100 %).

2.4.3.3. C-I: Reaction of (L)$_2$Sc(CH$_2$SiMe$_3$)$_2$ with C$_6$F$_3$I to form a C-I bond and (L)$_2$Sc(C$_6$F$_3$)$_2$

a. **Preparative scale** (L)$_2$Sc(CH$_2$SiMe$_3$)$_2$ (0.15 g, 0.21 mmol) and C$_6$F$_3$I (27.6 µL, 0.21 mmol) were combined in C$_6$D$_6$ (1 mL) in a J-Young teflon valve NMR tube. Immediately, a colorless solid precipitated from the reaction mixture. This solid was washed with hexanes (3 x 1 mL) and the volatiles were removed *in vacuo* to afford (L)$_2$Sc(C$_6$F$_3$)$_2$ as a colorless solid. Yield: 0.15 g, (86 %). The organic product Me$_3$SiCH$_2$I, identified in the NMR tube reaction below, is unstable and decomposes over time in solution to a dark-colored material. Diffraction quality crystals of (L)$_2$Sc(C$_6$F$_3$)$_2$ were grown from a toluene solution at -20 ºC. $^1$H NMR (C$_6$D$_6$, 500 MHz): 7.18 (2 H, t, $^3$J$_{HH}$ = 8 Hz, 4-C$_6$H$_3$), 7.13 and 6.92 (2 H each, dd, $^3$J$_{HH}$ = 8 Hz, $^4$J$_{HH}$ = 1 Hz, 2,6-C$_6$H$_3$), 3.41 (2 H, d, $^3$J$_{HH}$ = 13 Hz, OCM$_2$C$_2$H$_3$), 3.25 – 2.91 (12 H, overlapping m, NCH$_2$CH$_2$N and HCM$_2$), 2.80 (2 H, d, $^3$J$_{HH}$ = 13 Hz, OCM$_2$C$_2$H$_3$), 1.63 (6 H, s, CMe$_2$), 1.60 and 1.16 (6 H each, d, $^3$J$_{HH}$ = 7 Hz, HCM$_2$), 1.11 (6 H, s, CMe$_2$), 0.99 and 0.94 (6 H each, d, $^3$J$_{HH}$ = 7 Hz, HCM$_2$) ppm. $^{13}$C {$^1$H} NMR (C$_6$D$_6$, 125 MHz): 215.3 (NCN), 147.4 (3,5-C$_6$H$_3$), 146.9 (1-C$_6$H$_3$), 137.7 (4-C$_6$H$_3$), 124.4 and 123.7 (2,6-C$_6$H$_3$), 73.6 (CM$_2$), 62.5 (OCMeC$_2$H$_3$), 53.0 and 52.8 (NCH$_2$CH$_2$N), 28.6 (HCM$_2$), 28.2 (CM$_2$), 28.1 (HCM$_2$), 26.0, 25.5, 24.9 and 23.1 (HCM$_2$) ppm. Anal. Found (calcd for C$_{48}$H$_{33}$F$_3$N$_4$O$_2$Sc): C, 64.70 (64.85); H, 7.07 (7.17); N, 6.78 (6.88).

b. **NMR tube scale C$_6$F$_3$I**: To a solution of (L)$_2$Sc(CH$_2$SiMe$_3$)$_2$ (0.012 g, 0.016 mmol) in C$_6$D$_6$ (1 mL) in a J-Young teflon valve NMR tube was added C$_6$F$_3$I (2.2 µL, 0.016 mmol) to afford a clear, colorless solution. $^1$H NMR spectroscopy indicated the formation of (L)$_2$Sc(C$_6$F$_3$)$_2$ and Me$_3$SiCH$_2$I. Over the course of 24 h, the solution darkened in color and became dark pink. $^1$H NMR spectroscopy showed the presence of (L)$_2$Sc(C$_6$F$_3$)$_2$ and Me$_3$SiCH$_2$I; the latter decomposes slowly in solution over time, darkening the solution.

3. **Crystalllographic Details**
Crystals were mounted in an inert oil and X-ray crystallographic data were collected at 150 K on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo-Kα radiation (\( \lambda = 0.71073 \) Å), at 170 K on an Oxford Diffraction Xcalibur diffractometer using graphite monochromated Mo-Kα radiation, or at 100 K on an Oxford Diffraction Supernova diffractometer using mirror monochromated Cu-Kα radiation (\( \lambda = 1.54178 \) Å).\(^5\) Using the WinGX suite of programs, all structures were solved using direct methods and refined using a full-matrix least square refinement on \(|F|^2\) using SHELXL\(^9\).\(^7\) Unless otherwise stated, all non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed using a riding model and refined with fixed isotropic displacement parameters.\(^5\) Complex neutral-atom scattering factors were used.\(^5\) Refinement proceeded to give the residuals shown in Table 2.
**Table 2.** Selected experimental crystallographic data for a) [(L)ScR$_2$]$_2$, b) (L$_4$)ScR$_3$, c) (L)$_2$ScR , d) (L)$_2$ScCl, and e) (L)$_2$Sc(C$_8$F$_2$).

<table>
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<th>Crystal data</th>
<th>(L)ScR$_2$</th>
<th>(L$_4$)ScR$_3$</th>
<th>(L)$_2$ScR</th>
<th>(L)$_2$ScCl</th>
<th>(L)$_2$Sc(C$_8$F$_2$)</th>
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<tr>
<td>Chemical formula</td>
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<td>C$<em>{42}$H$</em>{49}$N$_2$O$_5$Sc$_2$Si</td>
<td>C$<em>{38}$H$</em>{58}$ClN$_2$O$_5$Sc</td>
<td>C$<em>{44}$H$</em>{58}$FeN$_2$O$_5$Sc</td>
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<td>Orthorhombic, $C222_1$</td>
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<td>150</td>
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<td>100</td>
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<td>90, 90, 90</td>
<td>90, 90, 90</td>
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<td>Mo $K\alpha$</td>
<td>Mo $K\alpha$</td>
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<td>Bruker SMART APEX CCD area detector</td>
<td>Xcalibur, Eos diffractometer</td>
<td>Xcalibur, Eos diffractometer</td>
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<td>0.0(2)</td>
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References

6 Weiss, C. J.; Marks, T. J. Dalton Trans. 2010, 39, 6576.
18 Marçalo, J.; De Matos, A. P. Polyhedron 1989, 8, 2431.
35 Deacon, G. B.; Forsyth, C. M. Organometallics 2003, 22, 1349.
38 Hayes, P. G.; Piers, W. E.; Parvez, M. Organometallics 2005, 24, 1173.
53 International Tables for Crystallography Dordrecht, 1992; Vol. C.