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

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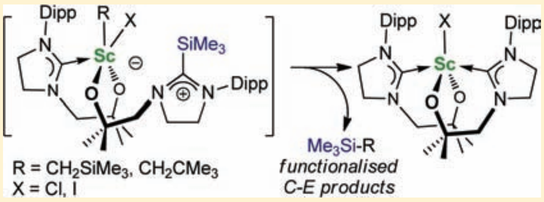
S Supporting Information



ABSTRACT: Two functional groups can be delivered at once to organo-rare earth complexes, (L)MR$_2$ and (L)$_2$MR (M = Sc, Y; L = ({1-C(NDipp-CH$_2$CH$_2$N)}CH$_2$CMe$_2$O), Dipp = 2,6-^{i}Pr$_2$-C$_6$H$_3$; R = CH$_2$SiMe$_3$, CH$_2$CMe$_3$), via the addition of E−X across the metal−carbene bond to form a zwitterionic imidazolinium−metal complex, (L^E)MR$_2$X, where L^E = {1-EC(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O, E is a p-block functional group such as SiR$_3$, PR$_2$, or SnR$_3$, and X is a halide. The "ate" complex (L^{Li})ScR$_3$ is readily accessible and is best described as a Li carbene adduct, ({1-Li(THF)C(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$, since structural characterization shows the alkoxide 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, (L^E)ScR$_3$ (E = SiMe$_3$ or CPh$_3$). 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 re-forming the inorganic metal carbene (L)MR(X) or (L)$_2$MX complex, respectively. Warming the tris(alkyl) complexes (L^E)MR$_3$ forms organic products arising from C−C or C−Si bond formation, which appears to proceed via the same elimination route. Treatment of (L)$_2$Sc(CH$_2$SiMe$_3$) with iodopentafluorobenzene results in the "reverse sense" addition, which upon thermolysis forms the metal aryl complex (L)$_2$Sc(C$_6$F$_5$) and releases the iodoalkane Me$_3$SiCH$_2$I, again facilitated by the reversible functionalization of the N-heterocyclic carbene 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 catalyzed by many metal complexes from across the periodic table, via various reaction types.[1] 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.[2] For example, the first example of methane activation was observed in the reaction between Cp*$_2$YCH$_3$ (Cp* = C$_5$Me$_5$) and ^{13}CH$_4$, which resulted in the interchange of labeled Y-^{13}CH$_3$ and unlabeled Y-^{12}CH$_3$ groups.[3] The methane interconversion reactions in these systems are nonproductive because the H atom always resides in the β position in the four-center σ-bond metathesis transition state. However, Tilley's group has demonstrated that silicon can take this β position, and they used this to generate complexes capable of catalytic carbon−silicon bond formation: the reaction of CH$_4$ with Ph$_2$SiH$_2$ in the presence of catalytic (10%) amounts of Cp*$_2$ScCH$_3$ affords Ph$_2$MeSiH and H$_2$ (Cp* = C$_5$Me$_5$). 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.[4] While other Cp*$_2$LnR alkyl complexes exhibit interesting hydrocarbon chemistry, such as β-carbon elimination from Cp*$_2$Sm(CH$_2$CMe$_3$) to form the bridging planar trimethylenemethane dianion in {Cp*$_2$Sm}$_2$(μ-η^3:η^3-C(CH$_2$)$_3$),[5] 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 catalyzes the controlled addition of H$_2$ and a main-group element functional group (amine, phosphine, thiol, alcohol) across an unsaturated C−C bond,[6] 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.[7] 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*-metalated complexes, and

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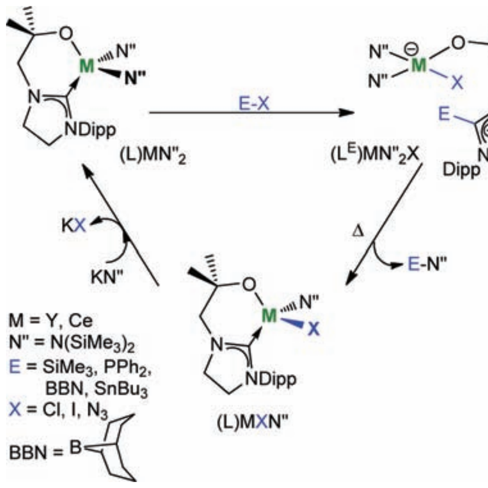
Scheme 1. Addition−Elimination Cycles of Reactivity for d^0 Metal Carbene Complexes with E−X



Teuben's group reported that $Cp^*_2Y(\eta^2\text{-}C,N\text{-}NC_5H_4)$ is formed from the hydride $[Cp^*_2YH]_2$ by the selective metalation of pyridine.[8] The hydride also metalates other arenes. The addition of a further equivalent of pyridine forms the adduct $Cp^*_2Y(\eta^1\text{-}2\text{-}NC_5H_4)(NC_5H_5NC_5H_5)$, which on heating first forms the nonaromatic C−C coupled product $Cp^*_2Y\{\kappa^1\text{-}2,2'\text{-}NC_5H_5(2\text{-}NC_5H_4)\}$ by insertion and 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 Sc^{III} chemistry in which two pyridine ligands were C−C coupled to form a ligated de-aromatized bipyridine[9] in a mechanism also proposed to occur via σ-bond metathesis chemistry, since other oxidation states are not generally accessible for group 3 metals.[10]

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 (NHC) as a reactive donor ligand.[11] 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 M^n/M^{n+2} 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 = SiR_3, BR_2, PR_2, SnR_3; X = Cl, N_3) to $(L)MN''_2$ (M = Y, Ce; L = $\{1\text{-}C(NDippCH_2CH_2N)\}CH_2CMe_2O$) to afford $(L^E)MN''_2X$ (L^E = $\{1\text{-}EC(NDippCH_2CH_2N)\}CH_2CMe_2$, Dipp = 2,6-^{i}Pr$_2$-$C_6H_3$), followed by thermally induced elimination of E−N″, and a final salt metathesis step to regenerate $(L)MN''_2$.

A small but rising number of examples of non-innocent behavior of the imidazolinium NHC unit are being reported, and these instances include reactions of early transition metal and f-block NHC 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-^{t}Bu-C_6H_2O)CH_2CH_2(3,5-^{t}Bu-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 behavior and converting the carbene C to an sp^3-hybridized carbanion, 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 imidazolium 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 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]

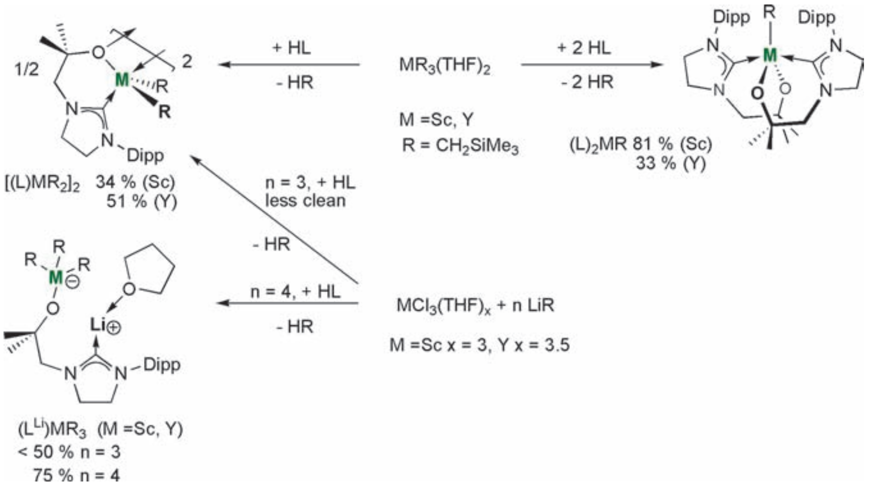
Aware of the absence of two-electron redox reactivity for the rare earth metals, the clean and reversible amido functionalization chemistry elucidated in Scheme 1, and the potentially useful hydrocarbon reactivity that low-coordinate f-block complexes show, we have sought to extend the addition−elimination 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 (CH_2SiMe_3) and neopentyl (Np = CH_2CMe_3) were chosen as targets with which to study the NHC labilization chemistry; both mono- and bis(ligand) compounds of the rare earth Y^{III} and Sc^{III} cations are accessible using these anions. The mono(carbene) alkyl complexes $[(L)MR_2]_2$ (M = Sc or Y, R = CH_2SiMe_3) can be made readily from the thermally sensitive tris(alkyl) complexes by a protonolysis reaction between $MR_3(THF)_2$ and HL in hexanes or hexanes/THF at 0 °C and isolated in 62% (Sc) or 51% (Y) yield. The preparation of the same complexes from an *in situ* reaction of $MCl_3(THF)_n$ (n = 3, Sc; n = 3.5, Y) and 3 equiv of LiR is less clean since the "ate" complex $(L^{Li})MR_3$ forms more readily than the neutral complex, so extra purification steps are required.[17] The "ate" complex can be made specifically from treatment of $MCl_3(THF)_n$ with 4 equiv of LiR and 1 equiv of HL (Scheme 2). The alkyl complexes $[(L)MR_2]_2$ are dimeric, at least in the solid state, and show much lower air - and thermal stability than the heterobimetallic "ate" complexes, and the Sc complexes are much more readily isolated than the Y complexes, presumably due to the greater degree of steric protection afforded by the ligands to Sc. The three complexes $[(L)ScR_2]_2$, $[(L)YR_2]_2$, and $(L^{Li})MR_3$ have all been structurally characterized by single-crystal X-ray diffraction techniques. The structures are discussed below.

The bis(carbene) alkyls $(L)_2MR$ (M = Sc or Y, R = CH_2SiMe_3) can also be made from the tris(alkyl) complexes $MR_3(THF)_2$ by

Scheme 2. Syntheses of Rare Earth Metal Carbene Alkyl Complexes

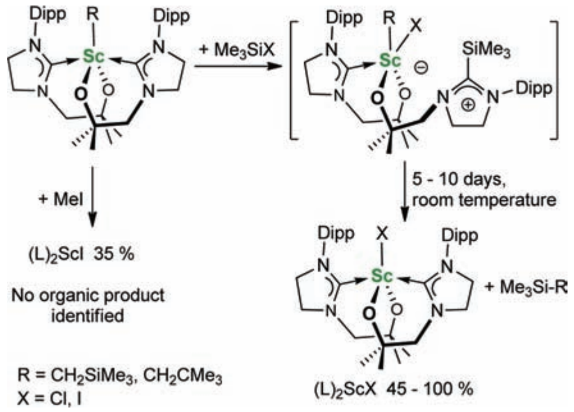


treatment with 2 equiv of the proligand HL in hexanes (Sc) or toluene (Y) at 0 °C. All reaction mixtures were stirred at room temperature before the volatiles were removed *in vacuo* to give the final products in 33% ((L)$_2$YR) or 81% ((L)$_2$ScR) yield (Scheme 1). These complexes are significantly more thermally stable than the mono(L) complexes and have thus been used for the majority of reactivity studies described below. The complex (L)$_2$ScR can be heated to 80 °C in C$_6$D$_6$ without noticeable signs of decomposition. The ^{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)$_2$ScR, four doublets define the $\underline{\mathrm{CHMe_2}}$ protons of the Dipp groups, and two singlets appear for the CMe$_2$ alkoxy arm protons. The $\underline{\mathrm{CH_2}}$SiMe$_3$ alkyl resonances show geminal coupling ($^2J_{HH}$ = 11 Hz) and appear as two doublets, implying the restricted rotation of the scandium alkyl Sc−CH$_2$SiMe$_3$ bond. In the analogous (L)$_2$YR, a doublet of doublets represents the $\underline{\mathrm{CH_2}}$SiMe$_3$ protons due to the coupling to yttrium ($^1J_{YH}$ = 3 Hz) in addition to the geminal coupling of the protons ($^2J_{HH}$ = 11 Hz). The synthesis and characterization of the neopentyl complex (L)$_2$ScR (R = CH$_2$CMe$_3$) has also been carried out successfully in 47% yield; details are included in the Supporting Information.

Addition−Elimination Reactions of Metal Carbene Alkyl Complexes To Form Carbon−Silicon and Carbon−Carbon Bonds. 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 Supporting Information.

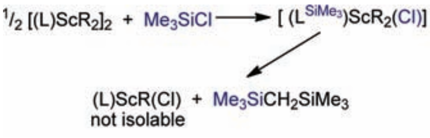
Reactions of (L)$_2$Sc(CH$_2$SiMe$_3$) and (L)$_2$Sc(CH$_2$CMe$_3$) with Halosilanes and Haloalkanes: C−Si Bond Formation. Treatment of the bis(ligand) Sc neosilyl or neopentyl complex (L)$_2$ScR with 1 equiv of trimethylsilyl chloride or iodide in benzene results in the formation of a clear, colorless solution which slowly (over 5 days for R = CH$_2$SiMe$_3$ and 10 days for R = CH$_2$CMe$_3$) at room temperature forms a clean mixture of (L)$_2$ScCl and the product of C−Si bond formation, Me$_3$SiCH$_2$SiMe$_3$ or Me$_3$SiCH$_2$CMe$_3$, 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 5 day reaction period, an unstirred reaction between (L)$_2$ScR (R = CH$_2$SiMe$_3$) and Me$_3$SiCl had deposited single crystals of the Sc product (L)$_2$ScCl which were suitable for a single-crystal structural analysis; details are given below.

Scheme 3. Formation of C−Si Bonds from Addition of Halosilanes to d^0 Metal Carbene Complexes



In an effort to extend C−Si bond formation to C−C bond formation, we carried out the reactions of (L)$_2$MR (M = Sc or Y, R = CH$_2$SiMe$_3$ or CH$_2$CMe$_3$) with a number of alkyl halides (MeI, ^{i}PrCl, ^{i}PrI, ^{t}BuI, Ph$_3$CCl, CH$_2$CHCH$_2$Cl, BnBr, Me$_3$SiCH$_2$Cl) and aryl halides (PhCl, PhI, C$_6$F$_5$I). In a typical reaction, an equimolar quantity of each reagent was combined in a J-Young Teflon valve NMR tube in C$_6$D$_6$ (0.5 mL). The ^{1}H NMR spectrum was recorded immediately and then again after the reaction mixture had been heated to 80 °C for 16 h. In all but the tube containing (L)$_2$Sc(CH$_2$SiMe$_3$) and MeI or C$_6$F$_5$I (see below), no reaction occurred. In the reaction with MeI, no reaction was observed until the mixture was heated; after 2 h at 80 °C the scandium iodide inorganic product $(L)_2ScI$ was isolated in 35% yield, but no C−C bonded organic product $H_3C-CH_2SiMe_3$ was observed, suggesting decomposition of the CH_3I had occurred. The same outcome was observed in the presence or absence of daylight (where MeI is known to liberate free I_2), and MeI is thermally stable up to 270 °C. When the reaction was carried out with an excess of MeI, the solution became red-brown in color due to the formation of I_2. No haloalkane Me_3SiCH_2I was observed in the reaction mixture, a byproduct which might be expected from a reaction with I_2. X-ray-quality single crystals of $(L)_2ScI$ were grown from a toluene solution of this reaction mixture at room temperature, allowing us to confirm its structure; see below and the Supporting Information 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 C_6F_5I, a formally reverse sense addition across the $M-C_{carbene}$ bond and subsequent C−I bond formation occur, i.e., $(L)_2Sc(C_6F_5)$ and Me_3SiCH_2I are the products. This is discussed below.

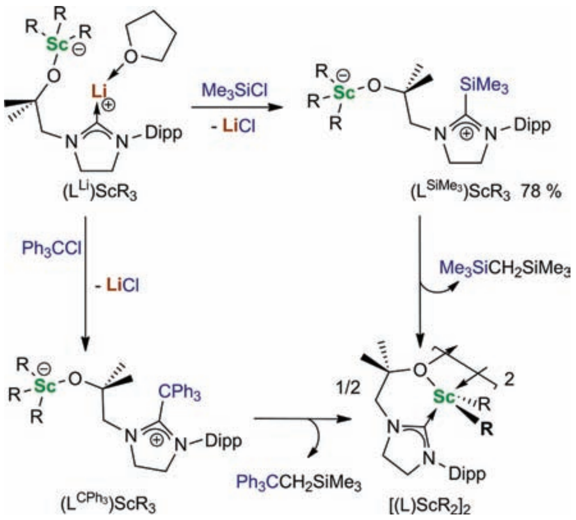
Reaction of $[(L)Sc(CH_2SiMe_3)_2]_2$ with Halosilanes and Haloalkanes: C−Si and C−C Bond Formation. The mono(ligand) neosilyl complex $[(L)ScR_2]_2$ ($R = CH_2SiMe_3$) reacts much more quickly than the bis(ligand) complex with 1 equiv of trimethylsilyl chloride in benzene to form a clear, colorless solution (over 3 h at 25 °C) which contains the product of C−Si bond formation, $Me_3SiCH_2SiMe_3$ (eq 1).



(1)

As before, the most reasonable mechanism for this reactivity involves the initial addition across the $M-C_{carbene}$ bond to form the quaternized NHC complex $(L^{SiMe_3})ScR_2(Cl)$, which decomposes at room temperature, cleanly eliminating $Me_3SiCH_2SiMe_3$. If this mechanism is occurring, then the scandium-containing byproduct should be $(L)ScR(Cl)$, but it is not observed. In the analogous amide chemistry, the product $(L)MN''Cl$ was usually observed to redistribute ligands to form equimolar $(L)MN''_2$ and $(L)MCl_2$. Here, neither $(L)ScR(Cl)$ nor $[(L)ScR_2]_2$ 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 $[(L)MR_2]_2$



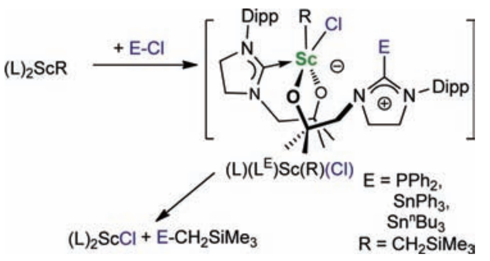
The heterobimetallic ScLi compound $(L^{Li})ScR_3$ allows another route to the introduction of a functional group via metathetical displacement of the lithium cation. Thus, treatment with either trimethylsilyl chloride or triphenylmethyl chloride at room temperature affords a colorless precipitate of lithium chloride and the 2-silylated or 2-alkylated imidazolinium scandium complex $(L^{SiMe_3})ScR_3$ or $(L^{CPh_3})ScR_3$, respectively after 1 or 2 h (Scheme 4). If the mixture is kept at 0 °C, the silylated imidazolinium complex $(L^{SiMe_3})ScR_3$ is isolable as a colorless powder in 78% yield, and it 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 Me_3SiCl. The increased stability may arise from the greater steric protection of the scandium center by the presence of three CH_2SiMe_3 ligands rather than two neosilyl ligands and one chloride ligand, which has a lesser steric demand.[18] Upon warming to room temperature, the isolated powder of $(L^{SiMe_3})ScR_3$ decomposes in the solid state, but if redissolved in toluene, it cleanly undergoes elimination chemistry: by integration of the ^1H NMR spectrum, ~0.9 equiv of the anticipated $[(L)ScR_2]_2$ was formed. A small amount of $(L)_2ScR$ (~0.1 equiv) was also observed, presumably as a result of ligand redistribution to this more stable product. Heating a toluene solution of $(L^{CPh_3})ScR_3$ results similarly in the straightforward spontaneous thermal elimination of $Ph_3C-CH_2SiMe_3$ to regenerate $[(L)ScR_2]_2$. This represents a new way to achieve carbon−carbon bond formation from a rare-earth complex. From the reaction mixture that formed $[(L)ScR_2]_2$ and $Ph_3C-CH_2SiMe_3$, 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 Ph_3C-Cl is very weak, estimated as 280 kJ mol^{-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 Ph_3C-X cleavage chemistry. This observation again supports the assignment of a general addition−elimination mechanism for the reactions. No reaction was observed between $(L^{Li})ScR_3$ and simpler alkyl or aryl halides such as ^iPrCl, ^iPrI, ^tBuI, $PhCH_2Br$, 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.

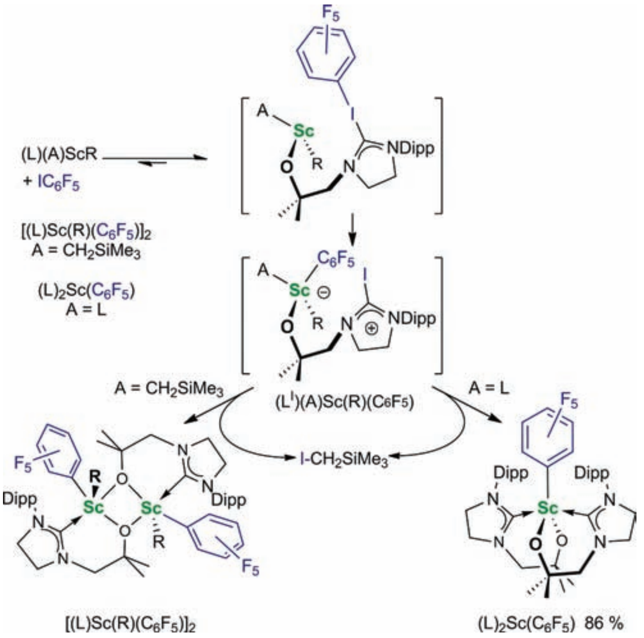
Halophosphines and Stannanes: C−P and C−Sn Bond Formation. The reaction of $[(L)ScR_2]_2$ ($R = CH_2SiMe_3$) at room temperature in C_6D_6 with 1 equiv of $^nBu_3SnCl$, Ph_3SnCl, or Ph_2PCl resulted in C−Sn and C−P bond formation to yield $^nBu_3SnCH_2SiMe_3$, $Ph_3SnCH_2SiMe_3$, and $Ph_2PCH_2SiMe_3$, 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

Scheme 5. Formation of C−Heteroatom Bonds from the Addition of Halogenated p-Block Reagents to $(L)_2ScR$ ($R = CH_2SiMe_3$)



intermediate imidazolinium complexes are observed by NMR spectroscopy, despite the reaction to form the P−C bond proceeding over the course of 5 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 $^nBu_3SnCH_2SiMe_3$ proceeds quantitatively over 17 h, but the formation of $Ph_3SnCH_2SiMe_3$ take up to 5 days to reach completion. The $^nBu_3SnCH_2SiMe_3$ product was identified by both EI-MS ($m/z = 363.1$ $[M-Me]^+$) and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance for the methylene ^{n}Bu carbons of $^nBu_3SnCH_2SiMe_3$ occurs at 10.7 ppm, and coupling to the NMR-active ^{119}Sn and ^{117}Sn isotopes was visible as tin satellites ($^2J_{^{119}SnC} = 162$ Hz, $^2J_{^{117}SnC} = 155$ 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 $[(L)ScR_2]_2$ ($R = CH_2SiMe_3$) with C_6F_5I proceeds instantly to afford the product arising from the addition in the reverse sense; 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_3SiCH_2I and $(L)Sc(R)(C_6F_5)$, which crystallizes as an alkoxide bridged dimer (eq 2).



The analogous reaction between $(L)_2ScR$ and C_6F_5I was found to proceed equally cleanly, with both $(L)_2Sc(C_6F_5)$ (isolated in 86% yield) and Me_3SiCH_2I identified as the products. X-ray-quality single crystals of $[(L)Sc(R)(C_6F_5)]_2$ and $(L)_2Sc(C_6F_5)$ were grown from toluene solutions of the reaction mixtures at −20 °C and room temperature, respectively. The molecular structure of $[(L)Sc(R)(C_6F_5)]_2$ is described in the Supporting Information, while that of monomeric $(L)_2Sc(C_6F_5)$ is shown in Figure 1e, below.

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 $M-C_{carbene}$ bond in a heterolytic fashion to form a quaternized imidazolinium complex. For example, $(L)_2ScR$ reacts with Me_3SiCl to form $(L^{SiMe_3})(L)ScR(Cl)$, $(\{1\text{-}Me_3SiC(NDippCH_2CH_2N)\}CH_2CMe_2O)(\{1\text{-}C(NDippCH_2CH_2N)\}CH_2CMe_2O)Sc(CH_2SiMe_3)Cl$ initially. The addition reaction appears to be driven by the formation of a strong M−X bond (Sc−Cl: 464 kJ mol^{-1} in $ScCl_3$, 331 kJ mol^{-1} for the diatomic ScCl; Y−Cl: 523 ± 84 kJ mol^{-1} for diatomic YCl) and the use of a polar substrate. Upon warming to room temperature, this "ate"-like complex cleanly eliminates $Me_3SiCH_2SiMe_3$, reforming a metal carbene complex, in this example $(L)_2ScCl$.[11] In the bis(ligand) complex reactions, no inorganic products other than $(L)_2ScX$ 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 charge on the Sc center, which seems unlikely. The bis(ligand) complex $(L)_2ScCl$ is readily reconverted back to the alkyl $(L)_2ScR$ 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 $(L)_2ScR$ with respect to $[(L)ScR_2]_2$. The tris(alkyl) complex $(L^{CPh_3})ScR_3$ 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 $Me_3SiCH_2SiMe_3$, 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 $Ph_3CCH_2SiMe_3$ from $(L^{CPh_3})ScR_3$ 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, e.g., a bulky phosphine PR_3 in combination with strongly electrophilic $B(R)(C_6F_5)_2$, can react to cleave H_2 (or other small molecules) in a heterolytic manner, affording $[HPR_3][HBR_3]$.[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 NHC. 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 bond dissociation energy (BDE) of an NHC-coordinated BH_3 molecule $1\text{-}H_3B-C(NDippCH)_2$ is lowered by ∼125 kJ mol^{-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

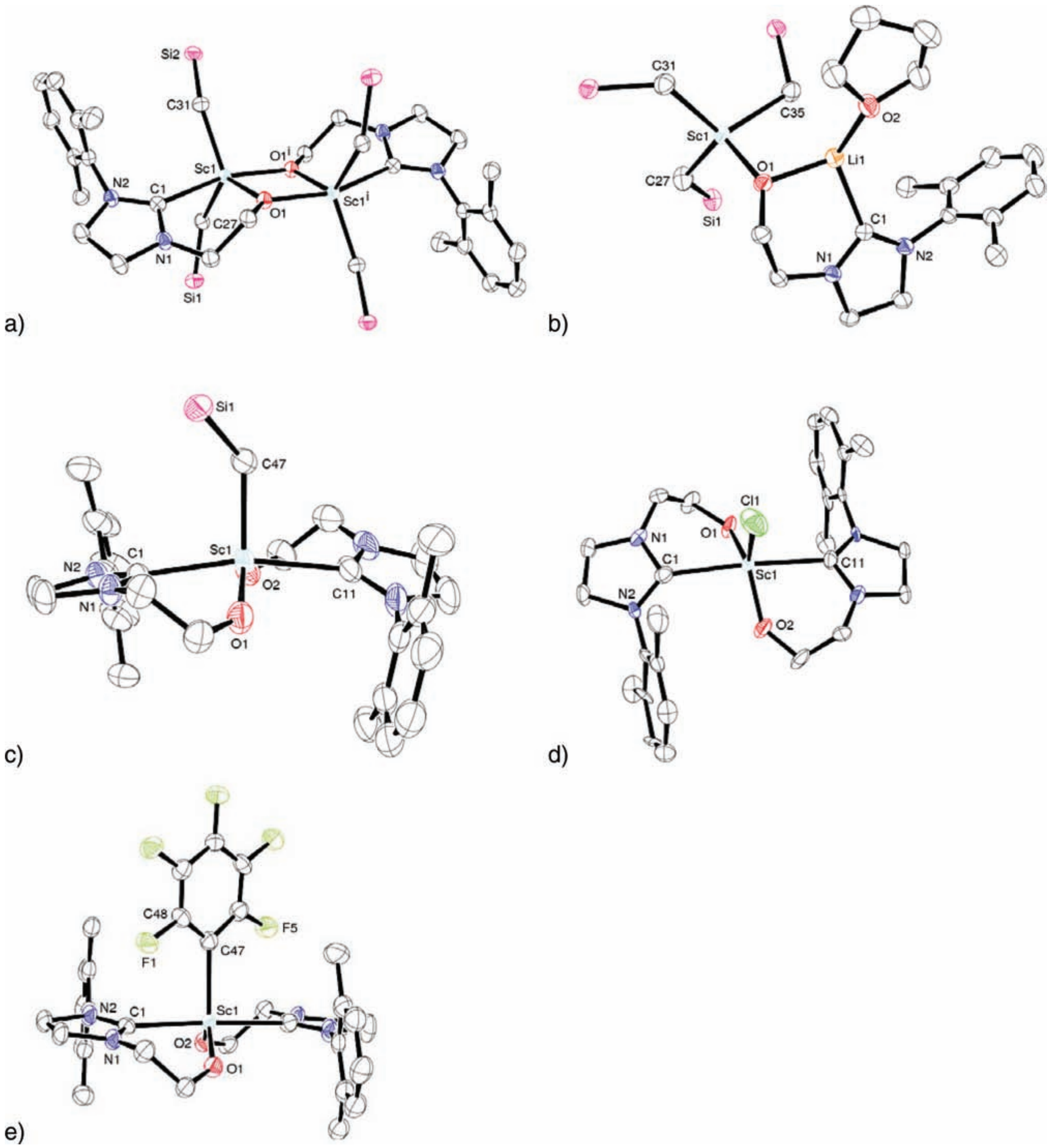


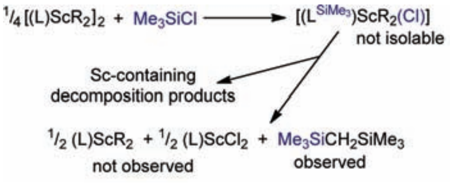
Figure 1. Thermal displacement drawings (50% probability ellipsoids) of the molecular structures of (a) $[(L)ScR_2]_2$, (b) $(L^{Li})ScR_3$, (c) $(L)_2ScR$, (d) $(L)_2ScCl$, and (e) $(L)_2Sc(C_6F_5)$. Methyl groups, H atoms, and lattice solvent molecules are omitted for clarity.

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 $(L)_2YR$ with Me_3SiCl, 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_3CCl), in an attempt to form carbon−carbon bonded products was not successful in this respect. Low yields of the iodide $(L)_2ScI$ are formed from reactions of $(L)_2ScR$ 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 $(L)_2ScR$ and PhI. The C−I bond strength in Me−I is 239 kJ mol^{-1}; that in Ph−I is 281 kJ mol^{-1}.[24,25] Alkyl halides such as *tert*-butyl chloride have previously been shown to act as a single-electron oxidant toward 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$''_2$ systems that the mono(ligand) products formed after elimination of the organic amine, i.e., (L)MN$''$Cl, were susceptible to ligand redistribution reactions, forming a 50:50 mixture of (L)MN$''_2$ and (L)MX$_2$.

If this were 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.



(3)

The heterobimetallic alkyl complex (L^{Li})ScR$_3$, in which the carbene binds to the lithium cation, allows a straightforward carbene C-alkylation to be carried out, and the quaternized intermediate, (L^{CPh_3})ScR$_3$, 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$_2$]$_2$ is also thermally stable. This represents a new type of C−C bond-forming reaction, one of particular potential use to give 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)$_2$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 kJ mol^{-1} in Me$_3$Sn−Cl,[27] but the polarity and formation of the strong Sc−Cl bond presumably drive the reaction. The use of two different tin reagents with very different sizes provides further information, since the quantitative formation of ^{n}Bu$_3$SnCH$_2$SiMe$_3$ takes 17 h, but that of Ph$_3$SnCH$_2$SiMe$_3$ takes up to 5 days. This must primarily be due to the difference 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 kJ mol^{-1} in Me$_3$SnCl, 439 kJ mol^{-1} in ^{n}Bu$_3$SnCl, and 350 ± 8 kJ mol^{-1} for the diatomic Sn−Cl),[28] but the polarity of the bond and the formation of a strong Sc−Cl bond (464 kJ mol^{-1} in ScCl$_3$ and 331 kJ mol^{-1} for the diatomic Sc−Cl)[28,29] are presumed to facilitate the reaction.

Precedent for the reverse addition of C$_6$F$_5$I to form the iodoimidazolinium intermediate (which is not directly observed) has been set. The free carbene {1-C(NAdCH)$_2$)} (IAd, where Ad = 1-adamantyl) reacts in THF with C$_6$F$_5$I to give the reverse ylide, 2-C$_6$F$_5$-I-C{N(Ad)CHCHN(Ad)}, i.e., a halonium methylide ylide, a zwitterion with a positive charge formally centered on the N-heterocyclic ring and a negative charge on the iodine atom, which exists in an equilibrium in solution with the free carbene and C$_6$F$_5$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.[30] It is interesting to compare the C−I BDE value[24] of 277 kJ mol^{-1} for C$_6$F$_5$−I with that for C$_6$H$_5$−I (281 kJ mol^{-1}), which was not reactive for this chemistry. The simple 2-iodoimidazolinium salt [2-I-C-(NAdCH)$_2$][I] can also be prepared by treatment of the free carbene IAd with I$_2$,[30] and [1-I-C(NEtCH)$_2$][I] was reported to be formed from the reaction of molybdenum or chromium carbonyl complexes (L)M(CO)$_5$ (M = Mo or Cr, L = {1-C(NEtCH)$_2$}) in chloroform with iodine.[31] Stack has reported the first example of reductive elimination of C$_{carbene}$−halogen bonds from IPrCu^{III} halide complexes (IPr = {1-C(NDippCH)$_2$)}) to form the corresponding 2-chloroimidazolium cation.[32] The formation of the iodoalkane Me$_3$SiCH$_2$I associated with the formation of the Sc-C$_6$F$_5$ containing complexes by elimination from the Sc-R and imidazolinium-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 σ-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$_6$ to afford Cp$^t_2$Ce(C$_6$F$_5$) (Cp^t =1,2,4-^{t}Bu-C$_5$H$_2$);[36] the latter reacts with C$_6$F$_5$SiH$_3$ to afford [Cp*$_2$Sm(C$_6$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 β-diketiminato complex [Sc(Me){(Ar)NC(Me)CHC(Me)N(Ar)}][MeB(C$_6$F$_5$)$_3$] affords [Sc(C$_6$F$_5$){(Ar)NC(Me)CHC(Me)N(Ar)}][Me$_2$B(C$_6$F$_5$)] (Ar = 2,6-^{i}Pr-C$_6$H$_3$).[38] Finally, protonolysis of the chiral metallacycle Ce(Cp^t)({1,2-^{t}Bu-4-CMe$_2$CH$_2$}C$_5$H$_2$) with C$_6$F$_5$H forms Ce(Cp^t)$_2$(C$_6$F$_5$).[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(N^{i}PrCH)$_2$}),[39] or by simple substitution reactions, as for (L)Au(C$_6$F$_5$) (L = {1-C(NMeCH)$_2$}).[41] Thus, the straightforward iodoarene addition across the M−NHC bond 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^{Li})ScR$_3$, (L)$_2$ScR, (L)$_2$ScCl, (L)$_2$ScI, (L)$_2$Sc(C$_6$F$_5$), and [(L)Sc(R)-(C$_6$F$_5$)]$_2$ were grown and the molecular structures determined by X-ray diffraction. The structures of [(L)ScR$_2$]$_2$, (L^{Li})ScR$_3$, (L)$_2$ScR, (L)$_2$ScCl, and (L)$_2$Sc(C$_6$F$_5$) are shown in Figure 1a−e, respectively, with selected metrical data collected in Table 1. The structures of [(L)YR$_2$]$_2$, (L)$_2$ScI and [(L)Sc(R)(C$_6$F$_5$)]$_2$ are discussed in the Supporting Information.

Single crystals of [(L)MR$_2$]$_2$ (M = Sc or Y, R = CH$_2$SiMe$_3$) 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)MR$_2$]$_2$ (M = Sc or Y) is dimeric in the solid state, with the alkoxy groups bridging the metal centers to form an M$_2$O$_2$ core which is centered over a crystallographic inversion center. Each metal center is five-coordinate, in a distorted trigonal bipyramidal geometry where the silylalkyl groups and one alkoxy bridging group define the equatorial plane. The L

Table 1. Selected Bond Lengths (Å) and Angles (°) of $[(L)ScR_2]_2$, $(L^{Li})ScR_3$, $(L)_2ScR$, $(L)_2ScCl$, and $(L)_2Sc(C_6F_5)$

	$[(L)ScR_2]_2$	$(L^{Li})ScR_3$	$(L)_2ScR$	$(L)_2ScCl$	$(L)_2Sc(C_6F_5)$
$M-C_{carbene}$	2.4572(16)	2.114(5) (M = Li)	2.442 (av.)	2.416 (av.)	2.422 (av.)
$Sc1-C_{alkyl}$	2.247 (av.)	2.245 (av.)	2.282 (av.)	–	2.417(6)
M-O	2.0821(11)	1.904(5) (M = Li)	1.945 (av.)	1.879(3)	1.918(4)
C1−Sc1−C11	–	–	166.4 (av.)	174.48(16)	177.2(2)
O1−Sc1−O2	–	–	131.8 (av.)	127.9(2)	120.96(19)

ligand is not parallel with the C_2O_2 plane but pitched away from the plane defined by the C_2O_2 core by ~28°. The $Sc-C_{carbene}$ (2.4572(16) Å) and $Sc-C_{alkyl,average}$ (2.247 Å) bond lengths are comparable to those previously reported for other complexes: $Sc-C_{carbene}$ = 2.350(3) Å and $Sc-C_{alkyl,average}$ = 2.209 Å in $(L)ScR_2$ (L = $IndCH_2CH_2\{1\text{-}C(NCHCHNMes)\}$),[17] $Sc-C_{carbene}$ = 2.343(4) Å and $Sc-C_{alkyl,average}$ = 2.201 Å in $(L)ScR_2$ (L = $FluCH_2CH_2\{1\text{-}C(NCHCHNMes)\}$).[42]

Crystals of $(L^{Li})ScR_3$ were grown from a toluene solution at −20 °C. The displacement ellipsoid plot is shown in Figure 1b. Lithium NHC complexes remain rare.[43] The molecular structure of $(L^{Li})ScR_3$ contains the shortest $Li-C_{carbene}$ distance (2.114(5) Å) reported to date. Existing examples range from 2.124(4) Å in $[Li(L)]_2$ (L = $^tBuNCH_2CH_2\{1\text{-}C(NCHCHN^tBu)\}$)[44] to 2.237(3) Å in $[Li(L)(C\equiv C^tBu)]_4$ (L = $\{1\text{-}C(NMeCMe)_2\}$).[45] 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 $[(L)ScR_2]_2$ (2.4572(16) Å) and much shorter than expected on the basis of the differences in ionic radii ($Li^{I,6C.N.}$ = 0.76 Å, $Sc^{III,6C.N.}$ = 0.745 Å).[46]

The coordination geometry at the scandium center is distorted tetrahedral, with the $Sc-C_{alkyl,average}$ bond length (2.245 Å) very similar to that in $[(L)ScR_2]_2$ (2.247 Å). The Li^I ion forms part of a six-membered metallacyclic ring where five of the atoms (O1−Li1−C1−N1−C8) are, unusually, virtually coplanar and Li1 is in a distorted trigonal coordination environment, sitting 0.471 Å above the plane defined by O1−O2−C1.

Crystals of $(L)_2ScR$ were grown from a toluene solution at −30 °C. The displacement ellipsoid plot is shown in Figure 1c. $(L)_2ScR$ crystallized with four molecules in each asymmetric unit of the unit cell. It is noted that one molecule was largely disordered. Comparable to all of the $(L)_2ScX$ 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 for scandium alkyl complexes.

Crystals of $(L)_2ScCl$ were grown from C_6D_6 at room temperature from the reaction mixture of $(L)_2ScR$ and Me_3SiCl. The displacement ellipsoid plot is shown in Figure 1d. The scandium center 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−C1−Sc1 = 115.1(3)°, N2−C1−Sc1 = 136.6(3)°), with the *N*-Dipp groups being forced backward in order to minimize unfavorable interactions. A C_2 axis is present through the Sc1−Cl1 bond.

Crystals of $(L)_2Sc(C_6F_5)$ were grown from a saturated toluene solution at −20 °C. The displacement ellipsoid plot is shown in Figure 1e. $(L)_2Sc(C_6F_5)$ crystallized with two molecules in each asymmetric unit of the unit cell; 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 coplanar (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 $Sc-C_{carbene}$ bond length (2.412(5) Å) is comparable to that in $(L)_2ScI$ (2.431(2) Å). The $Sc-C_{aryl}$ bond length in $(L)_2Sc(C_6F_5)$ (2.412(5) Å) is long. Comparison with $(L)Y(C_6F_5)_2(THF)$ (L = $1\text{-}NPh\text{-}2\text{-}CHNPh\text{-}C_6H_4$) (2.492(3) Å) confirms this, even when taking into account the 0.155 Å difference in ionic radii of Sc^{III} and Y^{III}.[46] The $Sc\cdots F_{average}$ 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 C_6F_5 group to the scandium center (C48−C47−Sc1 = 125.0(4) Å and C52−C47−Sc1 = 123.89(4) Å) to indicate the presence of any stabilizing $Sc\cdots F$ interactions (see Supporting Information for discussion of $Sc\cdots F$ interactions in $[(L)Sc(R)(C_6F_5)]_2$).

■ 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 catalytic reactions that combine NHCs with Lewis acidic metal catalysts[47] 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,[48] 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), distilled under reduced pressure, and 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 (δ = 0 ppm). Chemical shifts are quoted in δ (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. $ScCl_3(THF)_3$, $YCl_3(THF)_{3.5}$, $Sc(CH_2SiMe_3)_3(THF)_2$, $Y(CH_2SiMe_3)_3(THF)_2$, $Sc(CH_2CMe_3)_3(THF)_{1.5}$, $Y\{CH(SiMe_3)_2\}_3(THF)_2$,[49] and HL[50] were prepared with reference to published methods. Ph_3CCl 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_3SnCl was sublimed (10^{-4} Torr, 90 °C), and Ph_2PCl was distilled under reduced pressure (10^{-1} Torr, 120 °C) prior to use. All other reagents were purchased and used without further purification.

2.1. Syntheses of Mono(L) Complexes. 2.1.1. Synthesis of (L)Sc(CH_2SiMe_3)$_2$

a. Preparation from Sc(CH_2SiMe_3)$_3$(THF)$_2$. At 0 °C, to a slurry of $Sc(CH_2SiMe_3)_3(THF)_2$ (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 $(L)Sc(CH_2SiMe_3)_2$ 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 °C. ^{1}H NMR (C_6D_6, 500 MHz): 7.26 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 7.16 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.33−3.20 (2 H, br m, $\underline{H}CMe_2$), 3.25 and 2.92 (2 H each, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 2.17 (2 H, s, $OCMe_2C\underline{H_2}$), 1.61 (6 H, s, CMe_2), 1.53 and 1.14 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me_2}$), 0.21 (9 H, s, SiMe), −0.21 (2 H, br s, $C\underline{H_2}SiMe_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 147.0 (1-C_6H_3), 137.3 (2,6-C_6H_3), 129.5 (4-C_6H_3), 125.2 (3,5-C_6H_3), 75.9 ($\underline{C}Me_2$), 54.3 and 52.0 (NCH_2CH_2N), 28.3 ($H\underline{C}Me_2$), 26.4 and 24.1 ($HC\underline{Me_2}$), 4.6 (SiMe) ppm. The NCN, $C\underline{Me_2}$, and $CH_2Si\underline{Me_3}$ resonances could not be located. Anal. Found (calcd for $C_{27}H_{51}N_2OScSi_2$): C, 62.18 (62.26); H, 8.77 (9.87); N, 5.48 (5.38).

b. In Situ Preparation from ScCl$_3$(THF)$_3$. At −78 °C, 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 $LiCH_2SiMe_3$ (0.29 g, 3.1 mmol) in hexanes (20 mL) to afford a clear, colorless solution. The reaction mixture was stirred at 0 °C for 2 h, and then a slurry of $[H_2L]Cl$ (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 *in vacuo* to give a white solid. Extraction into cold (0 °C) toluene (2 × 10 mL) afforded a clear, pale yellow solution. The volatiles were removed *in vacuo* afford a white solid. The synthesis of $(L)Sc(CH_2SiMe_3)_2$ was confirmed by ^{1}H NMR spectroscopy. This route was not as clean as the simple protonolysis reaction and required recrystallization for purification.

2.1.2. Synthesis of (L)Y(CH_2SiMe_3)$_2$. At 0 °C, to a solution of $Y(CH_2SiMe_3)_3(THF)_2$ (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 × 5 mL), and dried *in vacuo* to afford $(L)Y(CH_2SiMe_3)_2$ 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 °C. ^{1}H NMR (C_6D_6, 500 MHz): 7.27−7.02 (3 H, overlapping m, 4-C_6H_3 and 3,5-C_6H_3), 3.20 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 3.14 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 2.89 (2 H, t, $^3J_{HH}$ = 11 Hz, NCH_2CH_2N), 2.11 (2 H, s, $OCMe_2C\underline{H_2}$), 1.56 (6 H, s, CMe_2), 1.50 and 1.15 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me_2}$), 0.26 (18 H, s, SiMe), −0.65 to −0.96 (2 H, br m, $C\underline{H_2}SiMe_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): 215.4 (d, $^1J_{YC}$ = 30 Hz, NCN), 146.7 (1-C_6H_3), 136.8 (2,6-C_6H_3), 129.7 (4-C_6H_3), 125.0 (3,5-C_6H_3), 74.5 ($\underline{C}Me_2$), 60.8 ($OCMe_2\underline{C}H_2$), 54.0 and 52.4 (NCH_2CH_2N), 37.6 ($^1J_{YC}$ = 38 Hz, $\underline{C}H_2SiMe_3$), 30.5 (CMe_2), 28.4 ($H\underline{C}Me_2$), 25.8 and 24.8 ($HC\underline{Me}_2$), 4.8 (SiMe). Anal. Found (calcd for $C_{27}H_{51}N_2OSi_2Y$): 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(NDippCH$_2$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 °C was added dropwise a solution of $LiCH_2SiMe_3$ (1.1 g, 11 mmol). The reaction mixture was allowed to warm to 0 °C 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 *in vacuo* to yield a white powder. Extraction into toluene (3 × 15 mL) and removal of the volatiles under reduced pressure gave a white powder, which was washed with hexanes (3 × 15 mL) and dried once more to afford ({1-Li(THF)C(NDippCH$_2$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_6D_6, 600 MHz): 7.08 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C_6H_3), 6.96 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C_6H_3), 3.13 (2 H, t, $^3J_{HH}$ = 6 Hz, C_2H_4O), 3.12 (2 H, s, $OCMe_2C\underline{H_2}$), 2.85 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 2.90 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}CMe_2$), 3.05 (2 H, t, $^3J_{HH}$ = 10 Hz, NCH_2CH_2N), 1.51 (6 H, s, CMe_2), 1.21 (2 H, t, $^3J_{HH}$ = 6 Hz, C_2H_4O), 1.15 and 1.09 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me_2}$), 0.42 (27 H, s, SiMe), −0.16 (6 H, s, $C\underline{H_2}SiMe_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): 221.1 (NCN), 147.6 and 147.4 (2,6-C_6H_3), 138.2 and 137.8 (1-C_6H_3), 128.9 and 128.8 (4-C_6H_3), 124.3 (3,5-C_6H_3), 74.0 ($\underline{C}Me_2$), 68.0 (C_2H_4O), 62.2 ($OCMe_2\underline{C}H_2$), 52.8 and 51.7 (NCH_2CH_2N), 35.4 ($\underline{C}H_2SiMe_3$), 30.9 ($C\underline{Me_2}$), 28.4 and 28.3 ($H\underline{C}Me_2$), 25.3 (C_2H_4O), 24.8 and 24.7 ($HC\underline{Me_2}$), 4.39 (SiMe) ppm. Anal. Found (calcd for $C_{35}H_{70}LiN_2O_2ScSi_3$): C, 60.12 (61.18); 10.09 (10.27); N, 4.45 (4.66). This analysis was performed on a sample of powdered single crystals.

The low C percentage is noted and presumed to be due to the formation of metal carbide in the analysis.

2.2.2. Synthesis of ({1-Me$_3$SiC(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$. At 0 °C, to a solution of ({1-(Li(THF)C(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$ (0.34 g, 0.51 mmol) in toluene (5 mL) was added a solution of Me$_3$SiCl (64 μL, 0.51 mmol) in toluene (5 mL). The reaction mixture was stirred for 2 h. The volatiles were removed *in vacuo* to afford ({1-Me$_3$SiC(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$ 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%). ^{1}H NMR (C$_6$D$_6$, 500 MHz): 6.99 (1 H, t, $^3J_{HH}$ = 8 Hz, 4-C$_6$H$_3$), 6.75 (2 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C$_6$H$_3$), 4.58 and 3.35 (2 H each, t, $^3J_{HH}$ = 12 Hz, NCH$_2$CH$_2$N), 2.46 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}$CMe$_2$), 3.30 (2 H, s, OCMe$_2$C$\underline{H_2}$), 1.52 (6 H, s, CMe$_2$), 0.93 (12 H, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me_2}$), 0.58 (27 H, s, CH$_2$Si$\underline{Me_3}$), 0.16 (6 H, br s, C$\underline{H_2}$SiMe$_3$), −0.43 (9 H, s, CSiMe$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125 MHz): 174.8 (NCN), 146.3 (1-C$_6$H$_3$), 132.4 (2,6-C$_6$H$_3$), 131.3(4-C$_6$H$_3$), 125.2 (3,5-C$_6$H$_3$), 73.02 ($\underline{C}$Me$_2$), 64.2 (OCMe$_2\underline{C}$H$_2$), 54.7 and 51.5 (NCH$_2$CH$_2$N), 31.5 (C$\underline{Me_2}$), 28.5 (H$\underline{C}$Me$_2$), 25.6 and 23.3 (HC$\underline{Me_2}$), 4.91 (CH$_2$Si$\underline{Me_3}$ and $\underline{C}$H$_2$SiMe$_3$),1.48 ($\underline{C}$Si$\underline{Me_3}$) ppm. Anal. Found (calcd for C$_{34}$H$_{71}$N$_2$OScSi$_4$): C, 59.89 (59.94); H, 10.41 (10.50); N, 4.14 (4.11).

2.3. Synthesis of Bis(L) Complexes. 2.3.1. Synthesis of (L)$_2$Sc(CH$_2$SiMe$_3$). a. From Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$. At 0 °C, to a clear, colorless solution of Sc(CH$_2$SiMe$_3$)$_3$(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 stirred at room temperature for 1.5 h to afford a clear, colorless solution. The volatiles were removed under reduced pressure to afford (L)$_2$Sc(CH$_2$SiMe$_3$) as a white solid. Yield: 1.1 g (81%). Diffraction-quality crystals were grown from a hexanes solution at −20 °C. ^{1}H NMR (C$_6$D$_6$, 500 MHz): 7.27 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C$_6$H$_3$), 7.26 (4 H, d, $^3J_{HH}$ = 8 Hz, 3,5-C$_6$H$_3$), 3.74 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C$\underline{H_2}$), 3.32 (2 H, m, $\underline{H}$CMe$_2$), 3.25−2.28 (10 H, overlapping m, NCH$_2$CH$_2$N and $\underline{H}$CMe$_2$), 2.56 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C$\underline{H_2}$), 1.58, 1.51, 1.21 and 1.16 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me_2}$), 0.87 and 0.60 (6 H each, s, CMe$_2$), 0.37 (9 H, s, CH$_2$Si$\underline{Me_3}$), −0.33 and −0.72 (1 H each, d, $^2J_{HH}$ = 11 Hz, C$\underline{H_2}$SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125 MHz): 147.8 and 147.1 (2,6-C$_6$H$_3$), 138.4 (1-C$_6$H$_3$), 128.4 (4-C$_6$H$_3$), 124.02 (3,5-C$_6$H$_3$), 72.7 ($\underline{C}$Me$_2$) 62.41 (OCMe$_2\underline{C}$H$_2$), 53.3 and 52.7 (H$\underline{C}$Me$_2$ and NCH$_2$CH$_2$N), 30.2 (C$\underline{Me_2}$), 28.7 ($\underline{C}$H$_2$SiMe$_3$), 28.3 (C$\underline{Me_2}$), 27.6, 25.9, 25.3, and 25.1 (HC$\underline{Me_2}$), 4.7 (SiMe) ppm. The NCN resonance could not be located. Anal. Found (calcd for C$_{42}$H$_{69}$N$_4$O$_2$ScSi): C, 68.50 (68.63); H, 9.26 (9.46); N, 7.74 (7.62).

b. From (L)$_2$ScCl. (L)$_2$ScCl (0.014 g, 0.020 mmol) and LiCH$_2$SiMe$_3$ (0.0019 g, 0.020 mmol) were combined in C$_6$D$_6$ in a J-Young Teflon valve NMR tube. The reaction mixture was heated to 80 °C for 12 h. The formation of (L)$_2$Sc(CH$_2$SiMe$_3$) was confirmed by ^{1}H NMR spectroscopy.

2.3.2. Synthesis of (L)$_2$Sc(CH$_2$CMe$_3$). At 0 °C, to a clear, colorless solution of Sc(CH$_2$CMe$_3$)$_3$(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 stirred at room temperature for 1.5 h to afford a clear, colorless solution. The volatiles were removed under reduced pressure to afford (L)$_2$Sc(CH$_2$CMe$_3$) as a white solid. Yield: 0.11 g (47%). Diffraction-quality crystals were grown from a hexanes solution at −20 °C. ^{1}H NMR (C$_6$D$_6$, 500 MHz): 7.30 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C$_6$H$_3$), 7.18 (4 H, m, 2,6-C$_6$H$_3$), 3.92 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C$\underline{H_2}$), 3.46 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}$CMe$_2$), 3.27 (2 H, m, NCH$_2$CH$_2$N), 3.11−2.87 (6 H, overlapping m, $\underline{H}$CMe$_2$ and NCH$_2$CH$_2$N), 2.64 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C$\underline{H_2}$), 1.62 and 1.52 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me_2}$), 1.41 (9 H, s, CMe$_3$), 1.22 and 1.16 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me_2}$), 0.91 and 0.67 (6 H each, s, CMe$_2$), 0.50 and 0.37 (1 H each, d, $^1J_{HH}$ = 12 Hz, C$\underline{H_2}$CMe$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 500 MHz): 147.9 and 147.1 (2,6-C$_6$H$_3$), 138.6 (1-C$_6$H$_3$), 124.0 (3,5-C$_6$H$_3$), 72.5 ($\underline{C}$Me$_2$), 62.3 (OCMe$_2\underline{C}$H$_2$), 53.3 ad 52.8 (NCH$_2$CH$_2$N), 36.9 (^{t}Bu), 31.6 (C$\underline{Me_2}$), 28.7 and 28.2 (H$\underline{C}$Me$_2$), 27.8 (C$\underline{Me_2}$), 26.0,25.8,25.5,and 25.1 (HC$\underline{Me_2}$) ppm. The resonance for the 4-C$_6$H$_3$ C was obscured by the C$_6$D$_6$ resonance and the NCN and C$\underline{H_2}$CMe$_3$ resonances could not be located. Anal. Found (calcd for C$_{43}$H$_{69}$N$_4$O$_2$Sc): C, 71.74 (71.83); H, 9.75 (9.67); N, 7.61 (7.79).

2.3.3. Synthesis of (L)$_2$Y(CH$_2$SiMe$_3$). To a clear, colorless solution of Y(CH$_2$SiMe$_3$)$_3$(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, then the volatiles were removed under reduced pressure to yield a pale yellow solid which was washed with hexanes (3 × 5 mL) and dried under reduced pressure to afford (L)$_2$Y(CH$_2$SiMe$_3$) as a white solid. Yield: 0.14 g (33%). ^{1}H NMR (C$_6$D$_6$, 600 MHz): 7.29 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C$_6$H$_3$) 7.17 (4 H, m, 3,5-C$_6$H$_3$), 3.63 (2 H, d, $^3J_{HH}$ = 14 Hz, OCMe$_2$C$\underline{H_2}$), 3.38−2.85 (12 H, overlapping m, NCH$_2$CH$_2$N and $\underline{H}$CMe$_2$), 2.67 (2 H, d, $^3J_{HH}$ = 14 Hz, OCMe$_2$C$\underline{H_2}$), 1.57, 1.49, and 1.19 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me_2}$), 0.87 and 0.79 (6 H each, s, CMe$_2$), 0.41 (9 H, s, SiMe), −0.48 and −1.04 (1 H each, dd, $^1J_{HH}$ = 11 Hz, $^1J_{YH}$ = 3 Hz, C$\underline{H_2}$SiMe$_3$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125 MHz): 217.9 (d, $^1J_{YC}$ = 33 Hz, NCN), 147.6 and 147.2 (2,6-C$_6$H$_3$), 137.7 (1-C$_6$H$_3$), 128.6 (4-C$_6$H$_3$), 124.1 and 124.0 (2,6-C$_6$H$_3$), 67.9 and 63.2 (OCMe$_2\underline{C}$H$_2$), 53.2 and 53.0 (NCH$_2$CH$_2$N), 31.2 and 28.7 (C$\underline{Me_2}$), 28.3 and 28.0 (H$\underline{C}$Me$_2$), 25.9, 25.6, 25.1, and 25.0 (HC$\underline{Me_2}$), 5.0 (SiMe) ppm. The $\underline{C}$H$_2$SiMe$_3$ 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)$_2$Sc(CH$_2$SiMe$_3$) with E−X to form C−Si bonded products. 2.4.1.1. Reaction of (L)$_2$Sc(CH$_2$SiMe$_3$) with Me$_3$Si−Cl to form a C−Si bond and (L)$_2$ScCl

a. Preparative Scale. (L)$_2$Sc(CH$_2$SiMe$_3$) (0.17 g, 0.23 mmol) and Me$_3$SiCl (29 μL, 0.23 mmol) were combined in C$_6$D$_6$ (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 × 2 mL), and dried *in vacuo* to afford (L)$_2$ScCl as a colorless solid. Yield: 0.071 g (45%). Diffraction-quality crystals were grown from a saturated C$_6$D$_6$ solution. ^{1}H NMR (C$_6$D$_6$, 500 MHz): 7.25 (2 H, t, $^3J_{HH}$ = 8 Hz, 4-C$_6$H$_3$), 7.19 and 7.14 (2 H each, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, 3,5-C$_6$H$_3$), 3.69 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C$\underline{H_2}$), 3.59 (2 H, sept, $^3J_{HH}$ = 7 Hz, $\underline{H}$CMe$_2$), 3.25−3.19 (2 H, m, NCH$_2$CH$_2$N), 3.11−3.03 (4 H, overlapping m, $\underline{H}$CMe$_2$ and NCH$_2$CH$_2$N), 2.92−2.82 (4 H, m, NCH$_2$CH$_2$N), 2.49 (2 H, d, $^3J_{HH}$ = 13 Hz, OCMe$_2$C$\underline{H_2}$), 1.72, 1.60, 1.21, and 1.21 (6 H each, d, $^3J_{HH}$ = 7 Hz, HC$\underline{Me_2}$), 0.98 and 0.50 (CMe$_2$) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$, 125 MHz): 215.2 (NCN), 147.8, 147.6, and 129.3 (1,2,6-C$_6$H$_3$), 128.6 (4-C$_6$H$_3$), 124.3 and 124.1 (3,5-C$_6$H$_3$), 73.3 ($\underline{C}$Me$_2$), 62.3 (OCMe$_2\underline{C}$H$_2$), 52.3 and 52.6 (NCH$_2$NCH$_2$), 29.4 (C$\underline{Me_2}$), 28.8 and 28.2 (H$\underline{C}$Me$_2$), 27.2 (C$\underline{Me_2}$), 25.8, 25.4, and 25.0 (HC$\underline{Me_2}$). Anal. Found (calcd for C$_{38}$H$_{58}$ClN$_4$O$_2$Sc): C, 67.16 (66.79); H, 8.91 (8.56); N, 7.85 (8.20).

b. NMR Tube Scale. To a solution of (L)$_2$Sc(CH$_2$SiMe$_3$) (0.024 g, 0.032 mmol) in C$_6$D$_6$ (1 mL) in a J-Young Teflon valve NMR tube was added Me$_3$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}H NMR spectroscopy, and the formation of (L)$_2$ScCl and Me$_3$SiCH$_2$SiMe$_3$ was observed.

2.4.1.2. Reaction of (L)$_2$Sc(CH$_2$SiMe$_3$) with E−X To Form a C−Si Bond and (L)$_2$ScI

NMR Tube Scale, Me$_3$SiI. To a solution of (L)$_2$Sc(CH$_2$SiMe$_3$) (0.066 g, 0.090 mmol) in C$_6$D$_6$ (1 mL) in a J-Young Teflon valve NMR tube was added Me$_3$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}H NMR spectroscopy, and the formation of (L)$_2$ScI was observed. The volatiles were distilled off and were shown to contain Me$_3$SiCH$_2$SiMe$_3$ by ^{1}H NMR spectroscopy.

Table 2. Selected Experimental Crystallographic Data for $[(L)ScR_2]_2$, $(L^{Li})ScR_3$, $(L)_2ScR$, $(L)_2ScCl$, and $(L)_2Sc(C_6F_5)$

	$(L)ScR_2$	$(L^{Li})ScR_3$	$(L)_2ScR$	$(L)_2ScCl$	$(L)_2Sc(C_6F_5)$
			Crystal Data		
chemical formula	$C_{54}H_{102}N_4O_2Sc_2Si_4$	$C_{35}H_{70}LiN_2O_2ScSi_3$	$C_{42}H_{69}N_4O_2ScSi$	$C_{38}H_{58}ClN_4O_2Sc$	$C_{44}H_{58}F_5N_4O_2Sc$
M_r	1041.68	687.10	735.06	683.29	814.90
crystal system, space group	monoclinic, $P2_1/c$	orthorhombic, $Pbca$	orthorhombic, $C222_1$	monoclinic, Pn	monoclinic, $C2/c$
temperature (K)	100	150	150	150	100
a, b, c (Å)	9.5128 (1), 19.2311 (3), 19.6980 (3)	10.1400 (2), 22.3379 (5), 38.2117 (9)	32.2095 (4), 32.7595 (4), 34.3193 (5)	8.9058 (1), 11.9061 (2), 18.4358 (3)	38.7236 (16), 23.2484 (10), 20.6479 (8)
α, β, γ (°)	90, 97.888 (1), 90	90, 90, 90	90, 90, 90	90, 91.217 (1), 90	90, 110.141 (5), 90
V (Å^3)	3569.49 (9)	8655.2 (3)	36212.6 (8)	1954.37 (5)	17451.8 (12)
Z	2	8	8	2	16
radiation type	Cu Kα	Mo Kα	Mo Kα	Mo Kα	Cu Kα
μ (mm^{-1})	2.53	0.28	0.22	0.29	1.95
crystal size (mm)	0.11 × 0.08 × 0.04	0.55 × 0.50 × 0.45	0.19 × 0.15 × 0.11	0.21 × 0.19 × 0.15	0.17 × 0.17 × 0.07
			Data Collection		
diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer	Bruker *SMART APEX* CCD area detector diffractometer	Xcalibur, Eos diffractometer	Xcalibur, Eos diffractometer	SuperNova, Dual, Cu at zero, Atlas diffractometer
absorption correction	Multiscan, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55[a]	Multiscan, SADABS	Multiscan, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.44[b]	Multiscan, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55[a]	Multiscan, CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.33.55[a]
T_{min}, T_{max}	0.944, 1.000	0.861, 0.884	0.964, 1.000	0.980, 1.000	0.572, 1.000
no. of measured, independent, and observed $[I > 2\sigma(I)]$ reflections	23809, 6985, 5376	98382, 10956, 9564	106897, 35881, 30576	22700, 8848, 6534	62621, 13666, 9691
R_{int}	0.059	0.064	0.026	0.020	0.059
			Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.091, 0.93	0.079, 0.161, 1.28	0.048, 0.117, 1.02	0.080, 0.227, 1.02	0.103, 0.388, 1.59
no. of reflections	6985	10956	35881	8848	13666
no. of parameters	310	412	1964	457	1033
no. of restraints	0	0	0	2	0
	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 12.1028P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 31.7562P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1646P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.24	0.51, −0.42	0.50, −0.84	1.34, −0.38	1.98, −1.14

[a] 05-01-2010 CrysAlis171 .NET (compiled Jan 5 2010, 16:28:46). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. [b] 25-10-2010 CrysAlis171 .NET (compiled Oct 25 2010, 18:11:34). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

2.4.1.3. Reaction of $(L)_2Sc(CH_2CMe_3)$ with E−X To Form C−Si Bonded Products. Me_3SiCl. To a solution of $(L)_2Sc(CH_2CMe_3)$ (0.012 g, 0.017 mmol) in C_6D_6 (1 mL) in a J-Young Teflon valve NMR tube was added Me_3SiCl (2.1 μL, 0.017 mmol) to afford a clear, colorless solution. Over the course of 10 days, the reaction was monitored by ^1H NMR spectroscopy, and the formation of $(L)_2ScCl$ and $Me_3SiCH_2CMe_3$ was observed. ^1H NMR: (C_6D_6, 400 MHz, 298 K): 1.26 (9 H, s, CMe_3), 0.14 (9 H, s, SiMe), 0.07 (2 H, s, CH_2) 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 ({1-Li(THF)C(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$ with E−X To Give C−C Bond Formation. Ph_3CCl. To a solution of ({1-Li(THF)C(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)Sc(CH$_2$SiMe$_3$)$_3$

(0.11 g, 0.16 mmol) in toluene (2 mL) was added a solution of Ph_3CCl (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 × 1 mL). The combined washings were dried *in vacuo* to afford an orange solid. ^1H NMR spectral analysis showed this to be a combination of $(L)Sc(CH_2SiMe_3)_2$ and $Ph_3CCH_2SiMe_3$. EI-MS: *m/z* 330.2 $[Ph_3CCH_2SiMe_3]^+$ (25%), 315.2 $[Ph_3CCH_2SiMe_3{-}Me]^+$ (6%), 243.1 $[Ph_3CCH_2SiMe_3{-}CH_2SiMe_3]^+$ (100%).

2.4.2.2. Thermolysis of ({1-Me$_3$SiC(NDippCH$_2$CH$_2$N)}CH$_2$CMe$_2$O)-Sc(CH$_2$SiMe$_3$)$_3$ To Give C−Si Bond Formation. $\{1\text{-}Me_3SiC(NDippCH_2CH_2N)\}CH_2CMe_2O)Sc(CH_2SiMe_3)_3$ (0.021 g, 0.031 mmol) was dissolved in C_6D_6 (1 mL) in a J-Young Teflon valve NMR tube. The reaction mixture was kept at room temperature for 2 h, after which time the ^1H NMR spectrum contained resonances for $Me_3SiCH_2SiMe_3$, $(L)Sc(CH_2SiMe_3)_2$ (~0.9 equiv), and $(L)_2Sc(CH_2SiMe_3)$ (~0.1 equiv).

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(CH$_2$SiMe$_3$) with Ph$_2$PCl To Form a C−P Bond and (L)$_2$ScClPh$_2$PCl. To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.051 g, 0.069 mmol) in C_6D_6 (1 mL) in a J-Young Teflon valve NMR tube was added Ph_2PCl (12.3 μL, 0.069 mmol) to afford a clear, colorless solution. Over the course of 5 days, the reaction was monitored by ^1H NMR spectroscopy, and the formation of $(L)_2ScCl$ and $Ph_2PCH_2SiMe_3$ in 95% yield was observed. ^1H NMR (C_6D_6, 500 MHz, 298 K): 7.45 (12 H, m, C_6H_4), 0.36 ($C\underline{H}_2SiMe_3$) ppm. EI-MS: *m/z*: 272.1 $[Ph_2PCH_2SiMe_3]^+$ (100%).

2.4.3.2. C−Sn: Reaction of (L)$_2$Sc(CH$_2$SiMe$_3$) with Tris(Hydrocarbyl) Tin Chlorides To Form a C−Sn Bond and (L)$_2$ScCl

a. ^{n}BuSnCl. To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.037 g, 0.051 mmol) in C_6D_6 (1 mL) in a J-Young Teflon valve NMR tube was added $^nBu_3SnCl$ (14 μL, 0.051 mmol) to afford a clear, colorless solution. Over the course of 17 h, the reaction was monitored by ^1H NMR spectroscopy, and the formation of 1 equiv of $(L)_2ScCl$ and 1 equiv of $^nBu_3SnCH_2SiMe_3$ was observed. ^1H NMR (C_6D_6, 500 MHz): 1.67 (6 H, m, $(C\underline{H}_2)_3CH_3$), 1.49 (6 H, m, $(C\underline{H}_2)_3CH_3)$), 1.06−0.94 (36 H, overlapping m, $4\text{-}(C\underline{H}_2)_3CH_3$ and $1\text{-}(CH_2)_3C\underline{H}_3$), 0.24 (9 H, s, SiMe), −0.13 (2 H, s, $C\underline{H}_2SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 29.7 ($(2,3\text{-}\underline{C}H_2)_3CH_3$), 27.9 ($2,3\text{-}(\underline{C}H_2)_3CH_3$), 14.0 ($4\text{-}(CH_2)_3\underline{C}H_3$), 10.7 ($1\text{-}(\underline{C}H_2)_3CH_3$, $^2J_{^{119}SnC}$ = 162 Hz, $^2J_{^{117}SnC}$ = 155 Hz), 1.9 (SiMe), −7.1 ($\underline{C}H_2SiMe_3$) ppm. EI-MS: *m/z* 363.1 $[^nBu_3SnCH_2SiMe{-}Me]^+$ (5%), 321.1 $[^nBu_3SnCH_2SiMe_3{-}^nBu]^+$ (100%), 264.0 $[^nBu_3SnCH_2SiMe_3{-}2^nBu]^+$ (18%), 207.0 $[^nBu_3SnCH_2SiMe_3{-}3^nBu]^+$ (66%), 102.0 $[^nBu_3SnCH_2SiMe_3{-}^nBu_3Sn]^+$ (18%).

b. Ph$_3$SnCl. $(L)_2Sc(CH_2SiMe_3)$ (0.019 g, 0.026 mmol) and Ph_3SnCl (0.010 g, 0.026 mmol) were combined in C_6D_6 (1 mL) in a J-Young Teflon valve NMR tube. Over the course of 5 days, the reaction was monitored by ^1H NMR spectroscopy, and the formation of $(L)_2ScCl$ and $Ph_3SnCH_2SiMe_3$ was observed. ^1H NMR (C_6D_6, 500 MHz): 7.62−7.60 (3 H, overlapping m, C_6H_4), 7.21−7.13 (overlapping m, $\text{-}C_6H_4$), 0.36 (2 H, s, $C\underline{H}_2SiMe_3$), 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 $(L)_2ScCl$ resonances. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 137.3 and 128.7 (C_6H_4), 1.7 ($\underline{C}H_2SiMe_3$), −5.0 (SiMe) ppm. The remaining $-C_6H_4$ resonances are obscured by residual protio solvent and $(L)_2ScCl$ resonances. EI-MS: *m/z* 423.1 $[Ph_3SnCH_2SiMe_3{-}Me]^+$ (10%), 361.1 $[Ph_3SnCH_2SiMe_3{-}Ph]^+$ (14%), 351.0 $[Ph_3SnCH_2SiMe_3{-}CH_2SiMe_3]^+$ (100%).

2.4.3.3. C−I: Reaction of (L)$_2$Sc(CH$_2$SiMe$_3$) with C$_6$F$_5$I To Form a C−I Bond and (L)$_2$Sc(C$_6$F$_5$)

a. Preparative Scale. $(L)_2Sc(CH_2SiMe_3)$ (0.15 g, 0.21 mmol) and C_6F_5I (27.6 μL, 0.21 mmol) were combined in C_6D_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 × 1 mL), and the volatiles were removed *in vacuo* to afford $(L)_2Sc(C_6F_5)$ as a colorless solid. Yield: 0.15 g (86%). The organic product Me_3SiCH_2I, identified in the NMR tube reaction below, is unstable and decomposes over time in solution to a dark-colored material. Diffraction-quality crystals of $(L)_2Sc(C_6F_5)$ were grown from a toluene solution at −20 °C. ^1H NMR (C_6D_6, 500 MHz): 7.18 (2 H, t, $^3J_{HH}$ = 8 Hz, $4\text{-}C_6H_3$), 7.13 and 6.92 (2 H each, dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz, $2,6\text{-}C_6H_3$), 3.41 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 3.25−2.91 (12 H, overlapping m, NCH_2CH_2N and $\underline{H}CMe_2$), 2.80 (2 H, d, $^3J_{HH}$ = 13 Hz, $OCMe_2C\underline{H}_2$), 1.63 (6 H, s, CMe_2), 1.60 and 1.16 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$), 1.11 (6 H, s, CMe_2), 0.99 and 0.94 (6 H each, d, $^3J_{HH}$ = 7 Hz, $HC\underline{Me}_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): 215.3 (NCN), 147.4 ($3,5\text{-}C_6H_3$), 146.9 ($1\text{-}C_6H_3$), 137.7 ($4\text{-}C_6H_3$), 124.4 and 123.7 ($2,6\text{-}C_6H_3$), 73.6 ($\underline{C}Me_2$), 62.5 ($OCMe_2\underline{C}H_2$), 53.0 and 52.8 (NCH_2CH_2N), 28.6 ($H\underline{C}Me_2$), 28.2 ($C\underline{Me}_2$), 28.1 ($H\underline{C}Me_2$), 26.0, 25.5, 24.9, and 23.1 ($HC\underline{Me}_2$) ppm. Anal. Found (calcd for $C_{44}H_{58}F_5N_4O_2Sc$): C, 64.70 (64.85); H, 7.07 (7.17); N, 6.78 (6.88).

b. NMR Tube Scale, C$_6$F$_5$I. To a solution of $(L)_2Sc(CH_2SiMe_3)$ (0.012 g, 0.016 mmol) in C_6D_6 (1 mL) in a J-Young Teflon valve NMR tube was added C_6F_5I (2.2 μL, 0.016 mmol) to afford a clear, colorless solution. ^1H NMR spectroscopy indicated the formation of $(L)_2Sc(C_6F_5)$ and Me_3SiCH_2I. Over the course of 24 h, the solution darkened in color and became dark pink. ^1H NMR spectroscopy showed the presence of $(L)_2Sc(C_6F_5)$ and Me_3SiCH_2I; the latter decomposes slowly in solution over time, darkening the solution.

3. Crystallographic 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 (λ = 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 (λ = 1.54178 Å).[51] Using the WinGX suite of programs, all structures were solved using direct methods and refined using a full-matrix least-squares refinement on $|F|^2$ using SHELXL-97.[52] 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.[53] Complex neutral-atom scattering factors were used.[54] Refinement proceeded to give the residuals shown in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data have been deposited with the CCDC, codes 824248−824254 and 824414. This material is available at www.ccdc.cam.ac.uk.

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