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Transmetalation Reactions of a Scandium Complex Supported by a Ferrocene Diamide Ligand

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Efforts to transfer to aluminum the heterocyclic ligand of a ring-opened imidazole scandium complex, which was previously reported, are presented. A ring-opened imidazole aluminum compound was formed at 50 °C and characterized as a trialuminum complex. At high temperature (85 °C), the formation of an unusual scandium/aluminum methylidene was observed. The reaction products were characterized by standard spectroscopic techniques and X-ray crystallography. Density functional theory calculations were used to understand the electronic structure of the scandium/aluminum methylidene complex.

Introduction

A great amount of research has been directed toward exploring the reactivity of aromatic heterocycles because of their biological and industrial relevance.[1–15] Our group has been studying their behavior in the presence of d^0f^n metal complexes supported by ferrocene-based chelating ligands and found that a few distinct behaviors emerged depending on the substrate employed.[16–29] That body of research was prompted by the unusual behavior of the scandium complex $(NN^{fc})Sc(CH_2Ar)(THF)$ [**1-(CH₂Ar)(THF)**, where $NN^{fc} = 1,1'\text{-fc}(NSi^tBuMe_2)_2$ and $Ar = 3,5\text{-Me}_2C_6H_3$] toward 1-methylimidazole (eq 1).[21] A total of 2 equiv of the substrate was transformed, leading to the product, **2**, which contained an imidazole−imine−amide moiety with one ring-opened imidazole fragment. Other early transition metals, such as tantalum,[30] niobium,[31,32] and titanium,[33,34] have been reported to mediate the cleavage of aromatic N-heterocycles.[9] The reaction of **1-(CH₂Ar)(THF)** is unusual in that it involves

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Scheme 1. Reaction of **2** with AlMe₃ and the Proposed Mechanism
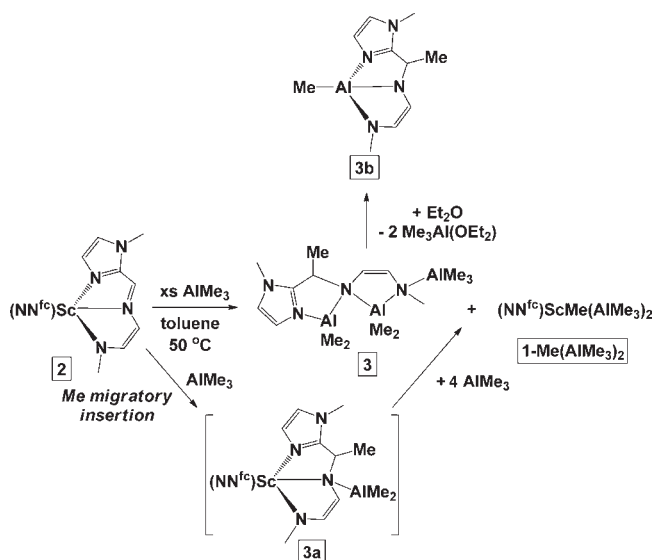
only σ bonds,[18] as opposed to previous examples, which took advantage of multiple bonds to drive the reactions.
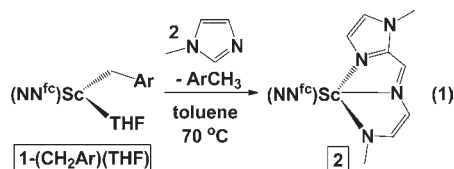
Given the unusual planar, tridentate nature of the imidazole−imine−amide ligand in **2**, we became interested in determining whether this fragment can be removed from scandium and used as a ligand for a different metal. Herein, we discuss the results of transmetalation reactions with **2**. During these studies, a new scandium methylidene complex was isolated. The rational synthesis and characterization of this scandium methylidene are also reported.

Results and Discussion

Transmetalation between 2 and AlMe₃. In addition to transferring the imidazole−imine−amide ligand of **2** to another metal, transmetalation would allow us to recycle the ferrocene diamide scandium fragment. Given the utility of Me₃SiCl in transmetalating reactions that involve electrophilic metal centers,[35−42] our first attempts to generate a scandium compound that can be reused in the synthesis of **2** involved this reagent. The expected scandium chloride product, [(NN^fc)Sc(μ-Cl)]₂, was previously obtained from the reaction of Me₃SiCl with

Figure 1. Thermal-ellipsoid (50% probability) representation of **3**; irrelevant hydrogen atoms were removed for clarity. Selected metrical parameters for **3** (distances in Å and angles in deg): Al(1)−N(3), 1.9966(13); Al(1)−N(4), 1.9553(14); Al(2)−N(2), 1.9449(13); Al(2)−N(3), 1.9977(15); Al(3)−N(4), 2.0238(15); C(4)−C(5), 1.5027(22); C(5)−C(6), 1.5228(21); C(5)−N(3), 1.5120(18); C(9)−C(10), 1.3268(22); N(3)−Al(1)−N(4), 90.84(6); N(2)−Al(2)−N(3), 84.45(6); Al(1)−N(3)−Al(2), 109.17(6); C(4)−C(5)−N(3), 109.76(13); C(6)−C(5)−N(3), 113.58(12); C(4)−C(5)−C(6), 109.76(13).

1-(CH₂Ar)(THF).[35] Heating **2** in the presence of excess Me₃SiCl for 2 days at 70 °C, however, showed no transformation.

Given the lack of reactivity between **2** and Me₃SiCl, a stronger Lewis acid, AlMe₃, was employed.[43−47] The reaction of **2** with 8 equiv of AlMe₃ was carried out in toluene, at 50 °C, for 16 h. The formation of two major products was observed (Scheme 1). The products were separated and isolated based on their different solubility properties: a hexane extraction led to the previously reported (NN^fc)ScMe(AlMe₃)₂ [**1-Me(AlMe₃)₂**],[35] while a toluene extraction allowed the isolation of a colorless solid, which was identified by NMR spectroscopy, X-ray crystallography, and elemental analysis as the trialuminum complex **3**.

The solid-state structure of **3**, determined by single-crystal X-ray diffraction, is shown in Figure 1. Three pseudotetrahedral aluminum centers featuring similar Al−N distances were found. The average Al−N distance of 1.98 Å compares well to analogous distances in similar multinuclear complexes.[48−51] While the C=C bond from the imine−amide ligand was preserved, the N=C bond was

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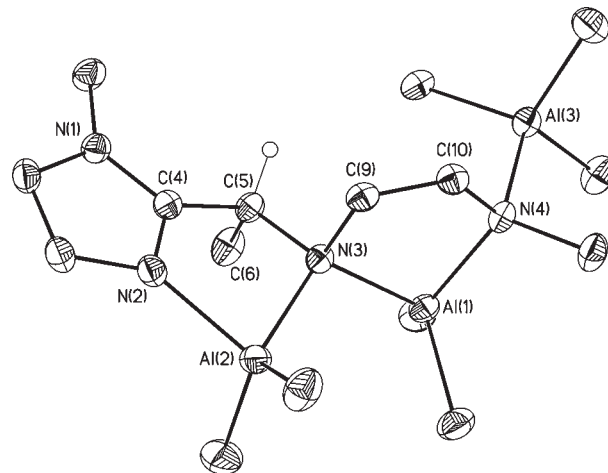
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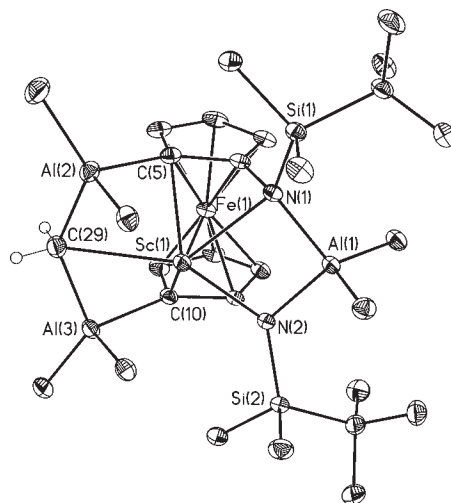
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not, as shown by the presence of the methyl substituent and the pyramidal character of the C(5) and N(3) atoms.

The methyl group that migrated from aluminum to the imine functionality was characterized, in the ^{1}H NMR spectrum of **3**, by a distinct doublet at 1.23 ppm, which corresponded to three protons; a quartet at 4.00 ppm, corresponding to one proton, was assigned to the methine hydrogen atom. Two sets (based on coupling constants) of doublets were identified in the olefinic region, consistent with the presence of the two C=C bonds. The aluminum methyl groups were characterized by a sharp singlet at 0.05 ppm and a broad singlet at −0.33 ppm, representing 3 and 18 protons, respectively. In order to assign the four olefinic peaks of **3**, an HMQC experiment was performed (see the Supporting Information). The protons showing resonances at 5.53 and 4.70 ppm were directly related to peaks at 124.9 and 123.5 ppm in the ^{13}C NMR spectrum, while those with resonances at 5.98 and 5.45 ppm correlated with peaks at 136.4 and 121.9 ppm in the ^{13}C NMR spectrum. We assigned the former set to the isolated C=C moiety and the latter to the imidazole ring, by comparison with the NMR spectral characteristics of **2**.[21] The HMQC spectrum of **3** also confirmed that protons with chemical shifts ranging from 0 to −0.3 ppm corresponded to aluminum methyl groups by correlating those protons to carbon resonances at chemical shifts characteristic of Al−C bonds.[52]

It is proposed that the formation of **3** starts with a methyl migratory insertion[51] from an AlMe₃ fragment, which coordinates to a nitrogen donor to give **3a** (Scheme 1; the AlMe₂ fragment is shown coordinated to the original imine nitrogen, although other formulations for **3a**, with different coordination modes for AlMe₂, are possible). This proposal is supported by the fact that alkyl migratory insertions were observed for uranium analogues of **2**.[20,23,53] The first step is rate determining because using substoichiometric amounts of AlMe₃ did not allow the observation of reaction intermediates. A series of steps, involving transmetalation and AlMe₃ coordination in a sequence that is difficult to predict, leads to **3**. The formation of **3**, with a coordinated AlMe₃ moiety, is likely a consequence of the presence of excess AlMe₃. The coordination of AlMe₃ is reversible, as shown by the fact that, after **3** was dissolved in diethyl ether and left at −33 °C for two weeks, a colorless solid precipitated out from the solution; its ^{1}H NMR spectrum (see the Supporting Information) showed several peaks similar to those for **3**: four doublets in the olefinic region that were shifted from those of **3**, one quartet around 4 ppm, and one doublet at 1.36 ppm corresponding to three protons. There was, however, only one singlet that integrated to three protons in the Al*Me* region. Compound **3b** was less soluble in hydrocarbon solvents than **3**, in agreement with having fewer methyl groups than **3**.

Because **3** transformed into **3b** in the presence of diethyl ether, we became interested in determining whether an equilibrium existed between **3** and AlMe₃ in solution in the absence of an external Lewis base. In addition, although samples of **3** could be obtained analytically

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Figure 2. Thermal-ellipsoid (50% probability) representation of **4**; irrelevant hydrogen atoms were removed for clarity. Selected metrical parameters for **4** (distances in Å and angles in deg): Sc(1)−Fe(1), 2.6580(4); Sc(1)−C(29), 2.6921(18); Sc(1)−N(1), 2.3627(13); Sc(1)−N(2), 2.3334(14); Sc(1)−Al(1), 3.0712(6); Sc(1)−Al(2), 2.6658(6); Sc(1)−Al(3), 2.6773(6); Al(1)−N(1), 1.9578(14); Al(1)−N(2), 1.9612(14); Al(2)−C(29), 1.9765(18); Al(2)−C(5), 2.0743(17); Al(3)−C(29), 1.9738(18); Al(3)−C(10), 2.0763(17); N(1)−Sc(1)−N(2), 78.00(5); N(1)−Sc(1)−C(29), 136.16(5); N(2)− Sc(1)−C(29), 136.53(5); C(5)−Sc(1)−C(10), 94.42(5); N(1)−Sc(1)− C(5), 64.56(5); N(2)−Sc(1)−C(10), 64.81(5); C(5)−Sc(1)−C(29), 73.78(6); C(10)−Sc(1)−C(29), 74.07(5); N(1)−Al(1)−N(2), 97.89(6); Al(2)−C(29)−Al(3), 135.55(10); C(5)−Al(2)−C(29), 97.96(7); C(10)− Al(3)−C(29), 98.58(7).

pure, a set of small peaks, which were similar to those of **3** and different from those of **3b**, were always observed in the ^{1}H NMR spectra of **3** (see the Supporting Information for details). Therefore, a variable-temperature ^{1}H NMR spectroscopy study was conducted (see the Supporting Information for details). Upon heating in C₆D₆ in 10 °C increments, from room temperature to 85 °C, only the expected shifting of peaks with temperature was observed together with a very small change in the ratio of peaks corresponding to **3** and those corresponding to the different species. On the basis of this data, we concluded that any equilibrium in solution between **3** and a form without a coordinated AlMe₃ moiety was not significant in the range of temperatures studied.
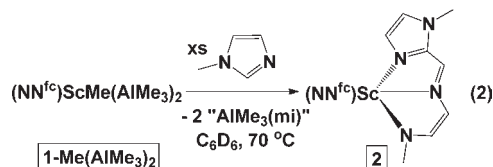
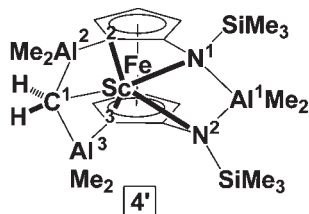Because **1-Me(AlMe₃)₂** is the scandium product of the reaction between **2** and AlMe₃, we were interested in determining whether **1-Me(AlMe₃)₂** can form **2** with 1-methylimidazole. Indeed, the reaction of **1-Me(AlMe₃)₂** with 8 equiv of 1-methylimidazole (mi) in C₆D₆ led to the formation of **2** after 8 h at 70 °C (eq 2). As indicated by ^{1}H NMR spectroscopy, the reaction was quantitative (see the Supporting Information for details). Although AlMe₃ reacts with 1-methylimidazole to form an adduct and thus prevents us from developing a catalytic cycle for the ring opening of 1-methylimidazole, this reaction (eq 2) shows that regeneration of the scandium starting material can be accomplished.

Table 1. Comparison of the Metrical Parameters Calculated for the Model Complex **4′** (ADF) with Those from the X-ray Crystal Structure (Experimental) of **4**

Complex	Parameter	ADF	Experimental
	Sc–C^1	2.68 Å	2.69 Å
	Sc–N^1	2.35 Å	2.36 Å
	Sc–N^2	2.35 Å	2.33 Å
	Sc–C^2	2.42 Å	2.38 Å
	Sc–C^3	2.41 Å	2.39 Å
	Al^2–C^1	2.00 Å	1.98 Å
	Al^3–C^1	2.00 Å	1.97 Å
	Fe–Sc	2.69 Å	2.66 Å
	N^{1}ScN^2	77.4°	78.0°
	C^{1}ScC^2	75.1°	73.8°
	C^{1}ScC^3	74.9°	74.1°
	C^{2}ScC^3	89.7°	94.4°
	Al^{2}C^{1}Al^3	136.8°	135.6°
	N^{1}Al^{1}N^2	95.7°	97.9°

Scandium/Aluminum Methylidene Complex. In order to determine whether different products would be obtained in the reaction between **2** and AlMe$_3$ under conditions other than those described above, the mixture was heated at 85 °C for 48 h, after which ^{1}H NMR spectroscopy indicated the complete disappearance of **2** and then of **1-Me(AlMe$_3$)$_2$**. The formation of a small amount of **3** was observed along with that of a major product, **4** (eq 3; **3** and **4** were likely formed in a 1:1 ratio, but the prolonged heating of the reaction mixture led to the decomposition of **3**). The X-ray crystal structure of **4** (Figure 2) indicated that an interesting scandium methylidene complex supported by AlMe$_2$ fragments was obtained. In addition, the ferrocene diamide ligand became tetraanionic. On the basis of the neutrality of the complex and considering trivalent scandium and aluminum centers, we assigned the moiety containing C(29) as a methylidene.
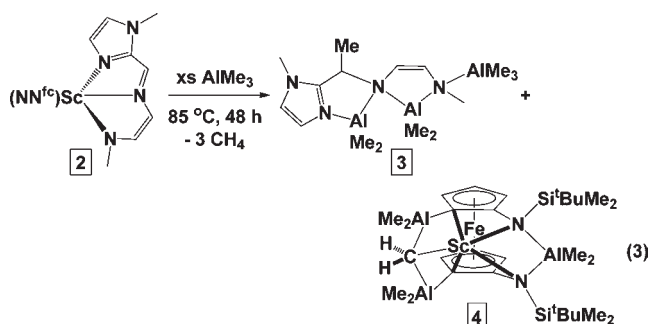
Although group 4−6 metal alkylidenes are relatively well known,[54−57] analogous group 3 metal and lanthanide complexes are scarce.[58,59] The complex **4** is only the second example of a characterized scandium methylidene, with the first being (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$ (PNP = N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2$).[60] Also relevant is the complex (DPPMS$_2$)ScCl(py)$_2$ [DPPMS$_2$ = SP(Ph)$_2$CH$_2$P(Ph)$_2$S], which features a short Sc−C distance to the ancillary ligand and shows nucleophilic carbene character.[61] The two methylidene complexes are both

supported by methylaluminum fragments, a situation encountered for analogous group 3 metal or lanthanide complexes[43,62−64] and for the Tebbe reagent, Cp$_2$Ti[μ_2-CH$_2$)(μ_2-Cl)AlMe$_2$].[65] Another structural similarity between **4** and (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$ is their pseudo-C_s symmetry in the solid state. The most important difference between the two complexes is the Sc−CH$_2$ distance: while this value is 2.3167(17) Å in (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$, it is 2.6921(18) Å in **4**, being longer than the Sc−CH$_3$ distances found in terminal scandium methyl complexes[66] or **1-Me(AlMe$_3$)$_2$** (2.38 Å)[35] and comparing well with the Sc−CH$_3$ distances found in bridging methyl compounds.[67]

Other metrical parameters for **4** also point to an unusual structure. For example, the Fe−Sc distance of 2.6580(4) Å is shorter by 0.36 Å than the sum of the iron and scandium covalent radii (3.02 Å)[68] and by almost 0.15 Å than the corresponding distance in [(NN^{fc})Sc(μ-Cl)]$_2$ [2.7986(7) Å],[35] making it the shortest Fe−Sc distance observed by us so far. The Sc−Al distances [2.6658(6) and 2.6773(6) Å] to the aluminum atoms that bind to the methylidene are also smaller than the sum of the scandium and aluminum covalent radii (2.91 Å).[68] The tetraanionic character of the ferrocene ligand is supported by the fact that the Sc−C distances to the deprotonated carbon atoms of 2.3837(16) Å [C(5)] and 2.3908(16) Å [C(10)] are significantly shorter than to the carbon atoms connected to the amide donors [2.5221(16) and 2.5380(16) Å]. In addition, the Al−C distances to the same carbon atoms of 2.0743(17) Å [C(5)] and 2.0763(17) Å [C(10)] are similar to the Al−C distances to their methyl groups (average of 2.01 Å).

Density functional theory (DFT) calculations were carried out with *ADF2009.01*[69−71] in order to probe the

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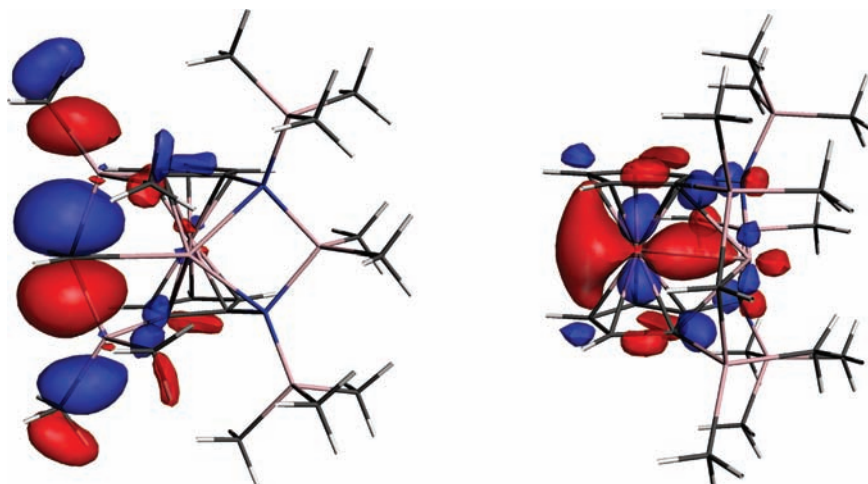(56) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
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Figure 3. HOMO−3 (left) and HOMO−2 (right) for a model (silyl-*tert*-butyl groups were replaced by methyl groups) of **4**.

electronic structure of **4**. Calculations were performed on a model of **4**, **4′**, in which the silyl-*tert*-butyl groups were replaced by methyl. Geometry optimizations were carried out with relativistic corrections, and the results indicated that the model showed metrical parameters similar to those obtained from the X-ray crystal structure of **4** (Table 1).

Given the agreement between the calculated and experimental parameters, **4′** was used as a model to understand the electronic structure of **4**, and the frontier molecular orbitals of **4′** were inspected (Figure 3 and the Supporting Information). HOMO−3 consisted of mostly the methylidene p orbital, indicating that this ligand has ionic character, similar to what was reported for (PNP)Sc-$(\mu_3$-CH$_2)(\mu_2$-Me)$_2$[AlMe$_2$]$_2$.[60] Bond orders were also calculated for comparison. In agreement with the longer Sc−C$_{methylidene}$ distance found in **4**, the Mayer bond order was 0.41, smaller than the corresponding bond order for (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$ (0.83).[60] DFT calculations also support a Sc−Fe interaction: HOMO−2 shows orbital overlap between the two atoms and the Mayer bond order value is 0.46. For reference, similar values were found for the bond orders corresponding to the Sc−N interactions (0.41) and to the scandium ferrocene−C interactions (0.35).

It was reasoned that the formation of **4** may proceed directly from **1-Me(AlMe$_3$)$_2$** and AlMe$_3$. Indeed, the reaction of **1-(CH$_2$Ar)(THF)** with excess AlMe$_3$ (8 equiv) at 85 °C led to **4** after 65 h (Scheme 2). The formation of **1-Me(AlMe$_3$)$_2$** was observed by ^{1}H NMR spectroscopy in the initial stages of the transformation. The correct stoichiometry [4 equiv of AlMe$_3$ vs **1-(CH$_2$Ar)(THF)**] gives similar conversions. One transmetalation [to form **1-Me(AlMe$_3$)$_2$**] and three C−H activations (likely methane liberation) occur by the end of the reaction. Similar C−H activations of the ferrocene cyclopentadienyl groups were observed by us in a uranium complex after heating it for an extensive period of time.[53] Although the formation of **4** from **1-Me(AlMe$_3$)$_2$** is apparently similar to the formation of methylidene or methine products reported by the Anwander

Scheme 2. Formation of **4**
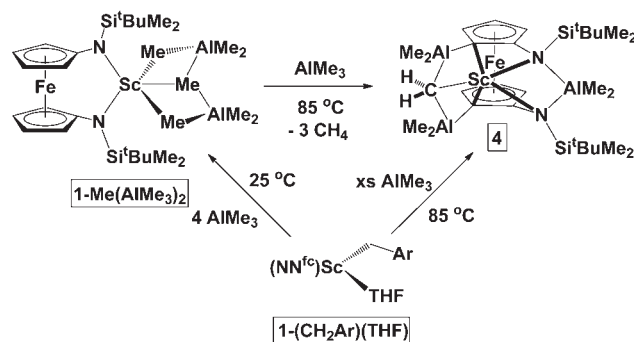
group,[43,62,64] a subtle difference between the two processes exists: in the present case, no Lewis base was added, while in the previous case, a base-induced C−H activation occurs. In principle, the methylidene **4** was formed by Lewis acid induced C−H activation because there is one more AlMe$_3$ unit in **4** than in **1-Me(AlMe$_3$)$_2$**, its starting material.

The methylidene **4** is C_s-symmetric in solution as determined by inspection of its ^{1}H NMR spectrum. Three peaks, which by integration represent two protons each, were found in the ferrocene region, indicating that the two cyclopentadienyl rings are equivalent. Other features, such as a single peak for the *tert*-butyl group and two peaks for SiCH_3 (Figure 2), also supported the symmetry of **4** in solution. The ^{13}C NMR spectrum of **4** was in agreement with its ^{1}H NMR spectrum and showed broad peaks for the carbon atoms directly bound to aluminum because of ^{13}C−^{27}Al coupling. A DEPT-135 experiment was carried out to identify the methylidene carbon atom of **4**; consequently, the peak at −4.7 ppm was assigned to it (see the Supporting Information for details).

A variable-temperature ^{1}H NMR spectroscopy experiment was undertaken to find out if **4** has a fluxional structure at high temperatures. Upon heating a C$_6$D$_6$ solution of **4** from room temperature to 85 °C (see the Supporting Information for details), only a slight shifting of all peaks was observed, indicating that, unlike (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$,[60] **4** does not exhibit fluxional behavior in solution at elevated temperatures. In addition, continued heating at 85 °C for 1 day led to no apparent change, as assessed by ^{1}H NMR spectroscopy.

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Although the Sc−C$_{methylidene}$ distance was fairly long in **4**, we became interested in determining whether the methylidene group could be transferred to suitable substrates. Because (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$ reacted with benzophenone to form the corresponding oxide (PNP)Sc(μ_3-O)(μ_2-Me)$_2$[AlMe$_2$]$_2$ and 1,1-diphenylethylene as an organic byproduct,[60] the same reaction was investigated with **4**. The reaction of **4** with benzophenone, however, was more complicated than in the case of (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$. Besides the 1 equiv of benzophenone necessary to transfer oxygen and form 1,1-diphenylethylene (identified by ^{1}H NMR spectroscopy), 2 equiv more was required to drive the reaction to completion after overnight heating at 50 °C (see the Supporting Information for details). It is likely that the more complicated reaction of **4** with benzophenone than that of (PNP)Sc(μ_3-CH$_2$)(μ_2-Me)$_2$[AlMe$_2$]$_2$ is a consequence of the presence of the doubly C−H activated ferrocene backbone, which might act as a nucleophile and attack the C=O moiety in benzophenone. Unfortunately, attempts to isolate and characterize the scandium product were unsuccessful. A similar situation was encountered by Anwander et al. when they investigated the reaction of a trinuclear yttrium methylidene complex, which required more than 1 equiv of a carbonyl substrate to consume all of the starting material and led to the formation of an intractable mixture of products.[64]

Conclusions. The reaction of the scandium benzyl complex (NN^{fc})Sc(CH$_2$Ar)(THF) [**1-(CH$_2$Ar)(THF)**] with 1-methylimidazole led to the formation of **2** by a series of transformations that were previously discussed.[18,21] The product **2** contains an imidazole−imine−amide moiety; efforts to transfer the heterocyclic ligand from **2** to aluminum were presented. A ring-opened imidazole aluminum compound was isolated at 50 °C and characterized as the trialuminum complex **3**; the scandium product was the methyl complex **1-Me(AlMe$_3$)$_2$**. This complex, **1-Me(AlMe$_3$)$_2$**, reacts, in turn, with 1-methylimidazole to generate **2**. At a high temperature (85 °C), the formation of a scandium/aluminum methylidene, **4**, was observed. The methylidene **4** has a rather unusual structure, featuring a long Sc−C$_{methylidene}$ distance, likely because of multiple interactions with aluminum centers, and a short Sc−Fe distance, which indicated a relatively strong Sc−Fe interaction. All reaction products were characterized by standard spectroscopic techniques and X-ray crystallography. DFT calculations were used to understand the electronic structure of **4** and indicated an ionic character of the methylidene ligand. The scandium/aluminum methylidene **4** is one of the few examples of f-element alkylidene complexes and thus provides an opportunity to understand such complexes.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[72] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories,

degassed three times, and stored over activated molecular sieves prior to use. Scandium oxide was purchased from Stanford Materials Corp., Aliso Viejo, CA, and used as received. **1-(CH$_2$Ar)(THF)**, **1-Me(AlMe$_3$)$_2$**, and **2** were prepared following published procedures.[21,35] NMR spectra were recorded on a Bruker300 or a Bruker500 spectrometer (work supported by the NSF Grants CHE-9974928 and CHE-0116853) at room temperature in C$_6$D$_6$ unless otherwise specified. Chemical shifts are reported with respect to an internal solvent (C$_6$D$_6$). CHN analyses were performed by Midwest Microlab, LLC, Indianapolis, IN.

Synthesis of 3. 2 (280.5 mg, 0.431 mmol) and 8 equiv of AlMe$_3$ (248.6 mg, 3.449 mmol) were combined in 5 mL of toluene in a Schlenk tube and stirred at 50 °C overnight. The volatiles were removed under reduced pressure, and the remaining solid was washed with hexanes. The suspension was filtered through Celite, the hexanes fraction was discarded, and the rest of the solid was extracted in toluene. A crude product was obtained by removing the volatiles from the toluene extraction. The product **3** was purified by recrystallization at −35 °C from toluene/hexanes. Yield: 93.8 mg, 61.7%. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 5.98 and 5.45 (d, J_{HH} = 0.84 Hz, 2H, mi−C*H*=C*H*), 5.53 and 4.70 (d, J_{HH} = 2.74 Hz, 2H, C*H*=C*H*), 4.00 (q, 1H, Me−C*H*), 2.55 and 2.00 (s, 6H, NC*H*$_3$), 1.23 (d, 3H, CH−C*H*$_3$), −0.05, −0.28, −0.30, and −0.31 (s, 21H, all AlC*H*$_3$). ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 154.9 (*C*=N), 136.4 and 121.9 (mi−*C*H*C*H), 124.9 and 123.5 (*C*H*C*H), 56.9 (Me−*C*H), 37.8 and 31.8 (N*C*H$_3$), 20.1 (CH−*C*H$_3$), −5.1, −5.8, −7.8, −8.5, and −9.2 (all Al*C*H$_3$). Anal. Calcd for C$_{16}$H$_{35}$N$_4$Al$_3$: C, 52.73; H, 9.68; N, 15.37. Found: C, 52.49; H, 9.57; N, 15.04.

Reaction of 2 with a Substoichiometric Amount of AlMe$_3$. Two J. Young tubes were each filled with **2** (20.0 mg, 0.0307 mmol) in C$_6$D$_6$. To the first was added a 0.045 mL C$_6$D$_6$ solution of AlMe$_3$ (0.686 M, 1 equiv), and to the second was added 0.090 mL of the same AlMe$_3$ solution (2 equiv). The two J. Young tubes were then immersed in a 50 °C bath. The reactions were monitored by ^{1}H NMR spectroscopy simultaneously. After 6 h at 50 °C, the first reaction reached 20% conversion (forming **1-Me(AlMe$_3$)$_2$** and **3**) based on the integration of **3** and starting material **2**, while the second reached 40% conversion. To the two J. Young tubes was then added 0.090 mL (2 equiv) of the same AlMe$_3$ solution at the same time, and they were reintroduced into the 50 °C bath. After 7 h at 50 °C, the two reactions reached 60% and 80% conversion, respectively. Again, to the two J. Young tubes were added 0.090 mL (2 equiv) and 0.045 mL (1 equiv) of the AlMe$_3$ stock solution, respectively. At this moment, both reactions had 5 equiv of AlMe$_3$, calculated from the initial point. After heating at 50 °C for an additional 7 h, both reactions reached completion with the formation of an equal amount of **1-Me(AlMe$_3$)$_2$** and **3**.

Transformation of 3 to 3b in Diethyl Ether. 3 (15.0 mg, 0.0426 mmol) was dissolved in 4 mL of diethyl ether and then kept in a freezer at −35 °C for 2 weeks. A colorless crystalline precipitate formed from the diethyl ether solution. The mother liquor was decanted, and the solid was washed with 2 mL of *n*-pentane. Yield: 8.7 mg, 58.6%. Compound **3b** was characterized by its similar but shifted peaks compared to **3** in the olefinic and aromatic regions and a single peak in the Al*Me* region that integrated to 3H against each olefinic peak that integrated to 1H.

Reaction of 1-Me(AlMe$_3$)$_2$ with 1-Methylimidazole (mi). **1-Me(AlMe$_3$)$_2$** (92.0 mg, 0.141 mmol) was combined with an excess of 1-methylimidazole (88.0 mg, 1.07 mmol) in C$_6$D$_6$ in a J. Young tube. The reaction mixture was heated to 70 °C and monitored by ^{1}H NMR spectroscopy. The solution turned to dark purple in 1 h, indicating the formation of **2**. After heating at 70 °C for 6 h, there was no starting material (**1-Me(AlMe$_3$)$_2$**) present, with **2** as the only product containing the ferrocene diamide ligand. Heating for a prolonged time (24 h) did not result in the formation of the transmetalation product **3**

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(or any of its forms), indicating that "AlMe$_3$(mi)" was inactive under the reaction conditions. The reaction mixture was worked up by removing the volatiles under reduced pressure. Efforts were made to isolate **2** in pure form. The side products, "AlMe$_3$(mi)", however, were not volatile and had solubility properties similar to those of **2**; therefore, the attempts to isolate pure **2** were not successful.

Reaction of 2 with AlMe$_3$ at 85 °C. 2 (20 mg, 0.031 mmol) was dissolved in 0.5 mL of C$_6$D$_6$ in a J. Young NMR tube, and 8 equiv of AlMe$_3$ (18 mg, 0.250 mmol) was added. The J. Young tube was first immersed in a 70 °C oil bath for 3 h and then in an 85 °C bath for 2 days and monitored by ^{1}H NMR spectroscopy routinely. After 45.5 h at 85 °C, ^{1}H NMR did not indicate new changes of the reaction mixture. The volatiles were removed under reduced pressure, and the remaining solid was washed with hexanes. The suspension was filtered through Celite, and the rest of the solid was extracted in toluene. The byproduct **3** was obtained mainly in the toluene fraction. A small amount of white **3** was crystallized out from the hexanes fraction at −35 °C. The yellow hexanes solution was decanted and placed at −35 °C. X-ray-quality crystals were formed from the solution overnight. X-ray diffraction indicated those crystals to be **4**.

Synthesis of 4. 1-(CH$_2$Ar)(THF) (179.7 mg, 0.265 mmol) and 8 equiv of AlMe$_3$ (152.7 mg, 2.118 mmol) were combined in 5 mL of toluene in a Schlenk tube and stirred at 85 °C for 65 h. The volatiles were removed under reduced pressure, and the remaining yellow solid was dissolved in 25 mL of hexanes. The solution was filtered through Celite. The resulting yellow solution contained both **4** and the byproduct Me$_2$Al(CH$_2$Xy-3,5) as determined by ^{1}H NMR spectroscopy. Because of the similar solubility properties of **4** and Me$_2$Al(CH$_2$Xy-3,5) in hexanes, crystals of **4** were collected from a series of recrystallizations. The first crop yielded 71.0 mg, 40.6%. The mother liquid was then concentrated to yield a second crop of 51.1 mg, 29.2%. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 4.43 and 4.40 (d, 4H, C*H*CHC*H* on Cp ring), 4.05 (t, 2H, CHC*H*CH on Cp ring), 1.04 (s, 18H, SiCC*H*$_3$), 0.35 and 0.06 (s, 12H, SiC*H*$_3$), −0.12 and −0.18 (s, 12H, CH$_2$AlC*H*$_3$), −0.12 and −0.22 (s, 6H, NAlC*H*$_3$), −1.35 and −1.42 (d, J_{HH} = 6.40 Hz, 2H, AlC*H*$_2$Al). ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 102.7 (*C*N on Cp ring), 96.7 (*C*Al on Cp ring), 87.6 (*C*HCHCH on Cp ring), 75.6 and 75.3 (*C*HCH*C*H on Cp ring), 28.7 (Si*C*CH$_3$), 22.8 (SiC*C*H$_3$), 11.1 and −10.7 (*C*H$_2$Al*C*H$_3$), −0.4 and −1.5 (Si*C*H$_3$), −0.8 and another peak overlapping with the peak at −0.4 (NAl*C*H$_3$), −4.2 (Al*C*H$_2$Al). Anal. Calcd for C$_{29}$H$_{56}$N$_2$Al$_3$FeScSi$_2$: C, 51.93; H, 8.42; N, 4.18. Found: C, 51.64; H, 8.18; N, 3.97.

Reaction of 4 with Benzophenone. 4 (8.6 mg, 0.013 mmol) and 3.6 equiv of benzophenone (8.3 mg, 0.046 mmol) were dissolved in C$_6$D$_6$ and heated to 50 °C. The reaction was monitored by ^{1}H NMR spectroscopy. The peak at 5.37 ppm, which is characteristic of the olefinic protons of 1,1-diphenylethylene, and the disappearance of the peaks in the ferrocene region of **4** were used to indicate the progress of the reaction. Although the methylidene proton resonance broadened immediately and disappeared shortly after, the formation of 1,1-diphenylethylene and consumption of **4** were rather slow. After heating at 50 °C for 50 h, the reaction reached completion. Based on integration of the spectrum for the reaction mixture, 3 equiv of benzophenone were consumed and 1 equiv of 1,1-diphenylethylene was formed.

X-ray Crystal Structures. X-ray-quality crystals were obtained from various concentrated solutions placed in a −35 °C

freezer in the glovebox. Inside the glovebox, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glovebox. The X-ray data collections were carried out on a Bruker AXS single-crystal X-ray diffractometer using Mo Kα radiation and a SMART APEX CCD detector. The data were reduced by *SAINT-PLUS*, and an empirical absorption correction was applied using the package *SADABS*. The structures were solved and refined using *SHELXTL* (Bruker 1998; *SMART*, *SAINT*, *XPREP*, and *SHELXTL*, Bruker AXS Inc., Madison, WI). All atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions unless specified otherwise. Tables with atomic coordinates and equivalent isotropic displacement parameters, with all of the bond lengths and angles, and with anisotropic displacement parameters are listed in the CIFs.

X-ray Crystal Structure of 3. X-ray-quality crystals were obtained from a concentrated toluene solution layered with hexanes. A total of 3806 reflections (−19 ≤ h ≤ 19, −10 ≤ k ≤ 10, −28 ≤ l ≤ 28) was collected at T = 100(2) K with 2θ$_{max}$ = 56.63°, of which 2813 were unique (R_{int} = 0.0424). The residual peak and hole electron density were 0.19 and −0.16 e A^{-3}. The least-squares refinement converged normally with residuals of R1 = 0.0378 and GOF = 0.920. Crystal and refinement data for **3**: formula C$_{16}$H$_{35}$N$_4$Al$_3$, monoclinic, space group $P2_1/c$, a = 14.598(3) Å, b = 7.5247(14) Å, c = 21.711(4) Å, β = 109.531(2)°, V = 2247.6(7) Å^3, Z = 4, μ = 0.173 mm^{-1}, F(000) = 792, R1 = 0.0563, wR2 = 0.0899 (for all data).

X-ray Crystal Structure of 4. X-ray-quality crystals were obtained from a concentrated hexanes solution. A total of 10 226 reflections (−21 ≤ h ≤ 21, −14 ≤ k ≤ 15, −30 ≤ l ≤ 30) was collected at T = 100(2) K with 2θ$_{max}$ = 61.56°, of which 8025 were unique (R_{int} = 0.0356). The residual peak and hole electron density were 0.55 and −0.50 e A^{-3}. The least-squares refinement converged normally with residuals of R1 = 0.0338 and GOF = 1.030. Crystal and refinement data for **4**: formula C$_{29}$H$_{56}$N$_2$Si$_2$ScFeAl$_3$, monoclinic, space group $P2_1/c$, a = 15.3292(14) Å, b = 10.7618(10) Å, c = 21.784(2) Å, β = 104.223(1)°, V = 3483.5(6) Å^3, Z = 4, μ = 0.777 mm^{-1}, F(000) = 1432, R1 = 0.0480, wR2 = 0.0922 (for all data).

DFT Calculations. The Amsterdam Density Functional (ADF) package (version *ADF2009.01*) was used to do geometry optimizations on Cartesian coordinates of the model compounds specified in the text. For all atoms, standard triple-ζ STA basis sets from the ADF database ZORA TZP were employed with 1s2p (Si, Al), 1s3p (Fe, Sc), and 1s (N, C) electrons treated as frozen cores. The local density approximation by Becke−Perdew was used together with the exchange and correlation corrections that are employed by default by the *ADF2009.01* program suite. Calculations were carried out using the scalar spin−orbit relativistic formalism.

Supporting Information Available: Experimental details for compound characterizations, full crystallographic descriptions (such as CIF), and DFT computational details. This material is available free of charge via the Internet at http://pubs.acs.org.