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Tebbe-like and Phosphonioalkylidene and -alkylidyne Complexes of Scandium

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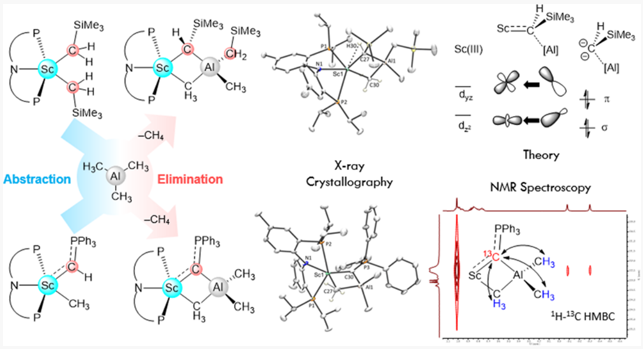
ABSTRACT: The bonding between scandium and carbon in a series of alkylidene- and alkylidyne-like moieties is compared. The Tebbe analogue complex (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (**2**) (PNP$^-$ = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2$) could be formed by adding AlMe$_3$ to (PNP)Sc(CH$_2$SiMe$_3$)$_2$ (**1**). The fluxional behavior of **2** is studied by a combination of 2D ^{13}C−^{1}H HMQC, HMBC, and other heteronuclear NMR spectroscopic experiments. The phosphonioalkylidene complex (PNP)Sc(CHPPh$_3$)(CH$_3$) (**3**) could be prepared from **2** by treatment with 2 equiv of the ylide H$_2$CPPh$_3$ or by methane elimination from (PNP)Sc(CH$_3$)$_2$ and 1 equiv of H$_2$CPPh$_3$. The reactivity of the alkylidene in **2** was further explored with N$_3$Ad, which gave insertion at the Sc−C bond, yielding (PNP)Sc(CH$_3$)[η^2-N$_3$AdCHSiMe$_3$Al(CH$_3$)(CH$_2$SiMe$_3$)] (**4**), while DMAP provided C−H activation across the alkylidene with loss of the Al−C bond to form (PNP)Sc(η^2-NC$_5$H$_3$NMe$_2$)(CH$_2$SiMe$_3$) (**5**). Utilizing the same approach that yielded **2**, methane elimination in **3** could further be promoted with Al(CH$_3$)$_3$ to furnish the first example of a scandium phosphonioalkylidyne complex, (PNP)Sc(μ_2-CPh$_3$)(μ_2-CH$_3$)Al(CH$_3$)$_2$ (**6**). Experimental and theoretical studies were combined to compare the bonding in **2**, **3**, and **6**, in order to understand the legitimacy of Sc−C multiple bond character.



INTRODUCTION

The nature of the metal−carbon multiple bonds involving rare-earth (RE) ions is an ongoing topic of debate. The empty orbitals of these metals are highly contracted f-orbitals and/or very high-energy d-orbitals, characteristics precluding formation of strong, covalent bonds with carbon-centered orbitals. In other words, the metal is commonly a hard Lewis acid, whereas the carbon-containing ligand is a soft Lewis base. While terminally bound RE alkylidenes can be generated in the gas phase via reaction with methane,[1a,b] there is a dearth of examples of RE systems featuring a legitimate π-bond between the two atoms in the condensed phase. Because the alkylidene moieties tend to bridge and/or oligomerize (Figure 1a),[2a−f] one strategy for stabilizing mononuclear systems is the use of metallacycles or rings, but this approach often diminishes the reactivity at the M═C bond in question (Figure 1b).[3a−e] An abstraction/elimination approach using trialkylaluminum reagents has also been employed to target such structures; however, more than one Al center may bind to the highly nucleophilic carbon, significantly diminishing the RE−C bond order (Figure 1c).[4a−f] Interestingly, the only crystallographically characterized example of a RE alkylidene that involves bridging strictly between two centers of different metals is Cp′(py)Sc(μ_2-CHSiMe$_3$)(μ_2-N^{t}Bu)IrCp* (Cp′ = C$_5$Me$_4$SiMe$_3$, Cp* = C$_5$Me$_5$) (Figure 1d).[5] More recently, the first examples of terminally bound RE-alkylidene structures have been obtained by delocalizing the excess charge within the metal−carbon−heteroatom multiple bonds, where the

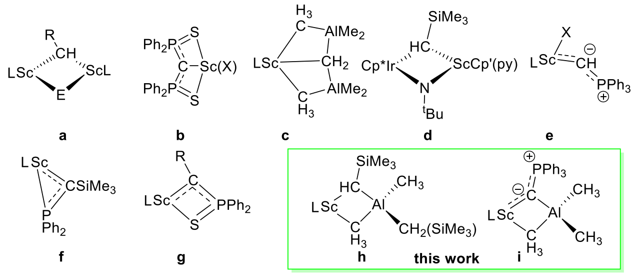


Figure 1. Bonding modes of alkylidenes or nucleophilic carbenes to the Sc(III) ion.

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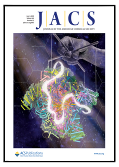

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heteroatom in question can be a phosphonium, PPh_3^{2+} (Figure 1e).[6] These systems avoid chelation of other heteroatom fragments, such as phosphino groups (PPh_2, Figure 1f),[3e] which sometimes compromise the reactive nature of the Sc−C multiple bonds, as in the case of $[P(S)Ph_2]^+$ (Figure 1g).[3d] Similar strategies have enabled isolation of rare and otherwise highly reactive titanium alkylidyne structures supported by either stabilization with trimethylaluminum, (PNP)Ti(μ_2-C^{t}Bu)(μ_2-CH_3)$AlMe_2$,[7a] or with a phosphonium substituent in the form of (PNP)Ti≡$CPPh_2Me$(OTf).[7b] Hence, we sought to extend this methodology to the synthesis of complexes containing scandium−carbon multiple bonds, utilizing the same pincer ligand. We report an $AlMe_3$-stabilized alkylidene that closely mirrors the structure of the iconic Tebbe reagent $Cp_2Ti(\mu_2\text{-}Cl)(\mu_2\text{-}CH_2)Al(CH_3)_2$ (Figure 1h).[8] We also explored the reactivity of the new reagent and compared its structure and bonding to those of the covalently linked PPh_3^{2+} (phosphoniomethylidene). Finally, we showcase the utility of $Al(CH_3)_3$ by integrating the two groups and disclose the first example of a phosphonioalkylidyne complex of scandium (Figure 1i).

■ EXPERIMENTAL SECTION

General Procedures. All operations were performed in an M. Braun glovebox or using standard Schlenk techniques under a nitrogen atmosphere unless otherwise stated. Anhydrous hydrocarbon solvents were purchased from Fisher Scientific. All anhydrous hydrocarbon solvents (pentane, hexanes, toluene, benzene) were purified and dried by passage through two columns of activated alumina and Q-5 drying agent in a two-column solvent system. All bulk solvents were kept over sodium and 4 Å molecular sieves. Toluene-d_8 and benzene-d_6 (Cambridge Isotope Laboratories) were dried and degassed over a potassium mirror prior to use. Celite and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. H_2CPPh_3,[9] (PNP)$ScCl_2$,[10] and (PNP)$Sc(CH_3)_2$[10] were prepared according to previous reports. $[H_3{}^{13}CPPh_3][I]$ was prepared from $^{13}CH_3I$ (Sigma-Aldrich, 99 atom % ^{13}C) and PPh_3 in THF and then deprotonated under identical conditions using the unlabeled derivative $[H_3CPPh_3][I]$. All other chemicals were purchased from commercial sources and degassed before being used. ^1H, ^{13}C, ^{31}P, ^{29}Si, HSQC, HMBC, and COSY NMR spectral data were recorded on Bruker AVII and AVIII 500 MHz, DRX 500 MHz, or AV-III 400 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are reported referenced to the internal residual proton, deuterium, or carbon resonances of toluene-d_8 (δ = 2.08 or 20.43) or benzene-d_6 (δ = 7.15 or 128.06). ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (δ = 0.0). ^{29}Si NMR chemical shifts are reported with respect to external $Si(CH_3)_4$ (δ = 0.0).

Statement on Elemental Analyses (EA). Each of the compounds that could be purified without significant impurities were submitted for EA to Midwest Microlab, each returning extremely low carbon values despite the request to use a combustion aid, and possibly attributable to formation of carbides. In the interest of transparency, those results are listed here. Comprehensive NMR spectral data of each compound are presented in the Supporting Information (SI), in lieu of EA and as proof of the bulk purity of material constitutions, which match those of the corresponding single-crystal X-ray diffraction structures being presented.

Synthesis of (PNP)Sc(CH_2SiMe_3)$_2$ (1). In 10 mL of toluene was suspended 300 mg (551 μmol) of (PNP)$ScCl_2$, and then this mixture was cooled to −35 °C. In a separate vessel, 104 mg (1.10 mmol) of $LiCH_2(SiMe_3)$ was dissolved in toluene and cooled to −35 °C. The cold solution of $LiCH_2(SiMe_3)$ was added dropwise to the suspension of (PNP)$ScCl_2$ with vigorous stirring. After being allowed to stir for 1.5 h, while coming to ambient temperature, the toluene was evacuated, leaving a cloudy oil, to which 1 mL of pentane was added; the mixture was stirred and evacuated again. The product was extracted with pentane (∼10 mL), filtered through Celite, concentrated to a volume of ∼2 mL (the solution appears very viscous as it is evaporating), and then placed into a −35 °C freezer overnight. Yellow crystals grow from which the mother liquor can be decanted, and then the crystals were rinsed with ∼0.5 mL of −35 °C pentane and dried under vacuum. This yielded 319 mg (492 μmol, 89.3%) of the product. ^1H NMR (500 MHz, benzene-d_6, 300 K): δ 7.06 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HP}$ = 4.2 Hz; 2 H, PNP aryl), 6.88 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.8 Hz; 2H, PNP aryl), 6.83 (d br, 2H, PNP aryl), 2.14 (s, 6H, PNP tolyl CH_3), 2.10 (m, 4H, ^{i}Pr $CH(CH_3)_2$), 1.22 (multiple overlapping resonances, 18H, ^{i}Pr $CH(CH_3)_2$), 0.85 (dd, $^3J_{HH}$ = 6.7 Hz, $^3J_{PH}$ = 9.3 Hz, 6H, ^{i}Pr $CH(CH_3)_2$), 0.49 (d, $^2J_{HH}$ = 11.3 Hz, 2H, −CH*H*−$SiMe_3$), 0.41 (d, $^2J_{HH}$ = 11.3 Hz, 2H, −*C*HH−$SiMe_3$), 0.35 (s, 13H, $Si(CH_3)_3$). ^{13}C NMR (101 MHz, benzene-d_6, 300 K): δ 159.75 (t, J_{PC} = 10.9 Hz; Ar), 133.17 (Ar), 133.03 (Ar), 128.00 (overlaps with solvent, Ar), 120.11 (t, J_{PC} = 3.3 Hz, Ar), 116.59 (dd, J_{PC} = 11.7, 8.8 Hz, Ar), 55.05 (br, $-CH_2Si(CH_3)_3$), 24.09 (t, J_{PC} = 2.7 Hz, ^{i}Pr $CH(CH_3)_2$), 20.81 (PNP tolyl CH_3), 20.29 (t, J_{PC} = 3.3 Hz, ^{i}Pr $CH(CH_3)_2$), 19.92 (t, J_{PC} = 3.6 Hz, ^{i}Pr $CH(CH_3)_2$), 19.77 (dd, J_{PC} = 6.3, 5.1 Hz, ^{i}Pr $CH(CH_3)_2$), 19.06 (t, J_{PC} = 5.9 Hz, ^{i}Pr $CH(CH_3)_2$), 16.25 (t, J_{PC} = 2.8 Hz, ^{i}Pr $CH(CH_3)_2$), 4.48 ($-CH_2-Si(CH_3)_3$). ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K): δ −4.66. $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 300 K): δ −1.41 (br, $\Delta\nu_{1/2}$ = 52 Hz). Anal. Calcd: C, 63.03; H, 9.65; N, 2.16. Found: C, 52.89; H, 9.14; N, 1.10.

Synthesis of (PNP)Sc(μ_2-$CHSiMe_3$)(μ_2-CH_3)[Al(CH_3)(CH_2SiMe_3)] (2). A 284 mg (438 μmol) portion of (PNP)Sc(CH_2SiMe_3)$_2$ was dissolved in ∼7 mL of pentane, and then while stirring vigorously, 219 μL of a 2 M hexanes solution of $Al(CH_3)_3$ (438 μmol) was added. This was allowed to stir for 1 h, and then the solution was filtered through glass fiber, concentrated to saturation (0.5−1 mL volume; the solution appears viscous as it is evaporating), and placed into a −35 °C freezer. Yellow crystals were obtained over time. After sitting for 2 days, 267 mg (379 μmol, 86.7%) could be collected following decantation of the mother liquor and rinsing the crystals with ∼0.5 mL of −35 °C pentane and drying under vacuum. ^1H NMR (500 MHz, benzene-d_6, 300 K): δ 7.37 (br, 1H, PNP aryl), 7.03 (d br, 1H, PNP aryl), 6.87 (br, 1H, PNP aryl), 6.81 (br, 2H, PNP aryl), 6.71 (br, PNP aryl), 2.26 (br, 1H, ^{i}Pr $CH(CH_3)_2$), 2.17 (s, 3H, PNP tolyl CH_3), 2.08 (s, 3H, PNP tolyl CH_3), 1.97 (br, 2H, ^{i}Pr $CH(CH_3)_2$), 1.57 (br, 1H, ^{i}Pr $CH(CH_3)_2$), 1.45 (d br, 3H, ^{i}Pr $CH(CH_3)_2$), 1.32 (d br, 3H, ^{i}Pr $CH(CH_3)_2$), 1.19 (d br, 3H, ^{i}Pr $CH(CH_3)_2$), 1.08 (d br, 3H, ^{i}Pr $CH(CH_3)_2$), 0.93 (br, 3H, ^{i}Pr $CH(CH_3)_2$), 0.80 (d br, 4H: 3H ^{i}Pr $CH(CH_3)_2$ + 1H Sc−CH−$Si(CH_3)_3$), 0.67 (br, 6H, ^{i}Pr $CH(CH_3)_2$), 0.48 (s, 9H, $Si(CH_3)_3$), 0.07 (s. 9H, $Si(CH_3)_3$), −0.38 (br, 2H, $-CH_2(Si(CH_3)_3$). ^{13}C NMR (101 MHz, benzene-d_6, 300 K): δ 161.49 (d br, Ar), 155.10 (d br, Ar), 137.25 (Sc-CH($Si(CH_3)_3$), 133.72 (Ar), 133.59 (Ar), 132.95 (Ar), 132.31 (Ar), 131.78 (Ar), 125.91 (Ar), 125.44 (Ar), 118.83 (d br, Ar), 114.51 (Ar), 114.31 (d br, overlapping with neighboring signal, Ar), 24.71 (br, 2C, ^{i}Pr $CH(CH_3)_2$), 21.03 (PNP tolyl CH_3), 20.81 (^{i}Pr $CH(CH_3)_2$), 20.75 (PNP tolyl CH_3), 20.55 (^{i}Pr $CH(CH_3)_2$), 19.95 (2C, ^{i}Pr $CH(CH_3)_2$), 19.11 (m br, 3C, ^{i}Pr $CH(CH_3)_2$, ^{i}Pr $CH(CH_3)_2$), 18.38 (2C, ^{i}Pr $CH(CH_3)_2$), 16.54 (^{i}Pr $CH(CH_3)_2$), 4.90 ($Si(CH_3)_3$), 3.56 ($Si(CH_3)_3$). ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K): δ −15.08 (a second, weak signal is revealed at 0.97 using an $^1H-^{29}Si$ HMBC experiment; see the SI). $^{31}P\{^1H\}$ NMR (162 MHz, benzene-d_6, 300 K): δ 7.10 (br $\Delta\nu_{1/2}$ = 129 Hz, PNP), −1.21 (br, $\Delta\nu_{1/2}$ = 92 Hz, PNP). Anal. Calcd: C, 61.42; H, 9.59; N, 1.99. Found: C, 59.25; H, 9.67; N, 1.70.

Synthesis of (PNP)Sc($CHPPh_3$)(CH_3) (3). In 8 mL of toluene was dissolved 184 mg (366 μmol) of (PNP)$Sc(CH_3)_2$ and the mixture cooled to −35 °C. In a separate vessel, 101 mg (366 μmol) of H_2CPPh_3 was dissolved into 8 mL of toluene and the mixture cooled to −35 °C. Once both mixtures were cold, the H_2CPPh_3 solution was added dropwise to the (PNP)$Sc(CH_3)_2$ solution with vigorous stirring. This mixture was stirred for 2 h, being allowed to come to ambient temperature, and then concentrated under vacuum to a volume of ∼4 mL and filtered through Celite, after which ∼4 mL of pentane was added. This new solution was concentrated to a total volume of ~3 mL and placed into a −35 °C freezer. After sitting in the freezer overnight, yellow crystals, with a slightly orange tint, grew and were separated from the mother liquor, rinsed with ~0.5 mL of −35 °C toluene and ~0.5 mL of −35 °C pentane, and dried under vacuum. This first crop of crystals yields 156 mg (204 μmol, 55.9%); the decanted solution and rinses could be combined and concentrated further and recrystallized to yield 64 mg more product for a total yield of 220 mg (288 μmol, 78.8%). ^{1}H NMR (500 MHz, benzene-d_6, 300 K): δ 7.72 (m, 6H, *o*-H *Ph*–PPh$_2$–CH–Sc), 7.36 (dd, $^{3}J_{\mathrm{HH}}$ = 8.6 Hz, $^{4}J_{\mathrm{HP}}$ = 4.4 Hz; 1H, PNP aryl), 7.19 (dd, $^{3}J_{\mathrm{HH}}$ = 8.6 Hz, $^{4}J_{\mathrm{HP}}$ = 4.7 Hz; 1H, PNP aryl), 7.08–7.05 (m, 9H, *m,p*-H *Ph*–PPh$_2$–CH–Sc), 6.98–6.96 (m, 2H, PNP aryl, two different positions on same ring overlapping), 6.92–6.90 (m, 2H, PNP aryl, two different positions on same ring overlapping), 3.42 (d, $^{2}J_{\mathrm{HP}}$ = 14.1 Hz, 1H, Sc–C*H*–PPh$_3$), 2.21 (s, 3H, PNP tolyl CH_3), 2.20–2.15 (m, 1H, ^{i}Pr C*H*(CH$_3$)$_2$, overlapping with tolyl peaks), 2.18 (s, 3H, PNP tolyl CH_3), 2.10 (m, 1H, ^{i}Pr C*H*(CH$_3$)$_2$, overlapping with residual toluene signal), 2.00–1.92 (m, 2H, ^{i}Pr C*H*(CH$_3$)$_2$), 1.29–1.13 (m, 18H, ^{i}Pr CH(CH_3)$_2$), 0.97 (dd, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, $^{3}J_{\mathrm{HP}}$ = 3.7 Hz; 3H, ^{i}Pr CH(CH_3)$_2$), 0.95 (dd, $^{3}J_{\mathrm{HH}}$ = 7.0 Hz, $^{3}J_{\mathrm{HP}}$ = 4.3 Hz; 3H, ^{i}Pr CH(CH_3)$_2$), 0.23 (t, $^{3}J_{\mathrm{HP}}$ = 1.9 Hz; 3H, Sc–CH_3). ^{13}C NMR (101 MHz, benzene-d_6, 300 K): δ 161.90 (d, $^{2}J_{\mathrm{CP}}$ = 21.7 Hz; PNP Ar), 160.19 (dd, $^{2}J_{\mathrm{CP}}$ = 21.4 Hz, $^{4}J_{\mathrm{CP}}$ = 2.3 Hz; PNP Ar), 137.56 (d, $^{1}J_{\mathrm{CP}}$ = 78.8 Hz; *ipso*-C *Ph*–PPh$_2$–CH–Sc), 133.39 (d, J_{CP} = 1.85 Hz; PNP Ar), 133.27 (d, J_{CP} = 1.3 Hz; PNP Ar), 132.78 (d, J_{CP} = 1.5 Hz; PNP Ar), 132.74 (d, J_{CP} = 1.3 Hz; PNP Ar), 132.66 (d, $^{2}J_{\mathrm{CP}}$ = 9.4 Hz; *o*-C *Ph*–PPh$_2$–CH–Sc), 129.79 (d, $^{3}J_{\mathrm{CP}}$ = 2.7 Hz; *p*-C *Ph*–PPh$_2$–CH–Sc), 128.13 (*m*-C *Ph*–PPh$_2$–CH–Sc), 127.63 (d, J_{CP} = 3.3 Hz; PNP Ar), 125.30 (d, J_{CP} = 3.5 Hz; PNP Ar), 121.85 (d, $^{3}J_{\mathrm{CP}}$ = 6.2 Hz; PNP Ar), 119.51 (d, $^{1}J_{\mathrm{CP}}$ = 18.3 Hz; PNP Ar), 117.88 (d, $^{3}J_{\mathrm{CP}}$ = 7.0 Hz; PNP Ar), 116.88 (d, $^{1}J_{\mathrm{CP}}$ = 18.6 Hz; PNP Ar), 73.99 (br, Sc–CH–PPh$_3$), 33.85 (br, Sc–CH$_3$), 24.20 (2C overlapping, ^{i}Pr CH(CH$_3$)$_2$), 20.96 (PNP tolyl CH$_3$), 20.78 (PNP tolyl CH$_3$), 20.28 (d, $^{3}J_{\mathrm{CP}}$ = 7.4 Hz; ^{i}Pr CH(CH$_3$)$_2$), 20.15 (d, $^{3}J_{\mathrm{CP}}$ = 6.0 Hz; ^{i}Pr CH(CH$_3$)$_2$), 20.05 (d, $^{3}J_{\mathrm{CP}}$ = 8.6 Hz; ^{i}Pr CH(CH$_3$)$_2$), 19.83 (d, $^{3}J_{\mathrm{CP}}$ = 7.2 Hz; ^{i}Pr CH(CH$_3$)$_2$), 19.33 (d obscured by neighboring signal, ^{i}Pr CH(CH$_3$)$_2$), 19.27 (2C overlapping, ^{i}Pr CH(CH$_3$)$_2$), 19.14 (d, $^{2}J_{\mathrm{CP}}$ = 4.5 Hz; ^{i}Pr CH(CH$_3$)$_2$), 17.04 (d, $^{3}J_{\mathrm{CP}}$ = 4.2 Hz; ^{i}Pr CH(CH$_3$)$_2$), 16.27 (d, $^{3}J_{\mathrm{CP}}$ = 5.6 Hz; ^{i}Pr CH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K): δ 5.10 (–CH–*P*Ph$_3$), 2.94 (br, $\Delta\nu_{1/2}$ = 80 Hz, PNP), 2.04 (br, $\Delta\nu_{1/2}$ = 69 Hz, PNP). Anal. Calcd: C, 72.33; H, 7.79; N, 1.83. Found: C, 62.81; H, 7.61; N, 1.16.

Synthesis of (PNP)Sc(CH$_3$)[η^2-N$_3$AdCHSiMe$_3$Al(CH$_3$)(CH$_2$SiMe$_3$)] (4). (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (189 mg, 268 μmol) and N$_3$Ad (47 mg, 265 μmol) were placed into a vial with a stir bar, dissolved in 7 mL of pentane and 3 mL of toluene, and allowed to stir for 1 h. The solution was concentrated to a volume of ~2 mL, filtered through glass fibers, and then placed in the −35 °C freezer for recrystallization. Pale yellow microcrystalline product deposits itself on the bottom of the vial, which is washed with −35 °C pentane/toluene (50/50) and dried under vacuum, giving 94 mg of product (107 μmol, 39.8%, ~85% purity). This product, despite multiple recrystallizations, could not be made totally pure, consistently containing another "(PNP)Sc"-containing compound; it is not clear whether this is an isomer of **4** or a different complex; however, many peaks appear to resemble those of **4**, suggesting that it may be a diastereomer. ^{1}H NMR (500 MHz, benzene-d_6, 300 K): δ 7.13 (m, 2H, PNP Aryl), 6.94 (dd, $^{3}J_{\mathrm{HH}}$ = 8.5 Hz, $^{4}J_{\mathrm{HH}}$ = 2.1 Hz; 1H, PNP Ar), 6.90–6.84 (m, 2H, PNP Ar), 6.75 (dd, $^{3}J_{\mathrm{HP}}$ = 5.5 Hz, $^{4}J_{\mathrm{HH}}$ = 2.0 Hz; 1H, PNP Ar), 2.93 (s, 1H, Ad–NNN–C*H*(Si(CH$_3$)$_3$)[Al]), 2.25 (br, 6H, CH_2 adamantyl 2,9,8-positions), 2.17 (s, 3H, PNP tolyl CH_3), 2.15 (s, 3H, PNP tolyl CH_3), 2.09 (br, 3H, C*H*, adamantyl 3,5,7-positions), 1.96–1.84 (m, 4H, ^{i}Pr C*H*(CH$_3$)$_2$), 1.73 (br, 3H, CH_2, adamantyl 4,6,10-positions), 1.62 (br, 3H, CH_2, adamantyl 4,6,10-positions), 1.30–0.80 (m, 24H, ^{i}Pr CH(CH_3)$_2$), 0.45 (s, 3H, Sc–CH_3), 0.37 (s, 9H, Al(CH$_2$(Si(CH_3)$_3$))), 0.05 (br, 9H, Ad-NNN–C*H*(Si(CH_3)$_3$)[Al]), −0.06 (s, 3H, Al–CH_3), −0.53 (d, $^{2}J_{\mathrm{HH}}$ = 12.2 Hz, Al(C*H*H(Si(CH$_3$)$_3$))), −0.64 (d, $^{2}J_{\mathrm{HH}}$ = 12.2 Hz, Al(C*H*H(Si(CH$_3$)$_3$))). ^{13}C{^{1}H} NMR (126 MHz, benzene-d_6, 300 K): δ 160.49 (d, $^{2}J_{\mathrm{CP}}$ = 21.0 Hz; PNP Ar), 159.4 (d, $^{2}J_{\mathrm{CP}}$ = 19.7 Hz; PNP Ar), 133.32 (2C, PNP Ar), 133.10 (PNP Ar), 132.34 (PNP Ar), 127.25 (d, $^{3}J_{\mathrm{CP}}$ = 4.2 Hz; PNP Ar), 126.56 (d, $^{3}J_{\mathrm{CP}}$ = 3.8 Hz; PNP Ar), 121.65 (d, $^{3}J_{\mathrm{CP}}$ = 6.1 Hz; PNP Ar), 118.30 (d, $^{3}J_{\mathrm{CP}}$ = 7.1 Hz; PNP Ar), 117.14 (d, $^{1}J_{\mathrm{CP}}$ = 23.3 Hz; PNP Ar), 116.53 (d, $^{1}J_{\mathrm{CP}}$ = 21.3 Hz; PNP Ar), 58.01 (N–C$_{\mathrm{quaternary}}$ Ad 1 position), 56.30 (Ad-NNN–CH(Si(CH_3)$_3$)[Al]), 43.75 (Ad CH$_2$ 2,9,8-positions), 40.48 (Sc–CH$_3$), 36.67 (Ad CH$_2$ 4,6,10-positions), 30.32 (Ad CH, 3,5,7-positions), 24.53 (d, $^{2}J_{\mathrm{PC}}$ = 6.6 Hz; ^{i}Pr CH(CH$_3$)$_2$), 24.18 (d, $^{2}J_{\mathrm{PC}}$ = 5.7 Hz; ^{i}Pr CH(CH$_3$)$_2$), 21.08 (d, $^{3}J_{\mathrm{CP}}$ = 10.8 Hz; ^{i}Pr CH(CH$_3$)$_2$), 20.79 (PNP Ar tolyl CH$_3$), 20.73 (PNP Ar tolyl CH$_3$), 20.00 ($^{1}J_{\mathrm{CP}}$ = 12.7 Hz; ^{i}Pr CH(CH$_3$)$_2$), 19.83–19.71 (m, 2C, ^{i}Pr CH(CH$_3$)$_2$), 19.65 (d, $^{3}J_{\mathrm{CP}}$ = 13.7 Hz; ^{i}Pr CH(CH$_3$)$_2$), 19.45–19.28 (2C, ^{i}Pr CH(CH$_3$)$_2$), 19.22 (d, $^{1}J_{\mathrm{CP}}$ = 13.3 Hz; ^{i}Pr CH(CH$_3$)$_2$), 18.58 (d, $^{3}J_{\mathrm{CP}}$ = 10.6 Hz; ^{i}Pr CH(CH$_3$)$_2$), 16.51 ($^{3}J_{\mathrm{CP}}$ = 5.6 Hz; ^{i}Pr CH(CH$_3$)$_2$), 3.40 (Al(CH$_2$(Si(CH$_3$)$_3$))), 2.53 (Al(CH$_2$(Si(CH$_3$)$_3$))), 0.44 (Ad–NNN–CH(Si(CH_3)$_3$)[Al]), −4.54 (Al–CH$_3$). ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K): δ 0.06 (Al(CH$_2$(*Si*(CH$_3$)$_3$))), −1.82 (Ad–NNN–CH(*Si*(CH$_3$)$_3$)[Al]). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K): δ 3.43 (br, $\Delta\nu_{1/2}$ = 110 Hz, PNP), 0.07 (br, $\Delta\nu_{1/2}$ = 84 Hz, PNP).

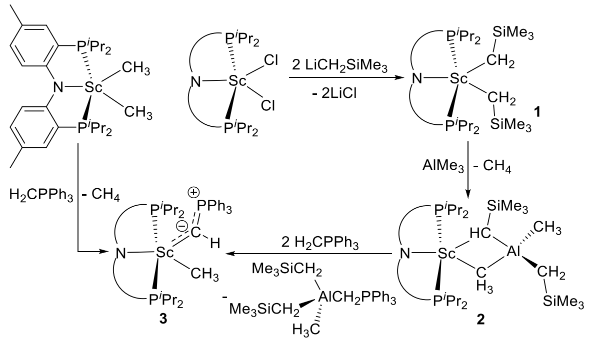
Synthesis of (PNP)Sc(η^2-NC$_5$H$_3$NMe$_2$)(CH$_2$SiMe$_3$) (5). *Note that these procedures were carried out with the glovebox lights turned off, as the product is slightly light-sensitive.* (PNP)Sc(μ_2-CHSiMe$_3$)(μ_2-CH$_3$)[Al(CH$_3$)(CH$_2$SiMe$_3$)] (120 mg, 170 μmol) was dissolved in 7 mL of pentane and stirred vigorously as a 3 mL solution of DMAP (41.6 mg, 341 μmol) in toluene was added. The resulting mixture was allowed to stir for 2 h at ambient temperature. The mixture was then filtered through glass fibers and the solvent was removed in vacuo. The product was then extracted with ~6 mL of 50/50 pentane/toluene, filtered through Celite, concentrated to saturation, and placed into the −35 °C freezer. Pale yellow microcrystalline solids formed in a yellow green solution. The final product was obtained following decantation of the supernatant, rinsing with −35 °C toluene, and drying under vacuum. This produced 86 mg of a product that was ~95% pure; multiple attempts to separate another "(PNP)Sc"-containing compound were made but were unsuccessful. ^{1}H NMR (500 MHz, benzene-d_6, 300 K): δ 8.29 (d, $^{3}J_{\mathrm{HH}}$ = 6.1 H; 1H, *ortho* to Sc–*N* in NC$_5$H$_3$NMe$_2$), 7.20 (m, PNP aryl), 7.14 (m overlapping with solvent peak, 1H), 7.00 (d, $^{4}J_{\mathrm{HH}}$ = 2.3 Hz; 1H, *ortho* to Sc–*C* in NC$_5$H$_3$NMe$_2$), 6.99–6.97 (m, 2H, PNP aryl), 6.94 (d, $^{3}J_{\mathrm{HH}}$ = 8.5 Hz; 1H PNP aryl), 6.83 (d, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz; 1H PNP aryl), 6.13 (dd, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, $^{4}J_{\mathrm{HH}}$ = 2.7 Hz; 1H, *meta* to Sc–*N* in NC$_5$H$_3$NMe$_2$), 2.27 (s, 6H, N(CH_3)$_2$), 2.21 (s, 3H, PNP tolyl CH_3), 2.17 (s, 3H, PNP tolyl CH_3), 2.05 (m, 1H, ^{i}Pr C*H*(CH$_3$)$_2$, the other methine peaks overlap with tolyl, dimethylamino, and residual solvent signals), 1.41 (dd, $^{3}J_{\mathrm{HP}}$ = 14.7 Hz, $^{3}J_{\mathrm{HH}}$ = 7.1 Hz; 3H, ^{i}Pr CH(CH_3)$_2$), 1.35–1.26 (m, 9H, ^{i}Pr CH(CH_3)$_2$), 1.14–1.04 (m, 9H, ^{i}Pr CH(CH_3)$_2$), 0.98 (dd, $^{3}J_{\mathrm{HP}}$ = 8.7 Hz, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz; 3H, ^{i}Pr CH(CH_3)$_2$), 0.41 (s, 9H, Si(CH_3)$_3$), 0.83 (d, $^{2}J_{\mathrm{HH}}$ = 11.6 Hz, 1H, Sc–C*H*H–Si(CH$_3$)$_3$), 0.23 (d, $^{2}J_{\mathrm{HH}}$ = 11.6 Hz, 1H, Sc–C*H*H–Si(CH$_3$)$_3$). ^{13}C NMR (101 MHz, benzene-d_6, 300 K): δ 212.75 (Sc–*C* in NC$_5$H$_3$NMe$_2$), 162.43 (d, $^{2}J_{\mathrm{CP}}$ = 20.4 Hz, PNP Ar), 160.20 (d, $^{2}J_{\mathrm{CP}}$ = 20.43 Hz, PNP Ar), 152.39 (*ipso* to N(CH$_3$)$_2$ in NC$_5$H$_3$NMe$_2$), 143.93 (*ortho* to Sc-*N* in NC$_5$H$_3$NMe$_2$), 132.86 (PNP Ar), 132.71 (PNP Ar), 132.33 (PNP Ar), 132.19 (PNP Ar), 127.08 (PNP Ar), 125.60 (PNP Ar), 121.09 (d, $^{3}J_{\mathrm{CP}}$ = 6.0 Hz; PNP Ar), 120.04 (d, $^{1}J_{\mathrm{CP}}$ = 20.0 Hz; PNP Ar), 118.78 (d, $^{3}J_{\mathrm{CP}}$ = 6.8 Hz; PNP Ar), 117.96 (d, $^{1}J_{\mathrm{CP}}$ = 19.4 Hz; PNP Ar), 110.88 (*ortho* to Sc–*N* in NC$_5$H$_3$NMe$_2$), 107.19 (*meta* to Sc–*N* in NC$_5$H$_3$NMe$_2$), 40.66 (Sc–CH$_2$–Si(CH$_3$)$_3$), 38.48 (N(CH$_3$)$_3$), 24.47 (2C overlapping, ^{i}Pr CH(CH$_3$)$_2$), 20.96 (PNP tolyl CH$_3$), 20.85 (PNP tolyl CH$_3$), 20.30 (d, $^{1}J_{\mathrm{CP}}$ = 9.5 Hz; ^{i}Pr CH(CH$_3$)$_2$), 20.14 (d, $^{3}J_{\mathrm{CP}}$ = 5.9 Hz; ^{i}Pr CH(CH$_3$)$_2$), 19.99 (^{i}Pr CH(CH$_3$)$_2$), 19.90 (^{i}Pr CH(CH$_3$)$_2$), 19.82 (^{i}Pr CH(CH$_3$)$_2$), 19.51 (d, $^{3}J_{\mathrm{CP}}$ = 6.1 Hz; ^{i}Pr CH(CH$_3$)$_2$), 19.27 (d, $^{3}J_{\mathrm{CP}}$ = 11.9 Hz; ^{i}Pr CH(CH$_3$)$_2$), 18.95 (d, $^{3}J_{\mathrm{CP}}$ = 11.6 Hz; ^{i}Pr CH(CH$_3$)$_2$), 17.36 (d, $^{3}J_{\mathrm{CP}}$ = 2.8 Hz; ^{i}Pr CH(CH$_3$)$_2$), 16.62 (d, $^{3}J_{\mathrm{CP}}$ = 4.8 Hz; ^{i}Pr CH(CH$_3$)$_2$), 4.90 (Si(CH$_3$)$_3$). ^{29}Si INEPT NMR (79 MHz, benzene-d_6, 300 K): δ −3.49. ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K): δ 0.98 (br $\Delta\nu_{1/2}$ = 67 Hz, PNP), −1.58 (br, $\Delta\nu_{1/2}$ = 73 Hz, PNP).

Synthesis of (PNP)Sc(μ_2-CPh_3)(μ_2-CH_3)Al(CH_3)$_2$ (6). (PNP)Sc($CHPPh_3$)(CH_3) (120 mg, 157 μmol) was dissolved in 5 mL of toluene and cooled to −35 °C. Once cooled, a hexanes solution of 2 M Al(CH_3)$_3$ (76 μ, 157 μmol) was added and the solution was stirred vigorously for 1 h, concentrated by vacuum to a volume of ~0.5 mL, and filtered through glass fibers. An equal volume of pentane was added to the solution, and it was concentrated to apparent saturation and then filtered once more. Crystals in $P2_1/n$ space group could be obtained by placing an open vial containing the concentrated solution into a jar and allowing for crystallization by evaporation at ambient temperature to give large yellow crystals after 1 day, from which the mother liquor was decanted and the solids were rinsed with −35 °C toluene and −35 °C pentane and then dried under vacuum (53 mg, 65 μmol, 41.1%). A similar procedure wherein the concentrated solution was placed into a freezer (−35 °C) gave crystals in $C2/c$ space group after about 1 week, but with inferior yields (and with widely varying degrees of purity), the best sample showing a 24% yield. ^{1}H NMR (500 MHz, benzene-d_6, 300 K): δ 7.68 (ddd, $^3J_{HP}$ = 11.6 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.8 Hz; 6H, *o*-H *Ph*−PPh_2−CH−Sc), 7.40 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HP}$ = 3.8 Hz; 1H, PNP aryl), 7.07−7.00 (m, 11H: 9H *m,p*-H *Ph*−PPh_2−CH−Sc + 2H PNP aryl), 6.93 (d, $^3J_{HP}$ = 5.0 Hz; 1H, PNP aryl), 6.82 (d, $^3J_{HH}$ = 8.6 Hz; 1H, PNP aryl), 6.77 (d, $^3J_{HP}$ = 5.7 Hz; 1H, PNP aryl), 2.24 (s, 3H, PNP tolyl CH_3), 2.11 (s, 3H, PNP tolyl CH_3, under the residual toluene peak), 2.15−2.00 (m, 3H, ^{i}Pr *C*H(CH_3)$_2$, one of these is under the benzylic position signal from toluene and PNP), 1.69 (m, 1H, ^{i}Pr *C*H(CH_3)$_2$), 1.49 (dd, $^3J_{HP}$ = 16.0 Hz, $^3J_{HH}$ = 6.9 Hz; 3H, ^{i}Pr CH(CH_3)$_2$), 1.21 (m, 6H, ^{i}Pr CH(CH_3)$_2$), 1.01 (s, 3H, Sc−CH_3−Al), 0.99 (m, 6H, ^{i}Pr CH(CH_3)$_2$), 0.89−0.80 (m, 6H, ^{i}Pr CH(CH_3)$_2$), 0.77 (dd, $^3J_{HP}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz; 3H, ^{i}Pr CH(CH_3)$_2$), −0.09 (s, 3H, Al−CH_3), −0.31 (s, 3H, Al−CH_3). ^{13}C NMR (101 MHz, benzene-d_6, 300 K): δ 161.80 (d, $^2J_{CP}$ = 21.3 Hz; PNP Ar), 158.31 (d, $^2J_{CP}$ = 18.1 Hz; PNP Ar), 138.09 (d, $^1J_{CP}$ = 79.9 Hz; *ipso*-C *Ph*−PPh_2−CH−Sc), 133.25 (3C, PNP Ar signals coincide), 133.03 (d, $^2J_{CP}$ = 9.6 Hz; *o*-C *Ph*−PPh_2−CH−Sc), 132.83 (PNP Ar), 132.45 (d, $^1J_{CP}$ = 15.2 Hz, Sc-C($AlMe_3$)(PPh_3)), 129.40 (d, $^4J_{CP}$ = 2.7 Hz; *p*-C *Ph*−PPh_2−CH−Sc), 129.34 (PNP Ar), 127.91 (*m*-C *Ph*−PPh_2−CH−Sc), 125.08 (PNP Ar), 123.71 (PNP Ar), 119.26 (d, $^1J_{CP}$ = 20.0 Hz; PNP Ar), 116.18 (d, $^3J_{CP}$ = 6.4 Hz; PNP Ar), 115.59 (d, $^1J_{CP}$ = 21.3 Hz; PNP Ar), 24.92 (Sc−CH_3−Al), 24.15 (2C, overlapping, ^{i}Pr CH(CH_3)$_2$), 21.00 (PNP tolyl CH_3), 20.60 (PNP tolyl CH_3), 20.50 (d, $^3J_{CP}$ = 6.6 Hz; ^{i}Pr CH(CH_3)$_2$), 20.15 (^{i}Pr CH(CH_3)$_2$), 20.02 (^{i}Pr CH(CH_3)$_2$), 19.67 (d, $^3J_{CP}$ = 6.1 Hz; ^{i}Pr CH(CH_3)$_2$), 19.25 (d, $^3J_{CP}$ = 7.3 Hz; ^{i}Pr CH(CH_3)$_2$), 18.82 (3C, ^{i}Pr CH(CH_3)$_2$ overlapping), 16.98 (^{i}Pr CH(CH_3)$_2$), 15.93 (^{i}Pr CH(CH_3)$_2$), −1.27 (Al−CH_3), −1.85 (Al−CH_3). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K): δ 6.75 (br d, $\Delta\nu_{1/2}$ = 54 Hz, $^2J_{PP}$ = 13 Hz; PNP), −1.31 (br, $\Delta\nu_{1/2}$ = 52 Hz, $^2J_{PP}$ = 13 Hz; PNP), −21.53 [−C($AlMe_3$)(*P*Ph_3)]. Anal. Calcd: C, 70.32; H, 7.87; N, 1.71. Found (attempt 1): C, 59.71; H, 8.00; N, 0.96. Found (attempt 2): C, 62.94; H, 8.16; N, 1.34.

■ RESULTS AND DISCUSSION

Isolation and Characterization of a Tebbe Analogue of Scandium. Our investigation began with a re-examination of the μ_2-bridging methylene fragment that closely resembles the Tebbe reagent as an intermediate en route to LM(μ_2-CH_2)(μ_2-CH_3)$_2$($AlMe_2$)$_2$ that we (L$^-$ = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2$, M = Sc) and Anwander (L$^-$ = 3,5-^{t}Bu,CH_3-trispyrazolylborate, M = La) reported some time ago.[4b,c] We hypothesized that a complex formed by a single equivalent of AlR_3 binding to the bridging carbon should be accessible with sterically demanding alkyl groups. For this reason, we first prepared the bis-alkyl complex (PNP)Sc(CH_2SiMe_3)$_2$ (**1**) in 89% yield from the transmetalation of (PNP)$ScCl_2$ with 2 equiv of $LiCH_2SiMe_3$ in toluene over 1.5 h. Complex **1** was fully characterized by multinuclear NMR spectroscopy in addition to single-crystal X-ray diffraction studies. Adding a single equivalent of $AlMe_3$ as a 2 M solution in hexanes to a pentane solution of **1** readily resulted in the formation of (PNP)Sc(μ_2-$CHSiMe_3$)(μ_2-CH_3)[Al(CH_3)(CH_2SiMe_3)] (**2**), isolable in 87% yield, along with the liberation of CH_4 (Scheme 1). While this complex was easily prepared at ambient temperature, it gradually decomposed in solution even when stored at low temperature, with loss of propylene (Figure S20, SI), akin to what was reported for similar complexes of Ce[11a] and Sc,[11b] but the resulting products could not be characterized.

Scheme 1. Synthesis of the Scandium Bis-Alkyl Complex 1, along with the Tebbe-like Complex 2 and Phosphonioalkylidene Complex 3[a]



[a]Two synthetic entries for complex **3** are shown in addition to the fluxional behavior of **2** in solution.

The solid-state structure determined by X-ray crystallography is shown in Figure 2 (top). Despite the lack of a formal multiple bond between Sc and C27, the Sc−$CHSiMe_3$ distance is surprisingly short at 2.0845(14) Å compared to what is found in the bridging CH_3 group [2.3641(14) Å] or the Sc−CH_2 distance in the methylidene complex (PNP)Sc(μ_3-CH_2)(μ_2-CH_3)$_2$[Al(CH_3)$_2$]$_2$ [2.3167(17) Å] that is stabilized by two Lewis acids.[3b] The solid-state structure of **2** also reveals what tantalizingly implies an α-H agostic interaction between the alkylidene hydrogen and the Sc(III) ion, with a Sc−H distance of 2.25(2) Å and acute Sc−C−H angle of 87.3(13)°, where the H atom was located and refined isotropically. Complex **2** shows a ^{1}H NMR spectrum where all resonances are extremely broadened, especially with respect to any protons that are bound to a carbon attached to the Al center, to the extent where cross-peaks are not observable in the HSQC spectrum at room temperature. One notable feature in complex **2** is the presence of two inequivalent $SiMe_3$ groups at 0.07 and 0.48 ppm in the ^{1}H NMR spectrum, although only the one incorporated into the alkylidene is visible in the ^{29}Si INEPT spectrum at −15.08 ppm at room temperature. The second weak signal can be found by a ^{1}H−^{29}Si HMBC spectrum (Figure S11, SI). What is most intriguing in the ^{13}C{^{1}H} NMR spectrum of **2** is the broad signal at 137 ppm with cross-peaks to a Si(CH_3)$_3$ moiety's ^{1}H resonances in the HMBC and a proton that corresponds to the α-H (Figure 2, bottom) in the HMQC spectrum; this highly downfield chemical shift is consistent with the presence of a bridging alkylidene species analogous to structure **d** depicted in Figure 1. While the two methyl groups and (trimethylsilyl)methyl group bound to Al are in rapid exchange in solution at ambient temperature, they resolve into three distinct species discernible in the ^{29}Si INEPTNMR experiment, with overlapping resonances in the ^{1}H and ^{31}P{^{1}H} spectra at 199 K; ostensibly,

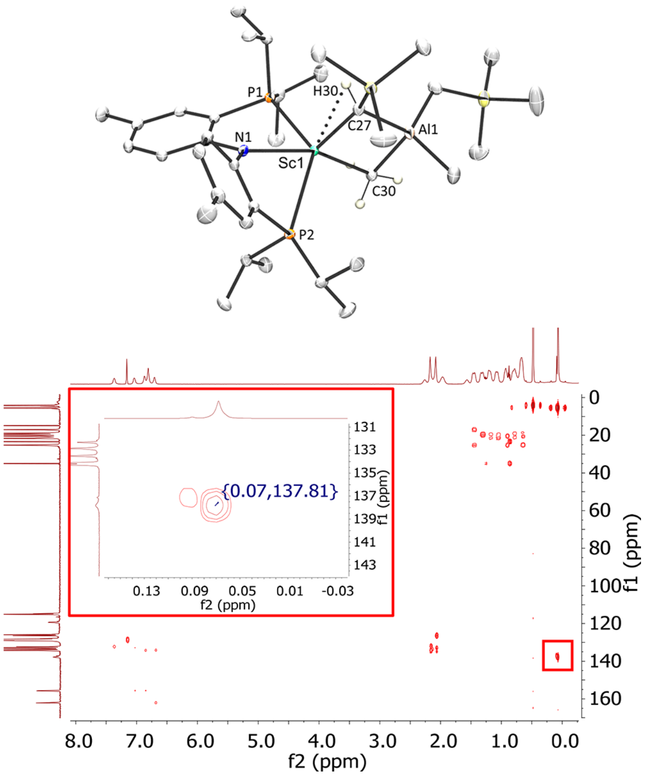


Figure 2. Top: Solid-state structures of the Tebbe analogue **2**. Solvent and hydrogens, with the exception of the *α*-hydrogen, have been omitted for clarity. Bottom: HMBC NMR spectrum of **2** displaying the cross-peak in the $^{13}C\{^{1}H\}$ trace at 137 ppm to the $Si(CH_3)_3$ hydrogens at 0.07 ppm in the ^{1}H NMR spectrum.

two are diastereomers, where a different methyl group bridges between Sc and Al, and one is a minor isomer, wherein the (trimethylsilyl)methyl moiety bridges. Complex **2** is a close analogue of the Tebbe complex, and hence, we explored some of its reactivity.

Reactivity of Complex 2. Although complex **2** could be categorized as a Tebbe-like reagent structurally, the ionicity and basicity in $Sc(\mu_2\text{-}CHSiMe_3)(\mu_2\text{-}CH_3)[Al(CH_3)(CH_2SiMe_3)$ are notably different compared to the Tebbe reagent, $Cp_2Ti(\mu_2\text{-}Cl)(\mu_2\text{-}CH_2)Al(CH_3)_2$. For example, compound **2** does not extrude the Lewis acidic protecting group $Al(CH_3)_2(CH_2SiMe_3)$ when treated with a Lewis base such as H_2CPPh_3. Instead, the alkylidene moiety deprotonates the ylide to give the phosphonioalkylidene methyl complex $(PNP)Sc(CHPPh_3)(CH_3)$ (**3**) along with what we propose to be the Lewis acid−base adduct $(Me_3SiCH_2)_2(CH_3)Al(CH_2PPh_3)$ (Scheme 1 and Figure S34, SI). Complex **3** could also be independently synthesized via $(PNP)Sc(CH_3)_2$ with 1 equiv of H_2CPPh_3 (Scheme 1). Complex **3** is relatively stable in the solid state, but it decomposes gradually in solution to a mixture of products that we have been unable to identify. In accord with the studies of Chen and co-workers,[6] complex **3** is characterized by a relatively far downfield $CHPPh_3$ resonance in the ^{13}C NMR spectrum, at 73.97 ppm [$^{1}J_{PC}$ = 22.5 Hz observed in the $^{31}P\{^{1}H\}$ spectrum by using the ^{13}C-enriched sample $(PNP)Sc(^{13}CHPPh_3)(CH_3)$ (**3**-^{13}C)], whereas the ^{1}H NMR spectrum reveals a doublet centered at 3.42 ppm ($^{2}J_{HP}$ = 14.1 Hz; $^{1}J_{CH}$ = 108.9 Hz in **3**-^{13}C), corresponding to the *α*-H for the phosphonioalkylidene. The $^{31}P\{^{1}H\}$ spectrum displays two inequivalent, but broad, resonances for the (PNP) ligand at 2.94 and −2.04 ppm and a sharper signal at 5.10 ppm for the phosphoniomethylidene, with an integration under the three resonances in a 1:1:1 ratio. However, the most definitive proof of **3** possessing a terminal phosphonioalkylidene unit stems from the solid-state structure depicted in Figure 2. Metrical parameters involving the $CHPPh_3$ moiety in **3** show a slightly longer $Sc{-}CHPPh_3$ distance of 2.121(2) Å from that reported by Chen and co-workers involving the complex $(nacnac)Sc(CHPPh_3)(X)$ (X^{-} = CH_3, OTf and I; nacnac^{-} = $[ArNC(CH_3)]_2CH$, Ar = 2,6-$^{i}Pr_2C_6H_3$) (see Table 1) but with a comparable C−P distance of 1.670(2) Å and an obtuse Sc−C−P angle of 145.42(14)°. The longer distance is not surprising given the higher coordination number at the Sc(III) ion in **3**. The $Sc{-}CHPPh_3$ distance is shorter than the $Sc{-}CH_3$ distance of 2.232(3) Å, implying Sc═C multiple bond character for the former, in accord with what was previously argued for in $(nacnac)Sc(CHPPh_3)(X)$. The formation of **3** from **2** and the phosphorus ylide H_2CPPh_3 suggests that the $Al{-}CHSiMe_3$ interaction is more stable than the $Sc{-}CHSiMe_3$ bonding; however, the alkylidene group $CHSiMe_3$ can depart with either the Sc or Al ion, depending on the substrate used.

Table 1. Selected Sc−C Bond Distances in the Alkylidene Units of Recently Reported Complexes, Including 2, 3, and 6

complex	Sc−C (Å)	ref
$(nacnac)Sc[C(SiMe_3)PPh_2](THF)$	2.089(3)	3e
$(nacnac)Sc(CHPPh_3)(CH_3)$	2.105(2)	6
$(nacnac)Sc(CHPPh_3)(OTf)$	2.060(3)	6
$(nacnac)Sc(CHPPh_3)(I)$	2.044(5)	6
2	2.0845(14)	this work
3	2.121(2)	this work
6	2.036(5)	this work

Electronic Structure. In order to better understand the electronic structure of **2**, density functional theory (DFT) calculations were carried out and the frontier orbitals were analyzed. The most salient features are summarized in Figure 3. The alkylidene moiety in a typical Sc(III)−alkylidene of the Schrock-type is best pictured as a dianionic ligand capable of donating four electrons, of which two are in a sp^2-hybridized *σ*-orbital and two are in a p-orbital that can engage a d_{yz}-orbital to afford a *π*-bond, as illustrated in Figure 3a.[12a−d] We have also calculated the structure of the experimentally elusive, hypothetical Sc−alkylidene **2*** without the Al Lewis acid stabilizer, which serves as a reference. The frontier orbitals drawn schematically in Figure 3a can readily be located in **2*** and are shown in the Supporting Information (Figure S59, SI). The Mayer bond order of Sc−C27 is calculated to be 1.69 in **2***, which is the reference value for a Sc═C double bond expected in the unmasked alkylidene without the Lewis acid. In comparison, a notably lower bond order of 1.13 is found in **2**, indicating that the double bond and alkylidene character is understandably lowered, but not completely erased when the Lewis acid is added. The C27−Al interaction is mainly electrostatic in nature with a bond order of 0.59. Despite careful inspection, we were unable to find any MO that promotes a covalent interaction between these two atoms. Instead, the positive electrostatic potential of the Al center lowers the fragment orbital energies of the alkylidene and changes the orientation of the silyl and hydrogen groups, as indicated in Figure 3b. As a result, the alkylidene becomes a

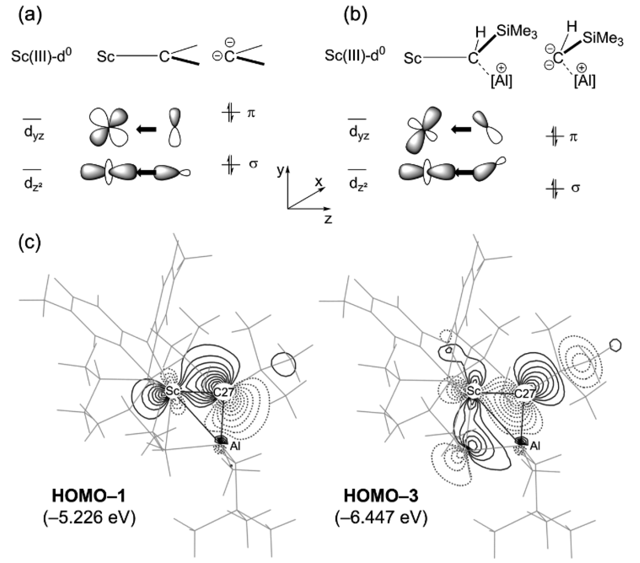


Figure 3. Conceptual MO diagram that compares the frontier orbitals of a typical Sc-alkylidene **2*** (a) to those of **2** (b). Contour plots of the relevant orbitals of **2** are shown in part (c).

weaker Lewis base and the two donor interactions are structurally distorted, as the contour plots of the two important frontier orbitals show in Figure 3c, as well as conceptualized illustration in Figure 3b. Nonetheless, the σ- and π-bond origins of the two bonding orbitals can easily be recognized. This electronic structure is in good agreement with the downfield-shifted NMR spectral signal observed for C27.

Compound **3** offers an interesting alternative way of stabilizing the excess charge of the alkylidene functionality, as explained above. Our DFT calculations reveal that the excess charge of the alkylidene remains mainly centered on the carbon in the phosphonioalkylidene. As the contour plots shown in Figure 4 illustrate, the HOMO is a lone-pair orbital centered on the alkylidene carbon with minimal interactions with the neighboring Sc or P atoms. Consequently, the Mayer bond order of the Sc−C bond is 1.02, which is mostly attributed to the σ-donor orbital HOMO−6, also shown in Figure 4. Thus, the phosphonio functionality again exerts only an electrostatic interaction, leading to the preservation of the Schrock-carbene character.

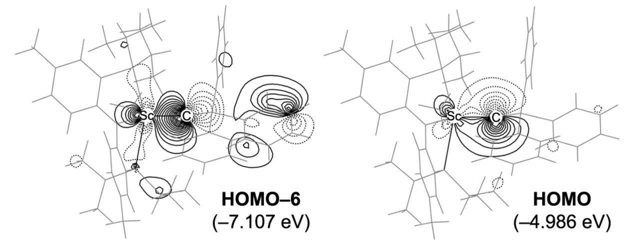


Figure 4. Contour plots of the most representative molecular orbitals that show the Schrock-carbene character of **3**.

Divergent Reactivity of 2. We also probed the reactivity of the alkylidene ligand in **2** with the azide N_3Ad (Ad = 1-adamantyl). Monitoring the addition of N_3Ad to **2** by NMR spectroscopy in benzene-d_6 showed two major products in roughly a 1:1 ratio (Figure S40, SI), but upon workup by recrystallization, these can be obtained in a ∼4:1 ratio. Single-crystal X-ray diffraction studies (Figure 5, center) reveal that insertion of the azide into the Sc−$CHSiMe_3$ bond occurs, accompanied by the complete transfer of the bridging methyl group from the Al to the Sc center to form the complex (PNP)Sc(CH_3)[η^2-$N_3AdCHSiMe_3Al(CH_3)(CH_2SiMe_3)$] (**4**) (Scheme 2) as the predominant product. This reactivity renders the alkylidene moiety in **2** more like a $AlMe_2$-substituted alkyl rather than a Lewis acid-stabilized alkylidene and, hence, follows the established pattern of reactivity of insertion to RE/early transition metal/actinide metal−carbon bonds with organic azides.[13a−e] The other major product observed in the in situ NMR monitoring experiment could not be separated as effectively, but given the similar resonances as those of **4**, such a species may simply be a diastereomer. It is also notable that the trimethylsilyl group formerly belonging to the bridging alkylidene appears to be in a hindered environment, giving rise to broadening of the ^1H NMR spectral signal of its methyl groups as well as a weaker signal in the ^{29}Si INEPT spectrum; the ^1H resonances belonging to the adamantyl group are also quite broad (Figure S31, SI). Complex **4** is also thermally robust in solution, not undergoing any noticeable transformation following heating at 60 °C overnight or for weeks at room temperature.

Conversely, the divergent reactivity of **2** can be demonstrated when this species is treated with 2 equiv of DMAP. In such a case, DMAP likely deprotects the alkylidene, and is subsequently coordinated by a second DMAP to form transient [(PNP)Sc=$CHSiMe_3$(DMAP)] (**B**), which deprotonates the *o*-CH of the pyridine to form (PNP)Sc(η^2-$NC_5H_3NMe_2$)(CH_2SiMe_3) (**5**) along with the Lewis acid−base adduct (Me_3SiCH_2)(H_3C)$_2$Al(DMAP), in accordance with Scheme 2. However, we concede that it may also be possible that DMAP coordinates to the Sc center first and is then deprotonated, and the resulting [(PNP)Sc(η^2-$NC_5H_3NMe_2$)][$Al(CH_3)_2(CH_2SiMe_3)_2$] subsequently converts to **5**. It is worth noting that addition of only 1 equiv of DMAP to **2** produces roughly half as much **5**, with the rest of the **2** remaining. Interestingly, bases such as 1,4-diazabicyclo[2.2.2]octane and trimethylphosphine do not react with **2**, suggesting that steric congestion precludes coordination of nucleophiles of even a modest steric profile. Multinuclear NMR spectroscopic studies are consistent with the formation of **5**, including a broad resonance in the $^{13}C\{^1H\}$ spectrum at 212.8 ppm corresponding to the Sc-bound carbon of the pyridyl moiety (Figure S44, SI). A solid-state structure, shown in Figure 5 (right), reaffirmed the formation of a Sc−pyridyl and −alkyl moieties in **5** [Sc−$C_{pyridyl}$, 2.219(3) Å; Sc−$N_{pyridyl}$, 2.148(2) Å; Sc−C_{alkyl}, 2.265(3) Å]. As a result, the alkylidene unit of complex **2** shows differing reactivity, implying that it is highly ionic with both scandium alkylidene character or, alternatively, as an alane-substituted alkyl. Such a small disparity in the electronegativity difference between Al and Sc (∼0.2) might impart the dual nature in the Sc($CHSiMe_3$)Al motif in **2**.[14]

A Scandium Phosphonioalkylidyne Complex. Having succeeded in synthesizing complex **2**, we reasoned that α-H elimination might be possible at the phosphoniomethylidene in **3**, mirroring our previous observation that (PNP)Ti=CH^tBu(R) (R = CH_3 or Ph) complexes are quite resistant to α-H abstraction but would readily eliminate RH when treated with $AlMe_3$ to form the Tebbe alkylidyne analogue (PNP)Ti(μ_2-C^tBu)(μ_2-CH_3)Al(CH_3)$_2$.[7a] Accordingly, treatment of **3** with Al(CH_3)$_3$ (2 M solution in hexanes) in a benzene or

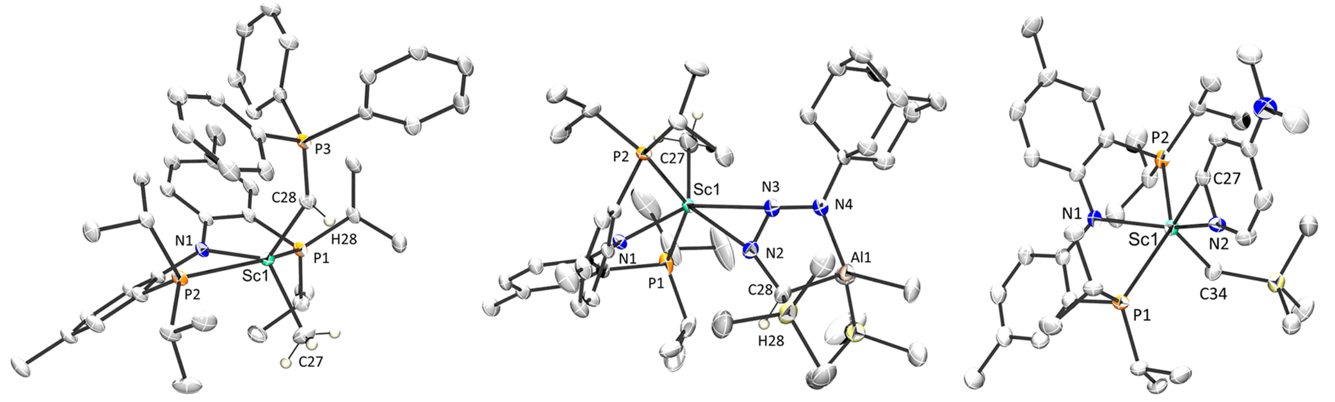
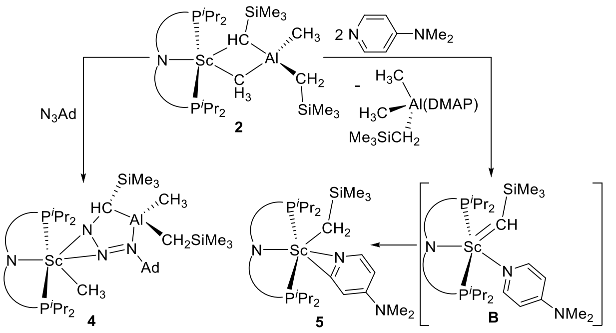
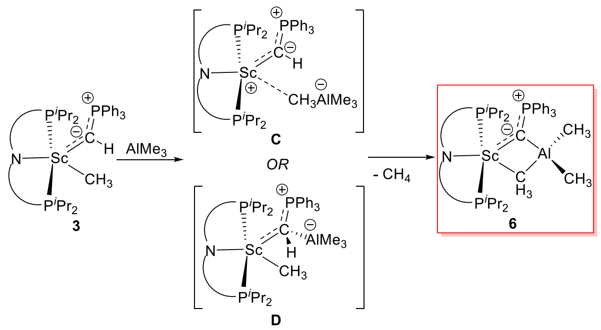


Figure 5. Solid-state structures of the Sc-based products **3** (left), **4** (center), and **5** (right) resulting from addition of H_2CPPh_3, N_3Ad, and DMAP, respectively, to **2**. Solvent, disorder, and hydrogens, with the exception of the α-hydrogen, have been omitted for clarity.

Scheme 2. Reaction of 2 with N_3Ad and DMAP to Give 4 and 5, Respectively



Scheme 3. Reactivity of 3 with $AlMe_3$ to Form either Zwitterion C or D Followed by Methane Extrusion to Produce 6



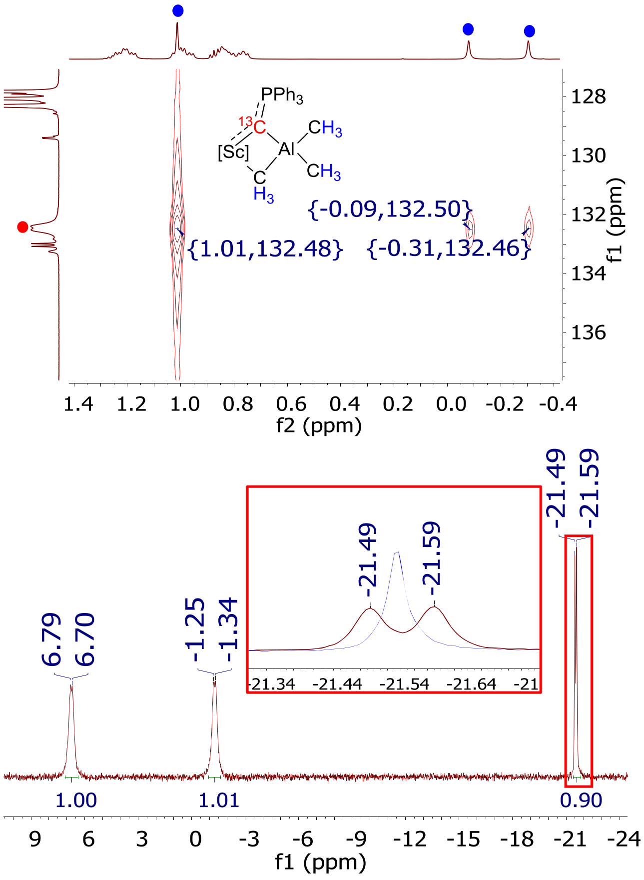


Figure 6. Top: ^{1}H−^{13}C HMBC spectrum of **6**-^{13}C. Bottom: ^{31}P{^{1}H} spectrum of **6**-^{13}C with an inset showing the superimposed spectrum of unlabeled **6**.

toluene solution resulted in immediate extrusion of CH_4 (^{1}H NMR: 0.16 ppm) and formation of several new products based on a combination of ^{1}H and ^{31}P NMR spectral data. Most notably, workup of the mixture and subsequent isolation of one such new product, in yields ranging from 24 to 41%, which is unstable in solution at 25 °C for extended periods, revealed spectral features consistent with a Sc═C bond and in accord with the formulation (PNP)Sc(μ_2-CPPh$_3$)(μ_2-CH$_3$)Al(CH$_3$)$_2$ (**6**) (Scheme 3). For instance, a highly downfield shifted resonance at 132.4 ppm with a coupling constant of $^1J_{PC}$ = 15.2 Hz (15.4 Hz in the ^{31}P NMR spectrum) was observed in the ^{13}C NMR spectrum with the aid of a ^{13}C-enriched sample, (PNP)Sc(μ_2-^{13}CPPh$_3$)(μ_2-CH$_3$)Al(CH$_3$)$_2$ (**6**-^{13}C), as shown in Figure 6. Strikingly, this ^{13}C chemical shift is 58.5 ppm further downfield than that of **3**, while the $^1J_{PC}$ coupling constant is 7.1 Hz smaller. It should be noted that this $^1J_{PC}$ coupling constant is markedly smaller than that found in terminal phosphonioalkylidyne (PNP)Ti≡CPPh$_2$CH$_3$(OTf), 32.5 Hz.[7b] The phosphonioalkylidene α-H resonance originally present in **3** was absent. Akin to **3**, the ^{31}P NMR spectrum indicates an asymmetrical complex with two very broadened signals, which in this case were resolvable as doublets. Two inequivalent phosphorus atoms of the PNP ligand appear at 6.75 and 1.30 ppm, with a highly shielded singlet resonance at −21.53 ppm (splitting into a doublet with the ^{13}C-labeled sample). This third resonance is even further upfield than free triphenylphosphine, reminiscent of what is observed for terminal phosphonioalkylidyne species (Figure 6).[15a−c] Unlike **2**, the $\mathrm{Al(CH_3)_3}$ unit is fixed firmly such that the methyl groups do not exchange at room temperature on the NMR time scale, similar to what was observed for the related (PNP)Ti(μ_2-$\mathrm{C^tBu}$)(μ_2-$\mathrm{CH_3}$)$\mathrm{Al(CH_3)_2}$.[7a] We propose complex **6** to form via methyl abstraction by $\mathrm{Al(CH_3)_3}$ to give putative [(PNP)Sc(CHPPh$_3$)][Al(CH$_3$)$_4$] (**C**), in which the strong anionic base $[\mathrm{Al(CH_3)_4}]^-$ deprotonates the phosphonioalkylidene α-H to liberate $\mathrm{CH_4}$ by forming $\mathrm{Al(CH_3)_3}$ and (PNP)Sc≡CPPh$_3$ or one of its other resonance forms by delocalizing the π-bond into the $\mathrm{PPh_3}^{2+}$ motif. The latter two fragments combine via an incomplete Al−C bond addition across the Sc−C multiple bonds to form the adduct **6**. However, an alternative mechanism is possible wherein $\mathrm{Al(CH_3)_3}$ is bound by the carbon of the phosphoniomethylidene group, generating (PNP)Sc[(μ_2-CHPPh$_3$)(Al(CH$_3$)$_3$)](CH$_3$) (**D**) and then promoting methane elimination.

The structural assignment of complex **6** was substantiated by X-ray crystallography across three independent molecules belonging to two separate space groups, $P2_1/n$ and $C2/c$ (Figure 7), with an average Sc−C(alkylidyne) distance of 2.036 Å, the shortest Sc−C distance recorded to date, being slightly shorter than Chen's recent (nacnac)Sc(CHPPh$_3$)(I) (see Table 1).[6] In the solid-state structure, both the alkylidyne carbon (CPPh$_3$) and a methyl bridge the $\mathrm{Sc^{3+}}$ and $\mathrm{Al^{3+}}$ centers. The C−PPh$_3$ bond distance (average 1.668 Å in the $P2_1/n$ structure, which has the lower R_1), which does not differ significantly from that of **3**, and the Sc−C−P angle of 149.54° (averaged from $P2_1/n$ structure) suggest that the nature of the C−P bond in the solid-state structures in both complexes is similar, in spite of the different $^1J_{\mathrm{CP}}$ coupling constants observed by NMR spectroscopy.

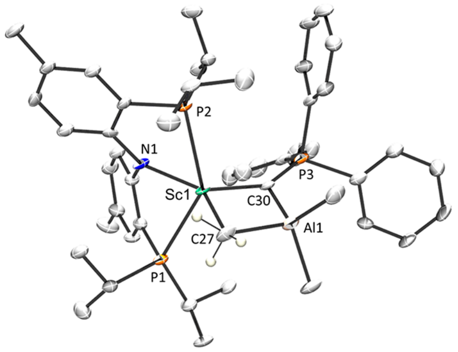


Figure 7. Solid-state structure of complex **6** showing thermal ellipsoids at the 50% probability level. Only the α-hydrogens are shown for clarity.

For a true alkylidyne, it is expected that all three p-orbitals of the carbon are utilized to give one σ- and two π-bonds. To gauge the impact of the Al fragment, we also calculated the structure and electronics of **6***, a hypothetical, $\mathrm{Al(CH_3)_3}$-free alkylidyne containing a simpler ScCPPh$_3$ fragment. We found that the Sc−C bond is expectedly short at 1.903 Å, and the bond order is calculated to be 1.88, indicating that the two π-bonds are weak but contribute notably to the bonding. As seen for **2**, the addition of the Al-based Lewis acid is anticipated to lead to a significant weakening of the triple bond character and localization of the charge on the alkylidyne carbon. Our calculations show that the bond order in **6** is only 1.31, which is higher than what was found in **2** and **3**, but remarkably low for a bond that is formally a triple bond. Figure 8 shows the three frontier orbitals that are responsible for the triple bond in **6**. HOMO−16 is the σ-bond, which is the major contributor to the alkylidyne binding. The two π-orbitals, HOMO−2 and HOMO−1, are mostly isolated and interact only very weakly with the metal center, which is the result of the positive electrostatic potential exerted upon the alkylidyne carbon by the Al and phosphonio groups.

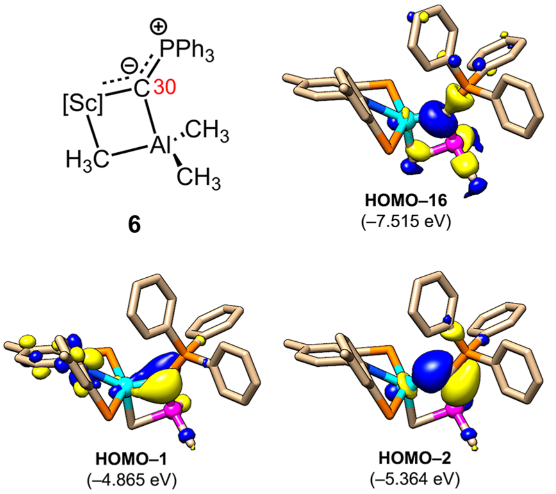


Figure 8. Three orbitals that are responsible for the triple bond character of **6**. All hydrogens and isopropyl groups on the PNP ligand are omitted for clarity. [Sc] represents the (PNP)Sc fragment. Isodensity value = 0.05 a.u.

■ CONCLUSION

In summary, the successful stabilization of rare unsaturated Sc−C bonds with a single trialkylaluminum unit has provided new insight into the nature of multiple bonds between carbon and RE metals. The Lewis acid-stabilized alkylidene (**2**), the terminal phosphonioalkylidene (**3**), and the Lewis acid-stabilized phosphonioalkylidyne (**6**) complexes of scandium have been prepared then spectroscopically and structurally analyzed. Both experimental and theoretical studies validate the multiple bond characters of Sc−C in **2**, **3**, and **6**. The Sc−alkylidene or Al−alkylidene bond of **2** breaks when it reacts with $\mathrm{N_3Ad}$ and DMAP, respectively showing the divergent reactivity of **2**. Both the phosphino and Al-based Lewis acids stabilize the alkylidene and alkylidyne moieties through electrostatic interactions only, resulting in a significant localization of the charge on the carbon, which becomes a much weaker Lewis base. We are currently probing the reactivity of **6** with various Lewis bases.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c02742.

NMR, XRD, and computational data for the compounds discussed (PDF)

X-ray crystallographic data for complex **1** (CIF)

X-ray crystallographic data for complex **2**·$^1/_2$$\mathrm{C_5H_{12}}$ (CIF)

X-ray crystallographic data for complex **3**·C_5H_{12} (CIF)
X-ray crystallographic data for complex **2** (CIF)
X-ray crystallographic data for complex **4** (CIF)
X-ray crystallographic data for complex **5**·$3C_7H_8$ (CIF)
X-ray crystallographic data for complex 2(**6**)·$3C_7H_8$ (CIF)
X-ray crystallographic data for complex $^1/_2$[2-(**6**)·$^1/_2C_7H_8$·$^1/_2C_5H_{12}$] (CIF)

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Notes

The authors declare no competing financial interest.

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