Group 3 Imides

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Evidence for the Existence of a Terminal Imidoscandium Compound: Intermolecular C–H Activation and Complexation Reactions with the Transient Sc=NAr Species**

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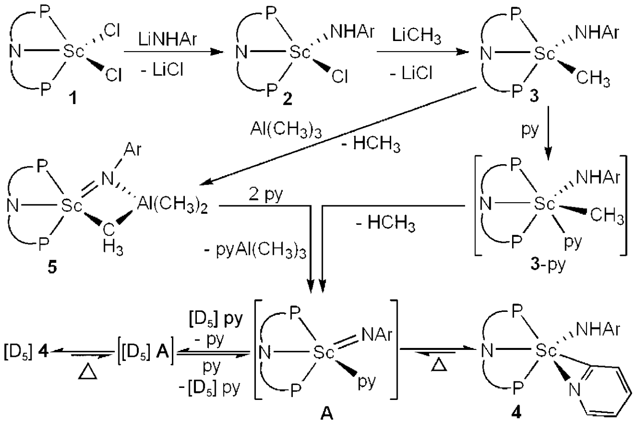
Terminal imide ligands in early-transition-metal chemistry have recently undergone a dramatic renaissance, given their potential applications in processes such as group transfer and catalysis.[1] Absent from this extensive list are Group 3 transition-metal imides, an antithesis given the inherent affinity of the highly electropositive metal ions for a hard donor such as nitrogen. To date, complexes of Group 3 transition-metal elements (including the lanthanides) with terminal imido ligands have been neither directly detected nor isolated; their existence during the formation of a narrow list of dinuclear or polynuclear bridging imides has only been speculated.[2–4] The inability to isolate a terminal imide linkage may be due to the discrepancy in energy between the lanthanide and imide-nitrogen orbitals,[4] rendering this type of bond highly polarized and thus prohibiting the formal M=NR or M≡NR bond that is prototypical among most early transition metals. As a result, such a mismatch in orbital energies should bestow unprecedented nucleophilic behavior to the imido nitrogen atom when coordinated to an ion such as a lanthanide. Herein, we present credible evidence for the existence of a terminal scandium imido complex by applying a combination of isotopic labeling and reactivity studies of a transient Sc=NR complex, evidenced by the intermolecular C–H activation of pyridine and benzene as well as complexation with $Al(CH_3)_3$.

The fact that we can generate transient, reactive titanium alkylidynes of the type [(PNP)Ti≡CR] (PNP = N[2-P-$(CHMe_2)_2$-4-methylphenyl]$_2$, R = Ph, $SiMe_3$, and *t*Bu, among other groups)[5] encouraged the search for an isolobal {(PNP)Sc≡NR} fragment, owing to the comparable atomic radii between titanium(IV) and scandium(III) when weighed against the other Group 3 congeners. Likewise, the PNP ligand type has been recently demonstrated to be an ideal ancillary support in the preparation of an unprecedented bridging phosphinidene moiety on lutetium(III).[6] For us, assembling the PNP ancillary ligand and Sc^{III} to form [(PNP)$ScCl_2$] (**1**) in 95% yield proved straightforward by treatment of Li(PNP) with [$ScCl_3(thf)_3$] in toluene at 70 °C over 48 h.[7,8] Bright yellow **1** can be readily transmetalated with LiNHAr (Ar = 2,6-*i*$Pr_2C_6H_3$) to afford [(PNP)Sc(NHAr)Cl] (**2**) in 76% yield (Scheme 1). To incorporate a good leaving group for deprotonation of the anilide, precursor **2** was alkylated with $LiCH_3$ to produce the yellow anilide methyl complex [(PNP)Sc(NHAr)(CH_3)] (**3**) in 72% yield subsequent to recrystallization from hexane at −35 °C (Scheme 1).[7] Although the ^{31}P NMR spectroscopic resonances for compounds **1**–**3** are unremarkable (7–2 ppm, $\Delta\nu_{1/2} >$ 90 Hz), presumably owing to effective coupling of the quadrupolar ^{45}Sc scalar with the ^{31}P nucleus, the ^1H and ^{13}C NMR spectra were clearly consistent with the proposed connectivity.[7] Notably, the ^1H NMR spectrum of compound **3** reveals an NH proton ($\delta = 5.98$ ppm) in addition to a methyl group resonating upfield at $\delta = 0.28$ ppm. Likewise, solid-state structural data for single crystals of **2**[9] and **3**[10] were collected (Figure 1). These molecular structures are related and both portray highly skewed {(PNP)Sc} scaffolds with the Sc–$N_{anilide}$ bonds being shorter (**2** 2.0073(17), **3** 2.0298(13) Å) than the Sc–N_{PNP} bonds (**2** 2.1385(16), **3** 2.1568(12) Å).[7]



Scheme 1. Synthesis of complexes **1**–**5**, subsequent C–H activation of pyridine to form **4** and complexation of **3** with $Al(CH_3)_3$ to produce **5**. A proposed mechanism is also depicted. Complexes **2**–**5** have been characterized by X-ray crystallography. The PNP caricature represents N[2-P$(CHMe_2)_2$-4-methylphenyl]$_2^-$; Ar = 2,6-*i*$Pr_2C_6H_3$.

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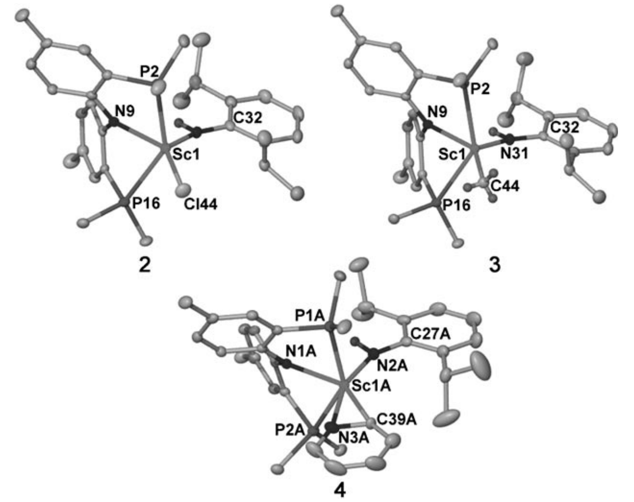


Figure 1. The molecular structures of complexes **2–4**. Methyl groups of isopropyl substituents on phosphorous, solvent, and hydrogen atoms (except α-hydrogen atoms) have been excluded for clarity.

Each anilide nitrogen atom lies in the plane formed by its substituents, and the orientation of the isotropically refined α-NH hydrogen atom is *anti* with respect to the N9-Sc-X groove (X = Cl, CH_3). The Sc···H distances (**2** 2.19(2), **3** 2.277(17) Å), coupled with the obtuse Sc-N-C32 angles (**2** 155.93(14)°, **3** 155.41(11)°), suggest significant α-hydrogen agostic interactions in the solid state, which is in accordance with these systems partaking in $N_{anilide}\rightarrow Sc$ π donation.

Only with exhaustive thermolysis (100 °C for several days in C_6D_6), does compound **3** eventually break down into a mixture of intractable materials. It was found, however, that complex **3** reacts readily with pyridine (py) at room temperature to form the pyridyl anilide complex [(PNP)Sc(NHAr)(η^2-NC_5H_4)] (**4**) concomitant with methane elimination.[7] Diagnostic spectroscopic features for complex **4** include an anilide NH resonance at $\delta = 6.18$ ppm in the ^{1}H NMR spectrum, as well as four inequivalent pyridyl resonances in the $\delta = 8.3$–6.6 ppm region.[7] The ^{13}C NMR spectrum unmistakably exposes a pyridyl carbon resonance at 217 ppm—identical to the chemical shift reported for the alkylidene pyridyl derivative [(PNP)Ti=CH*t*Bu(η^2-NC_5H_4)].[11] Single-crystal structural analysis of **4** also corroborates our NMR spectroscopic data, presenting a coordinatively saturated scandium center bearing an η^2-pyridyl ligand (Sc–N 2.229(3), Sc–C 2.243(3) Å, Figure 1).[12]

Intuitively, we would expect formation of **4** from **3** to occur by a σ-bond metathesis step, such as those reported in the literature.[13] However, isotopic labeling studies using precursor **3** and [D$_5$]py suggest otherwise, cleanly producing the isotopomer [(PNP)Sc(NDAr)(η^2-NC_5D_4)] ([D$_5$]**4**). Examination of the volatiles reveals only formation of CH_4, not CDH_3, thereby hinting that α-hydrogen abstraction precedes *ortho*-metalation of the pyridine substrate. In the isotopic labeling studies, no deuterium incorporation is observed into the anilide aryl framework or components of the PNP ancillary ligand when the final mixture is assayed by a combination of ^{1}H and ^{2}H NMR spectroscopy. Therefore, the isotopic labeling studies suggest that compound **3** undergoes an α-hydrogen abstraction step to furnish a terminal scandium imido intermediate, [(PNP)Sc = NAr(py)] (**A**), which rapidly promotes activation of the adjacent *ortho*-hydrogen of pyridine to give **4** (Scheme 1). Since complex **3** fails to extrude alkane under analogous conditions in the absence of a donor such as pyridine, an associative pathway to form putative **3**-py most likely transpires along the reaction coordinate to **A**.

The proposed synthetic pathway in Scheme 1 is further complimented by an independent route to **4**, explicitly via a masked scandium imide. Accordingly, when one equivalent of $Al(CH_3)_3$ in hexane is added to **3**, the formation of a new species is observed. In the ^{1}H NMR spectrum, a broad resonance integrating to nine hydrogen atoms ($\delta = 0.2$ ppm) is observed, as well as a broad resonance in the ^{31}P NMR spectrum centered at $\delta = 2.4$ ppm (which resolves into two broad resonances at $\delta = 2.1$ and 0.0 ppm upon cooling the mixture to −50 °C).[7] To determine the connectivity of this new product, single-crystal X-ray diffraction studies were relied upon; these data showed a zwitterionic scandium imide [(PNP)Sc{N(Ar)Al(CH_3)$_3$}] (**5**; Scheme 1).[14] The metrical parameters in the solid-state structure of **5** (Figure 2) are comparable to those of the isoelectronic titanium complex [(PNP)Ti{C(*t*Bu)Al(CH_3)$_3$}],[15] an alkylidyne analogue of Tebbe's reagent. The Sc–N imido bond in **5** is much shorter (1.9366(14) Å) than in precursors **2**, **3**, and **4**, as well as significantly contracted relative to that observed for the only reported scandium μ_2-imido complex [({$C_5H_4(CH_2)_2NMe_2$}Sc-{μ_2-NC(Ph)C_6H_{10}})$_2$] (2.056(2) Å).[3] DFT calculations and molecular orbital analysis converged well to the solid-state structure observed for **5**.[7] The natural bond order (NBO) calculations indicate a much stronger interaction Sc1–N2 (1.16) than that with the PNP amide nitrogen atom (Sc1–N1 0.50).[16] Likewise, the NBO for the bridging Al1–C39 of 0.48 is clearly smaller than that for the terminal Al–CH_3 group (0.90) and is thus consistent with a more ionic C39 group shared between scandium and aluminum. Inspection of the molecular orbitals for **5** confirms the ionic nature of the μ_2-CH_3 ligand (HOMO−8, Figure 3) as well as a π bond (HOMO−2) arising from Sc=NAr orbital overlap (Figure 3).[7] As anticipated for a d^0 metal center, the LUMO is purely metal based (Figure 3).

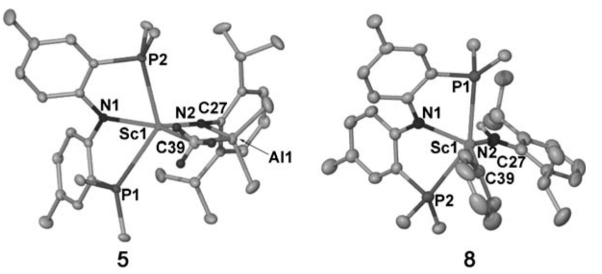


Figure 2. The molecular structures of complexes **5** and **8**. Methyl groups of isopropyl substituents on phosphorous, solvent, and hydrogen atoms (except α-hydrogen atoms) have been excluded for clarity.

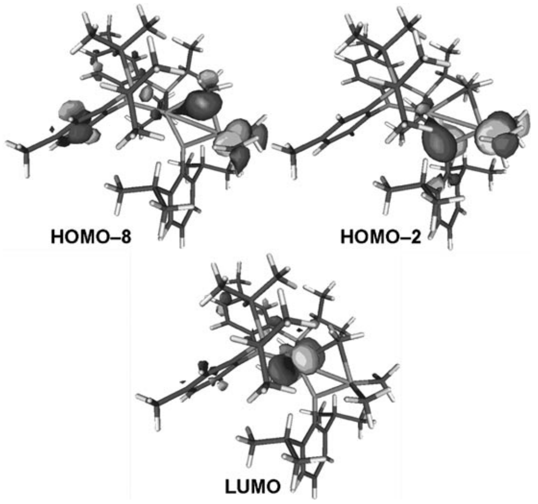
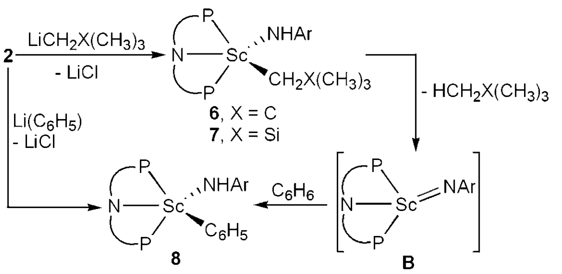


Figure 3. Selected frontier orbitals for **5** depicting isodensity at 0.05 au.

Formation of complex **5** likely traverses through a hypothetical zwitterion $[(PNP)Sc(NHAr)(\mu_2\text{-}CH_3Al(CH_3)_3)]$, which would then eliminate methane owing to the inherent superbasicity of the putative anion.[17] Piers and co-workers reported an analogous methide abstraction reaction with the surrogate $[(\{ArNC(CH_3)\}_2CH)Sc(NHR)\{\mu_2\text{-}CH_3B(C_6F_5)_3\}]$ (Ar = 2,6,-*i*$Pr_2C_6H_3$, R = *t*Bu, 2,6-*i*$Pr_2C_6H_3$), but were unable to promote elimination of methane via imido bond formation.[18] We cannot refute, however, the possibility of a smaller $Al(CH_3)_3$ unit coordinating first to the anilide nitrogen atom in **3** before alkane elimination furnishes the imido linkage.[2f] Complex **5** is indeed a masked form of a terminal scandium imido compound, given that treatment with two equivalents (or neat) pyridine results in immediate activation of the *ortho* C–H bond of pyridine to form **4**, concurrent with formation of the adduct $pyAl(CH_3)_3$ (Scheme 1).[7] Complex **4** is also found to be a resting state for intermediate **A** (Scheme 1), as the isotopomer $[D_5]$**4** can exchange with proteo-pyridine at 90 °C over 8 h and vice versa (Scheme 1).

Incorporation of a more sterically encumbering group in a scaffold such as $\{(PNP)Sc(NHAr)\}^+$ facilitates α-hydrogen abstraction. Accordingly, treatment of **2** with the alkyl reagents $LiCH_2X(CH_3)_3$ (X = C, Si) results in rapid formation of the anilide alkyl derivatives $[(PNP)Sc(NHAr)\{CH_2X(CH_3)_3\}]$ (**6** X = C, **7** X = Si; Scheme 2). As opposed to **3**, compounds **6** and **7** undergo C–H activation of benzene to form $[(PNP)Sc(NHAr)(C_6H_5)]$ (**8**) as the major product (**6**: 12 hrs, 70 °C, 45 % yield of isolated product; **7**: 24 hrs, 70 °C, 64 % yield of isolated product). Other observable products in the reaction mixture are minor and have not been identified. Upon treatment with C_6D_6, α-hydrogen abstraction in **6** and **7** once again precedes C–H bond activation of the solvent, as isotopically enriched $[(PNP)Sc(NDAr)(C_6D_5)]$ ($[D_6]$**8**) is produced (Scheme 2). No deuterium is incorporated into the leaving alkane, as implied by ^1H and ^2H NMR spectra of the reaction mixture. The formation of **8** from **6** and **7** implies that a putative low-coordinate imidoscandium intermediate [(PNP)Sc=NAr] (**B**) is likely produced along the reaction coordinate (Scheme 2). Therefore, the chemistry of putative **B** seems to resemble intermolecular 1,2-C–H bond additions involving Group 4–6 imide complexes.[1,19] Compound **6** is far more reactive than **7**, undergoing gradual decomposition in solution or as a solid at 25 °C. Therefore, compound **6** must be rapidly isolated after immediate formation from $LiCH_2C(CH_3)_3$ and **2** in hexane at −35 °C. Independently, complex **8** can be prepared in 74 % yield from **2** and LiC_6H_5 in toluene.[7] Diagnostic features include two broad overlapping resonances in the ^{31}P NMR spectrum at $\delta = 3.5$ and 3.0 ppm, as well as an anilide proton resonance at $\delta = 6.39$ ppm in the ^1H NMR spectrum. The solid-state structure of **8**[20] clearly portrays a phenyl ligand ($Sc\text{–}C_{ipso}$ 2.275(2) Å) resulting from C–H activation of the arene (Figure 2). Analogous to the molecular structures of **2**–**4**, the anilide hydrogen atom points away from the aryl moiety, while the phosphine arms of the PNP ligand are highly distorted from a transoid orientation (P-Sc-P 146.787(19)°).



Scheme 2. Intermolecular C–H activation of benzene promoted by intermediate **B** to produce **8**.

The work presented herein therefore supports the existence of a terminal scandium imido ligand. Systems such as **4**–**7** appear to be synthons of a reactive terminal scandium imido ligand, either by means of decomplexation with Lewis bases, a thermally induced 1,3-hydrogen shift, or by α-hydrogen abstraction. Our findings demonstrate, through experimental evidence, that imidoscandium complexes can be generated under mild conditions and can promote the activation of C–H bonds, including that of benzene. Mechanistic and computational studies derived from this new type of polarized ligand will be presented in due course.

Experimental Section

See the Supporting Information for full synthetic, spectroscopic, and structural details for all new compounds (**2**–**8**).

CCDC 692694, 692695, 692696, 692697, 692698 (**2**–**5**, **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[9] Crystal data for **2**: $C_{38}H_{58}ClN_2P_2Sc$, $M = 685.21$, monoclinic, space group $P2_1/c$, $a = 20.6443(16)$, $b = 11.3633(9)$, $c = 17.3145(13)$ Å, $\beta = 107.585(2)°$, $V = 3872.0(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.175$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha}$: 0.71073 Å, absorption coefficient 0.369 mm^{-1}, $F(000) = 1472$, 22269 reflections collected, 11154 independent reflections, $R_{int} = 0.0710$, GoF = 0.810, $R = 0.0436$ $[I > 2\sigma(I)]$, $wR^2 = 0.0701$ $[I > 2\sigma(I)]$.

[10] Crystal data for **3**: $C_{39}H_{61}N_2P_2Sc$, $M = 664.80$, monoclinic, space group $P2_1/c$, $a = 20.653(3)$, $b = 11.3736(14)$, $c = 17.400(2)$ Å, $\beta = 107.674(3)°$, $V = 3894.4(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.134$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha}$: 0.71073 Å, absorption coefficient 0.369 mm^{-1}, $F(000) = 1440$, 69288 reflections collected, 11386 independent reflections, $R_{int} = 0.0845$, GoF = 0.901, $R = 0.0355$ $[I > 2\sigma(I)]$, $wR^2 = 0.0778$ $[I > 2\sigma(I)]$.

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[12] Crystal data for **4**: $C_{45.50}H_{68}N_3P_2Sc$, $M = 763.93$, monoclinic, space group $P2_1/c$, $a = 25.0198(9)$, $b = 20.7333(8)$, $c = 19.0601(7)$ Å, $\beta = 90.2720(10)°$, $V = 9887.2(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.026$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha}$: 0.71073 Å, absorption coefficient 0.243 mm^{-1}, $F(000) = 3304$, 74624 reflections collected, 19728 independent reflections, $R_{int} = 0.0312$, GoF = 1.043, $R = 0.0602$ $[I > 2\sigma(I)]$, $wR^2 = 0.1923$ $[I > 2\sigma(I)]$.

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[14] Crystal data for **5**: $C_{44}H_{73}AlN_2P_2Sc$, $M = 763.92$, monoclinic, space group $C2/c$, $a = 24.3573(10)$, $b = 22.7846(9)$, $c = 18.4427(8)$ Å, $\beta = 114.9920(10)°$, $V = 9276.8(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.094$ Mg m^{3-}, $T = 150(2)$ K, $Mo_{K\alpha} = 0.71073$ Å, absorption coefficient 0.276 mm^{-1}, $F(000) = 3320$, 45314 reflections collected, 9461 independent reflections, $R_{int} = 0.0299$, GoF = 1.025, $R = 0.0354$ $[I > 2\sigma(I)]$, $wR^2 = 0.0901$ $[I > 2\sigma(I)]$.

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[20] Crystal data for **8**: $C_{44}H_{63}N_2P_2Sc$, $M = 726.86$, triclinic, space group $P\bar{1}$, $a = 11.7183(6)$, $b = 12.2735(6)$, $c = 17.2532(8)$ Å, $\alpha = 74.9370(10)$, $\beta = 73.8470(10)$, $\gamma = 62.5370(10)°$, $V = 2089.52(18)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.155$ Mg m^{-3}, $T = 150(2)$ K, $Mo_{K\alpha}$: 0.71073 Å, absorption coefficient 0.284 mm^{-1}, $F(000) = 784$, 23174 reflections collected, 7905 independent reflections, $R_{int} = 0.0319$, GoF = 1.013, $R = 0.0357$ $[I > 2\sigma(I)]$, $wR^2 = 0.0859$ $[I > 2\sigma(I)]$.