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# Synthesis and thermal behavior of dimethyl scandium complexes featuring anilido-phosphinimine ancillary ligands

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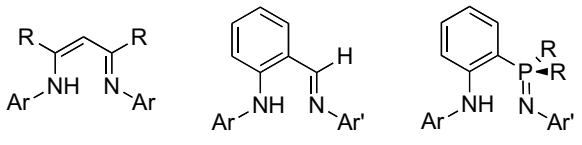
**Abstract**

A family of N,N donor ligands [1-(NHAr)-2-($PR_2$=$NAr'$)$C_6H_4$] (**1a–d**; Ar = 2,6-$^i$Pr$_2$-$C_6H_3$, R = Me, Ph, Ar′ = 2,4,6-$Me_3$-$C_6H_2$, 2-$^i$Pr-$C_6H_4$, 2,6-$^i$Pr$_2$-$C_6H_3$) has been prepared and fully characterized by multinuclear NMR spectroscopy and X-ray crystallography. Lithiation of the N–H unit and subsequent salt metathesis protocols with $ScCl_3THF_3$ provides an avenue to organometallic scandium complexes. The resultant base-free monomeric dichlorides $LScCl_2$, **3a–d**, have been fully characterized by NMR spectroscopy as well as X-ray crystallography (**3a**,**c**,**d**). Alkylation of the dichlorides using LiMe results in clean formation of dialkyl complexes $LScMe_2$ **4a–c**. Thermolysis of these materials under argon and hydrogen leads to decomposition products as a result of C–H activation of the ligand. Analysis of these results provides a qualitative assessment of the metalative resistance of each ligand framework.


*Keywords:* Scandium; Chelating ligands; Anilido-phosphinimine ligands; Thermal stability

## 1. Introduction

Ligand design is a regular exercise for organometallic chemists attempting to generate novel coordination environments, stabilizing particular oxidation states and preparing robust catalysts. With respect to group 3 chemistry [1], recent efforts have focused on the synthesis and reactivity of metal cations [2], hydrides [3] and metal to element double bonds [4]. In that regard, the β-diketiminato, or "NacNac" ligand (**I**) has been firmly established as a cyclopentadienide ("Cp") surrogate for organotransition metal chemistry [5] due to the steric and electronic [6] tunability of the ligand scaffold and its relatively straightforward synthesis [7]. This ancillary, featuring 2,6-disubstitution of the *N*-aryl groups, has proven an appropriate support for neutral [8] and cationic [9] organoscandium complexes. While neutral scandium bis-alkyl complexes exhibit moderate thermal stability, their cationic counterparts tend to be less robust, and decompose via C–H activation of one of the *ortho*-groups of the *N*-aryl units. This deactivation mode also operates for the organoyttrium congeners [10] and, thus, alternatives to NacNac were pursued.




I II III

We recently reported a new anilido-imine system (**II**), which was deployed as a support for organoyttrium cations [11]. Attempts to prepare organoyttrium hydride complexes from the same dialkyl starting materials were perpetually hampered by nucleophilic attack by the hydride at the imine carbon generating an undesirable dianionic ligand. To eliminate this possibility, the anilido-imine framework was modified through incorporation of a phosphinimine

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unit [12] in place of the imine, producing a new ancillary **III** [13]. The institution of the phosphorus(V) center should eliminate any nucleophilic attack of the ligand backbone, and the PN unit should allow for facile steric and electronic tunability. This system has been effectively utilized as a stabilizing ligand for neutral and cationic organoaluminum complexes [13] and recently for organoyttrium alkyls [14]. In this paper, we describe the synthesis of a family of anilido-phosphinimine ligands highlighting the modularity of the ligand framework. The thermal stability of the corresponding scandium dimethyl complexes is evaluated, as well as their ability to support organoscandium hydrides.

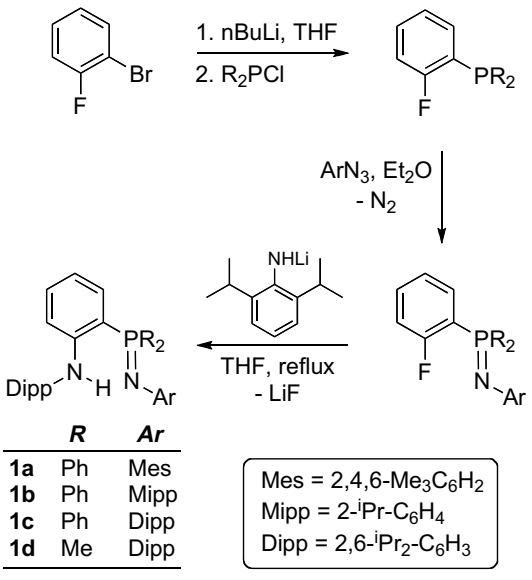
## 2. Results and discussion

### 2.1. Synthesis and characterization of anilido-phosphinimine ligands *1a–d*

The synthesis of ligand **1a** has been previously reported [13] and follows the slightly modified sequence outlined in Scheme 1. Of note, the preparation of *o*-$C_6H_4FPR_2$ (R = Me, Ph [15]) gives consistently higher yields when THF instead of diethyl ether (as originally reported) is employed. The lithiation step is kinetically much slower in ether, and the *in situ* generated aryl lithium begins to precipitate prior to addition of the phosphorus electrophile, which significantly lowers the yield. In THF however, the lithiation is very efficient and the aryl lithium remains dissolved in the more coordinating solvent at −78 °C. Oxidation of the phosphines under Staudinger conditions [16] can be performed in air with diethyl ether instead of under anaerobic conditions in MeCN and the resultant phosphinimines *o*-$C_6H_4FP(R_2)$=NAr′(R = Me, Ph; Ar′ = Mes, Mipp, Dipp) can be recrystallized from hexane. Incorporation of the formally P(V) center activates the *ortho* fluorine towards nucleophilic aromatic substitution, which gives similar yields whether the lithium anilide is added stoichiometrically or in slight excess. All of the ligands are obtained analytically pure as colorless crystals upon recrystallization from hot methanol in overall yields of 37–45% starting from bromo-2-fluorobenzene. This modular synthesis allows for a wide array of ligands to be prepared depending on the phosphine, azide and *N*-aryl substituents utilized; the current study will focus on the Dipp analide family depicted in Scheme 1.

Ligands **1a–d** have been comprehensively characterized by combustion analysis and multinuclear NMR spectroscopy ($^1H$, $^{13}C$, $^{31}P$). Signature spectral features include the N–H shift downfield of 9 ppm in the $^1H$ NMR spectra and singlets in the $^{31}P\{^1H\}$ NMR spectra between 0 and 6 ppm for **1a–c** which shifts further downfield when the more electron donating methyl groups are installed on phosphorus for **1d**. The X-ray structure of **1a** has been reported previously [13] and those of **1b** and **1c** are shown in Figs. 1 and 2, respectively; comparative metrical data for the three ligands whose structures have been determined are presented in Table 1.

The solid state structure of **1b** (Fig. 1) illustrates the characteristic twist within the ligand backbone with a C(27)–C(22)–P–N(1) torsion angle of 50.8(2)° which is even greater (c.f. 53.5(1)°) in the bulkier system **1c** (Fig. 2 and Table 1). Both angles are notably larger than the 44.1(2)° reported previously for **1a** [13], perhaps a result of the enhanced steric bulk of the aryl substituents on the phosphinimine nitrogen. As a result the aryl group of the PN unit is oriented significantly out of the plane while the anilido Dipp group lies orthogonal to the N–C–C–P plane. The phenyl rings on phosphorus occupy pseudoaxial and equatorial positions relative to the backbone plane. This ligand geometry contrasts with related *N*,*N*-bidentate




| | R | Ar |
|---|---|---|
| **1a** | Ph | Mes |
| **1b** | Ph | Mipp |
| **1c** | Ph | Dipp |
| **1d** | Me | Dipp |

Scheme 1.

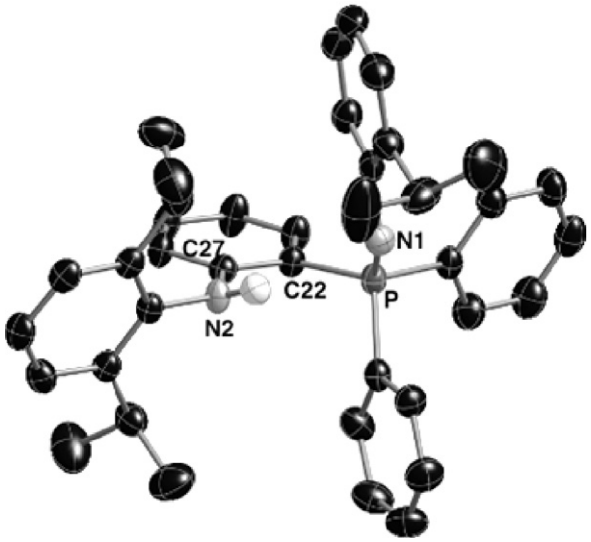



Fig. 1. Thermal ellipsoid diagram of **1b** at 50% probability. Selected bond lengths (Å) and angles (°): P–N(1), 1.575(2); P–C(22), 1.810(2); N(2)–C(27), 1.381(2); N(2)–C(27)–C(22)–P, 5.4(3); C(27)–C(22)–P–N(1), 50.8(2).

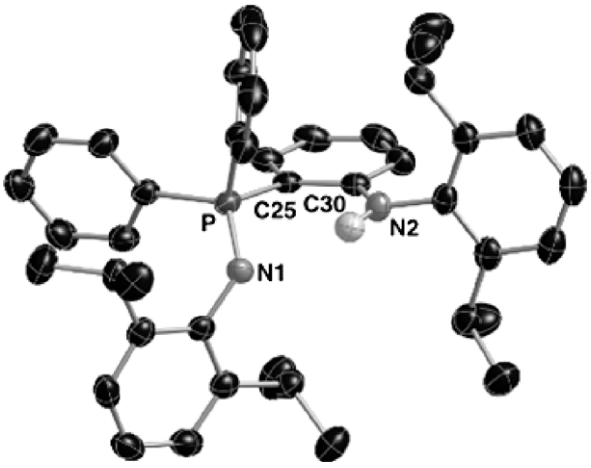
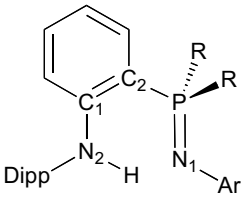



Fig. 2. Thermal ellipsoid diagram of **1c** at 50% probability. Selected bond lengths (Å) and angles (°): P–N(1), 1.558(2); P–C(25), 1.817(2); N(2)–C(30), 1.383(2); N(2)–C(30)–C(25)–P, 6.2(2); C(30)–C(25)–P–N(1), 53.5(1).

Table 1
Selected metrical parameters for **1a**–**c**



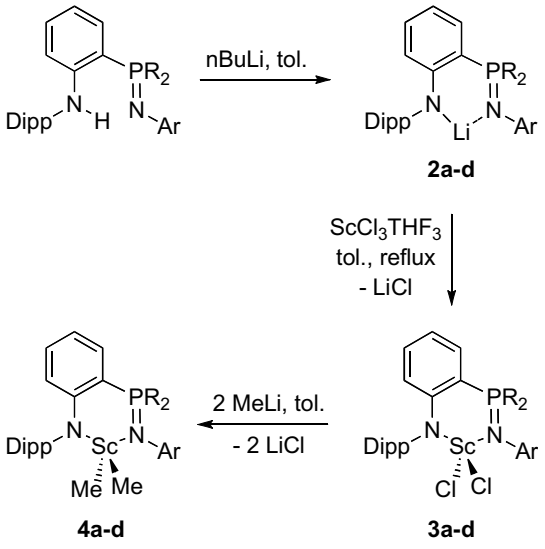

| Param | **1a** [13] | **1b** | **1c** |
|---|---|---|---|
| *Bond distances (Å)* | | | |
| N(2)–C(1) | 1.382(3) | 1.381(2) | 1.383(2) |
| C(2)–P | 1.817(2) | 1.810(2) | 1.817(2) |
| P–N(1) | 1.563(2) | 1.575(2) | 1.558(1) |
| *Bond angles (°)* | | | |
| N(2)–C(1)–C(2) | 120.1(2) | 120.45(16) | 121.30(13) |
| C(2)–P–N(1) | 116.45(10) | 116.57(9) | 113.87(7) |
| *Torsion angles (°)* | | | |
| N(2)–C(1)–C(2)–P | 3.7(3) | 5.4(3) | 6.2(2) |
| C(1)–C(2)–P–N(1) | 44.1(2) | 50.8(2) | 53.5(1) |

ligands like the β-diketiminates [5] and imine-anilido systems [11,17] where the flanking aryl groups are parallel to each other and perpendicular to the ligand plane. In the anilido-phosphinimine systems, the coordination core is protected on the PN flank by the phosphinimine aryl group and the pseudoaxial phenyl group on phosphorus. The P–N(1) contact at 1.575(2) Å for **1b** and 1.558(2) Å for **1c** are typical for P=N bonds of this type.

### 2.2. Dichloro- and dimethylscandium complexes

With a family of well characterized ligands in hand, we sought to evaluate their ability to support monomeric, base-free dichloro- and dimethylscandium complexes related to our previous work with β-diketiminato-[8] and anilido-imine [11] scandium complexes. Compound **1a** has been shown to react with $AlMe_3$ and $AlH_3 \cdot NMe_3$ to produce dimethyl- and dihydrido-aluminum complexes with concomitant loss of $CH_4$ and $H_2$ [13]. Attempts to prepare diakyl scandium complexes using alkane elimination protocols [18] with **1a**–**d** were unsuccessful, and thus a more traditional salt metathesis procedure was developed. Treatment of **1a**–**d** with *n*BuLi in toluene quantitatively generates the lithium salts **2a**–**d** that can be isolated as pale yellow solids by filtration and washing with hexanes (Scheme 2). Lithiated ligands **2a**–**d** are air and moisture sensitive materials but are stable indefinitely under argon at room temperature. Characterization by multinuclear NMR spectroscopy reveals the loss of the diagnostic N–H signal in the $^1H$ NMR spectra, and a downfield shift in the $^{31}P\{^1H\}$ NMR spectra to 18–20 ppm. The phosphinimine nitrogen chelates the lithium ion, effectively deshielding the phosphorus center leading to the downfield shift [13].

The anilido-phosphinimine scaffold can be attached to scandium by refluxing toluene solutions of **2a**–**d** with $ScCl_3THF_3$ for 8–10 h forming compounds $LScCl_2$ **3a**–**d** in moderate yields of 70–95% as off-white solids upon work-up. Compounds **3** are soluble in aromatic and halogenated solvents but largely insoluble in all aliphatic media. Spectroscopic analysis of **3a**–**d** indicates complete loss of coordinated THF donors and the $^{31}P\{^1H\}$ NMR spectra indicate a further downfield shift to the range of 29–33 ppm. Whereas the spectra for **3a**,**c**,**d** all exhibit sharp, resolved signals in the $^1H$ NMR spectrum, the mixed Mipp–Dipp dichloride **3b** exhibits broad signals for the Dipp isopropyl methynes and all of the isopropyl methyls at room temperature. Cooling $C_7D_8$ solutions below −30 °C freezes out the exchange processes and sharp septets and doublets are resolved. Presumably this behavior is a result of hindered rotation of the Dipp group and at




Scheme 2.

room temperature the compound is at the onset of the fast exchange regime.

Concentrated benzene solutions of **3a** and **3c** afford X-ray quality crystals when cooled to 0 °C and the molecular structures of these two compounds are shown in Figs. 3 and 4, respectively. The structure of **3a** is dimeric with the two distorted trigonal bypramidal scandium atoms each possessing two bridging chlorides and one terminal chloride within its coordination sphere, in addition to the chelating nitrogens of the ligand framework. It is presumed that this aggregation exists in benzene solution as well, since **3a** is only sparingly soluble in $C_6D_6$, which contrasts the other dichlorides studied here. As in the free ligand, the backbone atoms are not co-planar as illustrated by the C(13)–C(14)–P–N(2) torsion angle of 22.5(7)°, though it is much more planar than in **1a** (44.1(2)°) and **1b** (53.6(2)°). This is likely a result of the congested core of the dimer, necessitating the two ligands to arrange themselves approximately orthogonal to each other to minimize "across dimer" steric repulsions. The P–N contact is elongated from the free ligand to 1.628(5) Å indicating strong donation from the phosphinimine unit, but the distance is still consistent with a PN double bond. The terminal Sc–Cl contact of 2.345(2) Å is shorter than those in the bridging chlorides; these are asymmetrically bound, with Sc–Cl bond distances of 2.466(2) Å and 2.633(2) Å. This suggests that aggregation is weak and indeed addition of THF to $C_7D_8$ suspensions of **3a** promotes complete dissolution, giving rise to new $^1H$ and $^{31}P\{^1H\}$ signals corresponding to a five-coordinated monomeric scandium dichloride with one THF donor. The Sc–N contacts are equivalent within experimental error which highlights the strong donating capacity of the phosphinimine moiety (*vide infra*).

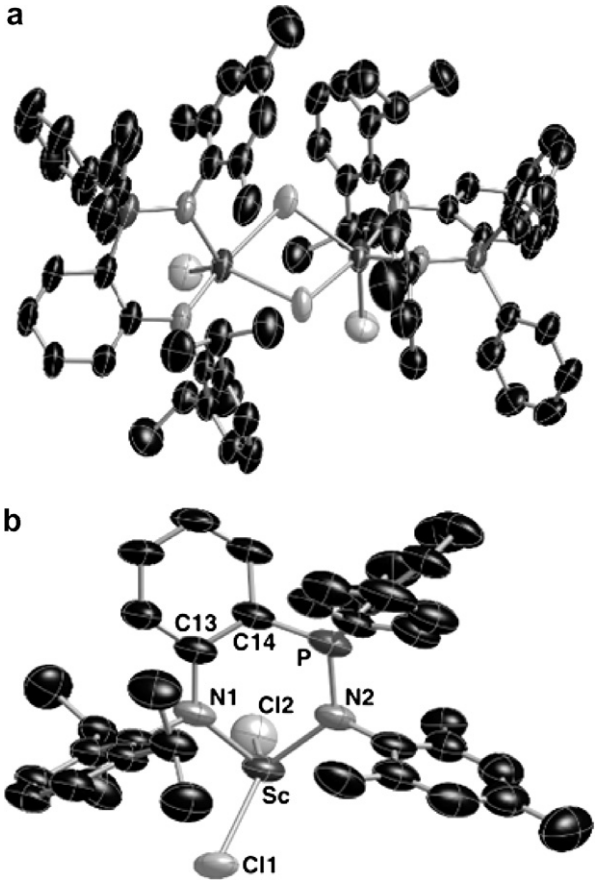



Fig. 3. Thermal ellipsoid diagram of **3a** at 50% probability. The dimeric structure is shown in (a) and the monomer moiety is shown in (b). Selected bond lengths (Å) and angles (°): P–N(2), 1.628(5); Sc–N(1), 2.107(5); Sc–N(2), 2.101(5); Sc–Cl(1), 2.466(2); Sc–Cl(2), 2.345(2); Sc–Cl(1′), 2.633(2); P–C(14), 1.767(7); N(1)–C(13), 1.385(7); N(1)–Sc–N(2), 92.5(2); N(1)–C(13)–C(14)–P, 16.9(9); C(13)–C(14)–P–N(2), 22.5(7).

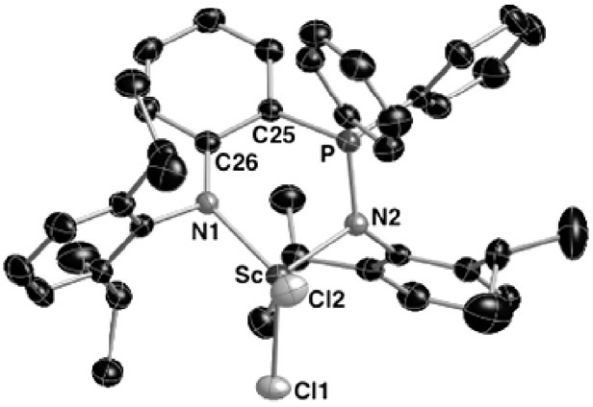



Fig. 4. Thermal ellipsoid diagram of **3c** at 50% probability. Selected bond lengths (Å) and angles (°): P–N(2), 1.630(2); Sc–N(1), 2.071(2); Sc–N(2), 2.106(2); Sc–Cl(1), 2.3373(7); Sc–Cl(2), 2.3341(6); P–C(25), 1.783(2); N(1)–C(26), 1.386(2); N(1)–Sc–N(2), 91.59(6); N(1)–C(26)–C(25)–P, 8.7(2); C(26)–C(25)–P–N(2), 48.1(2).

When the mesityl group is replaced by the bulkier Dipp group in **3c** a monomeric dichloride structure is obtained (Fig. 4). The four-coordinate scandium adopts a distorted tetrahedral geometry and does not retain any THF molecules. The P–N bond distance of 1.630(2) Å is comparable to that observed for **3a** however the ligand twist of 48.1(2)° is more reminiscent of the free ligand than of the dimer **3a**. The phenyl groups at phosphorus adopt the predicted axial and equatorial orientations, with the axial group and the adjacent Dipp group serving to protect regions of space above and below the ligand plane about the metal center. The inequivalent Sc–N contacts indicate asymmetric ligand binding with the anilide nitrogen more closely bound to the metal. The Sc–Cl distances of 2.3341(6) Å and 2.3373(7) Å are unremarkable.

Dichlorides **3** represent precursors to base-free dialkyl scandium complexes. Treatment of **3a-c** with ethereal solutions of methyl lithium at 0 °C produce dimethylscandium species **4a**–**c** in good yields following removal of LiCl by filtration. Addition of precisely 2 equiv. of MeLi is important as any excess produces lithiated ligands **2** which are difficult to remove from samples of **4**. Purified dimethyls **4** are stable indefinitely at room temperature under argon as solids, but show degrees of decomposition over time in solution (*vide infra*). Solution NMR spectra reveal $^{31}P$ shifts reside in the same region (~30 ppm) as their dichloride precursors. The $^1H$ spectra of **4** are analogous to **3** with the

exception that the ScMe groups give rise to resonances upfield of 0 ppm. Once again, the room temperature $^{1}H$ NMR spectrum of **4b** is broadened, however the spectrum becomes resolved below −30 °C (Fig. 5). Although the ligand provides an environment that lacks left–right, or top–bottom symmetry, the ScMe groups, which reside in chemically equivalent orientations, resonate as a singlet, even at temperatures below −80 °C. This suggests that the twist in the backbone is not static, and a dynamic process must exist in solution with a low barrier to inversion at scandium. $^{13}C\{^{1}H\}$ NMR spectra do not always reveal the ScMe resonance due to the close proximity to the quadrupolar scandium ($I = 7/2$); however, these resonances can be detected using an $^{1}H$–$^{13}C$ HMQC experiment, and they fall in the range 23–25 ppm. While **3a** is dimeric in the solid state, **4a** is likely a monomer due to the observed chemical shift of −0.26 ppm for the Sc–Me carbons, which is in the same range as the other monomeric dimethyl derivatives (*vide infra*).

X-ray quality crystals of **4b** and **4c** were grown from concentrated hexane solutions cooled to −35 °C and their molecular structures are shown in Figs. 6 and 7, respectively. Complexes **4b** and **4c** reveal four-coordinate, distorted tetrahedral scandium centers with distinct Sc–N bond distances of 2.134(3) Å and 2.145(3) Å for **4b** and 2.127(2) Å and 2.160(2) Å for **4c** with the shorter contacts arising from the anilide nitrogens indicating a moderate charge localization within the ligand backbone. The Sc–C distances are statistically equivalent and average 2.209(4) Å which is in agreement with other dimethylscandium complexes [8]. A similar coordination environment is observed for **4c** which is isostructural to **3c**. As seen in the structure of **4b**, the Sc–N contacts are elongated in **4c** relative to **4b**, however, N–Sc–N bond angle remains essentially unchanged.

Table 2 summarizes the metrical parameters of the three scandium-containing complexes (**3c**, **4c** and **5c**) featuring

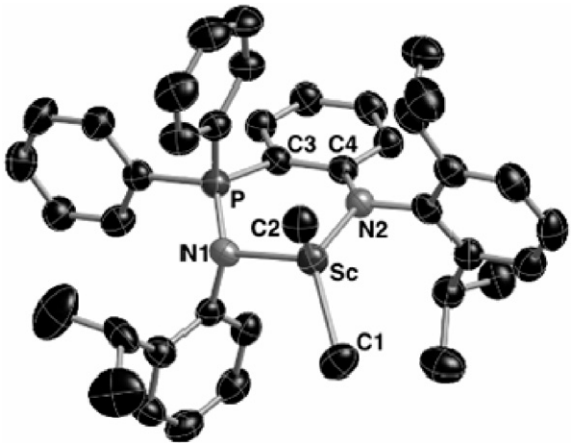



Fig. 6. Thermal ellipsoid diagram of **4b** at 50% probability. Selected bond lengths (Å) and angles (°): P–N(1), 1.616(3); Sc–N(1), 2.145(3); Sc–N(2), 2.134(3); Sc–C(1), 2.206(4); Sc–C(2), 2.211(5); P–C(3), 1.785(4); N(2)–C(4), 1.383(5); N(1)–Sc–N(2), 89.8(1); N(2)–C(4)–C(3)–P, 6.5(5); C(4)–C(3)–P–N(1), 43.4(4).

the ligand derived from **1c**. In all cases, closer Sc–$N_{anilide}$ contacts are observed vs. the Sc–$N_{phosphinimine}$ highlighting the charge localization in that position. Nevertheless, the disparities in the bond lengths (0.015–0.035 Å) is significantly smaller than for our previously reported yttrium complexes featuring the anilido-imine ligand (**II**) where the Y–$N_{anilide}$ contact was consistently shorter than the Y–$N_{imine}$ by $\geqslant$0.130 Å [11]. This suggests the phosphinimine unit possesses enhanced basicity vs. the imine function, making it an effective donor [12]. For **3c** and **4c** that feature chloride and methyl ligands, respectively, the two observed Sc–E contacts are statistically equivalent and does not suggest that a particular coordination site is more or less hindered.

Whereas the ligand systems with phenyl groups on phosphorus react cleanly with MeLi to afford dimethyl scandium complexes, the preparation of **4d**, in which the

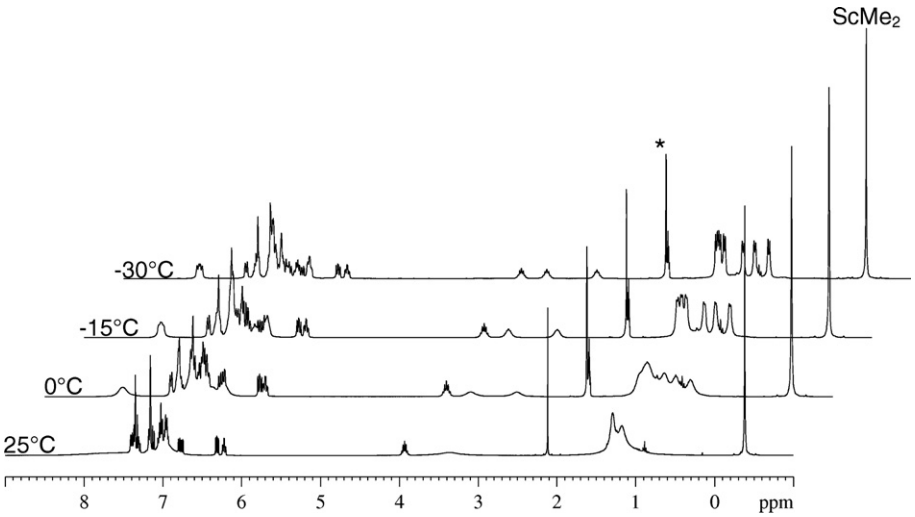



Fig. 5. Variable temperature 400 MHz $^{1}H$ NMR spectra of **4b** in $C_7D_8$ (*).

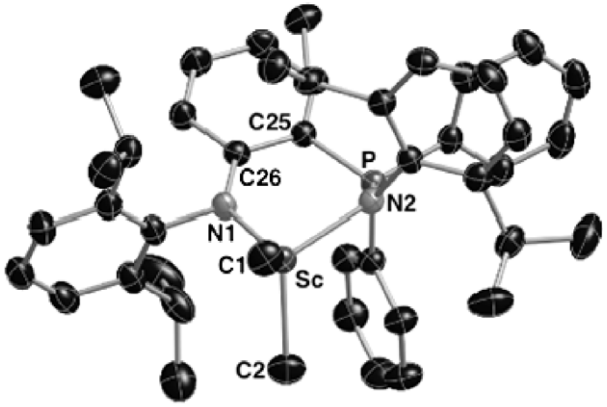
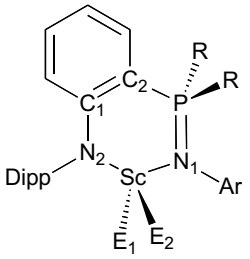



Fig. 7. Thermal ellipsoid diagram of **4c** at 50% probability. Selected bond lengths (Å) and angles (°): P–N(2), 1.629(2); Sc–N(1), 2.127(2); Sc–N(2), 2.160(2); Sc–C(1), 2.208(2); Sc–C(2), 2.209(2); P–C(25), 1.788(2); N(1)–C(26), 1.386(2); N(1)–Sc–N(2), 91.52(6); N(1)–C(26)–C(25)–P, 5.2(2); C(26)–C(25)–P–N(2), 47.1(2).

phenyl groups have been replaced with methyls, is not possible under the same conditions. Here, an asymmetric complex is obtained with a scandium methyl resonance at 0.5 ppm, which integrates to 3H and not the predicted 6H. The loss of symmetry and lower than expected methyl resonance intensity are indicative of a metalation process (see below and Scheme 3) wherein a methyl group is lost through C–H activation of the ligand. The presence of four well resolved isopropyl methynes indicates that metalation is not occurring at either of the Dipp groups, and must originate at the phosphorus methyls. The typical doublet for the $P(Me)_2$ is absent from the proton NMR spectrum and replaced with a complex multiplet characteristic of diastereotopic methylene protons. This was confirmed by a structural determination of the product (**5d**), and the structure is shown in Fig. 8.

Metalated product **5d** is a dimeric structure with the scandium methyls adopting a symmetric bridging geometry between the two distorted trigonal bipyramidal scandium centers. As the spectroscopy showed, the axial methyl group on phosphorus has succumbed to metalation, forming a tuck-in species with a Sc–C(2) distance of 2.338(3) Å that is 0.06 Å shorter than the bridging Sc–C(1) length of 2.399(3) Å. The N(2)–P–C(2)–Sc ring possesses a butterfly conformation with a torsion angle of 31.6(1)°. The backbone twist is in the range of the dimethyl complexes **4b**,**c** at 52.1(3)°, and has pushed the phosphinimine Dipp group away from the scandium allowing for dimerization. The N(1)–Sc–N(2) angle is approximately 5° more obtuse than in the dimethyl analogues with the scandium drawn into the ligand core by the metalated methylene unit.

Table 2
Selected metrical parameters for **3c**, **4c** and **5c**

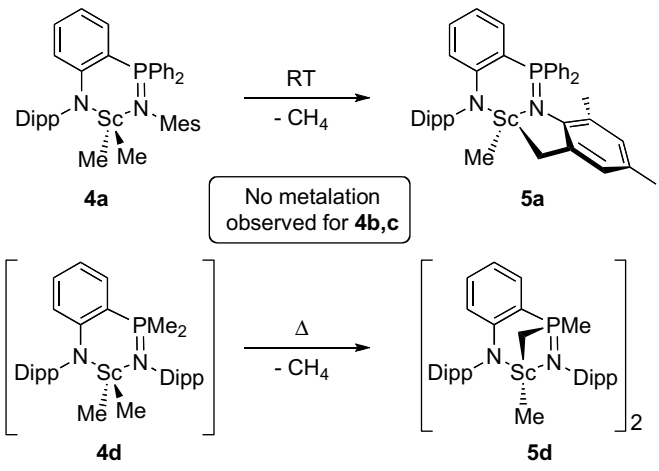



| Param.[a] | 3c | 4c | 5c[b] |
|---|---|---|---|
| *Bond distances (Å)* | | | |
| Sc–E(1) | 2.3373(7) | 2.208(2) | 2.365(3) |
| Sc–E(2) | 2.3341(6) | 2.209(2) | 2.307(4) |
| Sc–N(1) | 2.106(2) | 2.160(2) | 2.170(3) |
| Sc–N(2) | 2.071(2) | 2.127(2) | 2.155(3) |
| N(2)–C(1) | 1.386(2) | 1.386(2) | 1.393(4) |
| C(1)–C(2) | 1.431(3) | 1.427(3) | 1.427(5) |
| C(2)–P | 1.783(2) | 1.788(2) | 1.777(3) |
| P–N(1) | 1.630(2) | 1.629(2) | 1.608(3) |
| *Bond angles (°)* | | | |
| N(1)–Sc–N(2) | 91.59(6) | 91.52(6) | 89.32(10) |
| E(1)–Sc–E(2) | 104.08(2) | 100.99(9) | 88.64(13) |
| N(2)–Sc–E(1) | 113.34(5) | 112.52(8) | 107.16(12) |
| N(2)–Sc–E(2) | 121.44(5) | 125.37(8) | 94.93(12) |
| N(1)–Sc–E(1) | 119.24(5) | 116.49(8) | 161.48(13) |
| N(1)–Sc–E(2) | 107.73(4) | 110.93(8) | 81.41(11) |
| *Torsion angles (°)* | | | |
| N(2)–C(1)–C(2)–P | 8.7(2) | 5.2(2) | 4.4(4) |
| C(1)–C(2)–P–N(1) | 48.1(2) | 47.1(2) | 50.2(3) |

[a] E = Cl for **3c** and C for **4c** and **5c**.
[b] E(2) = C(42) from Fig. 9.

## 2.3. Thermal stability of scandium dialkyl complexes *4a–c*

The thermal instability of putative complex **4d** towards loss of methane is somewhat surprising given that the $sp^2$ hybridized C–H bonds of the phosphorus phenyl groups in compounds **4a**–**c** might be expected to be kinetically more prone [19] to such decomposition pathways. Given the potential of monomeric dialkyl scandium complexes in catalysis [9,20] and as precursors for elusive monomeric scandium hydrides [3,21] we were therefore interested in the thermal stability of compounds **4a**–**c** and their reactivity towards dihydrogen.




Scheme 3.

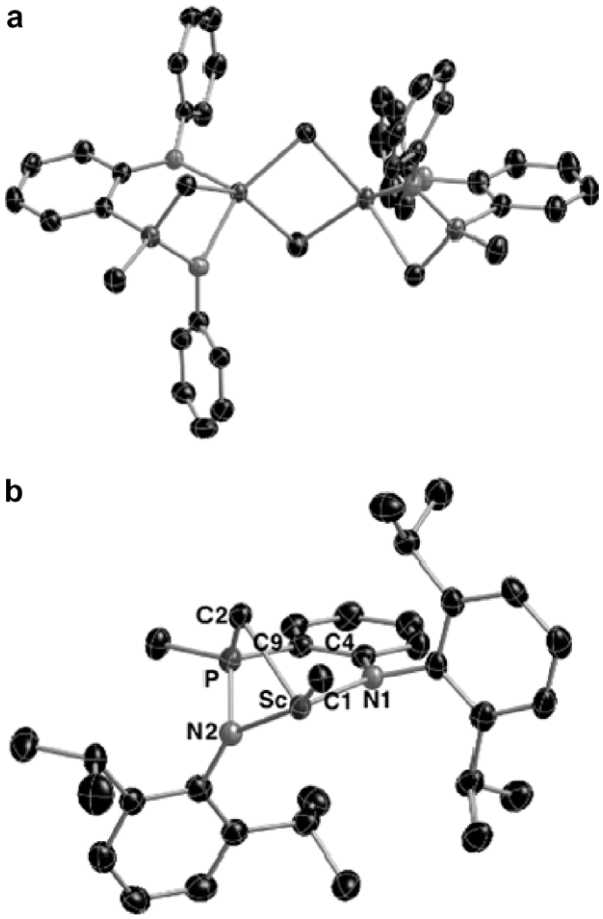
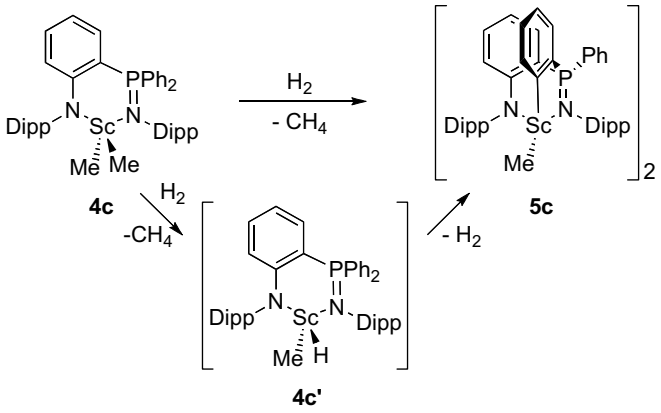



Fig. 8. Thermal ellipsoid diagram of **5d** at 50% probability. The dimeric structure with *iso*-propyl groups removed is shown in (a) and the monomer moiety is shown in (b). Selected bond lengths (Å) and angles (°): P–N(2), 1.641(2); Sc–N(1), 2.082(2); Sc–N(2), 2.144(2); Sc–C(1), 2.399(3); Sc–C(2), 2.338(3); P–C(4), 1.800(3); N(1)–C(9), 1.398(4); N(1)–Sc–N(2), 95.53(9); N(1)–C(9)–C(4)–P, 0.7(4); C(9)–C(4)–P–N(2), 52.1(3); N(2)–P–C(2)–Sc, 31.6(1).

Solutions of P=N mesityl substituted **4a** were found to decompose readily at room temperature through C–H bond activation of a mesityl methyl group (Scheme 3) and its chemistry was not examined further in this regard. In contrast, when $C_6D_6$ solutions of **4b**,**c** were heated at 65 °C in a J-Young NMR tube no decomposition was observed spectroscopically over 24 h. Given their promising thermal stability, compounds **4b** and **4c** were subjected to reaction with dihydrogen in an attempt to generate reactive scandium hydrides.

### 2.4. Hydrogen catalyzed C–H activation of *4c*

Alkyl- and dialkylscandium complexes have been known for some time to react readily with dihydrogen to produce hydrides [3,22] although well-defined monomeric hydrides have not been structurally verified and represent an attractive target. Stirring a hexane solution of **4c** under 4 atm of hydrogen at room temperature for 4 days (Scheme 4) leads to a pale yellow precipitate which can be isolated




Scheme 4.

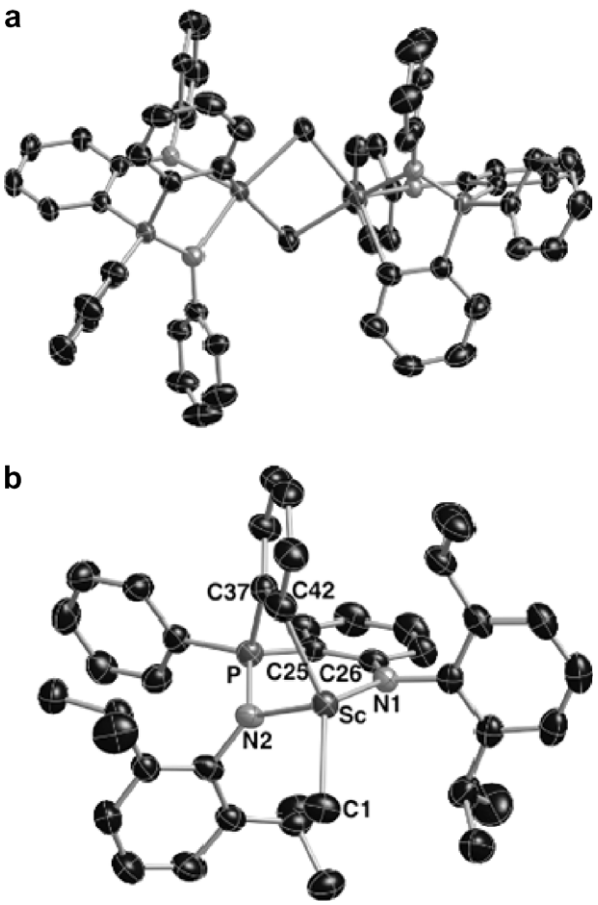



Fig. 9. Thermal ellipsoid diagram of **5c** at 50% probability. The dimeric structure with *iso*-propyl groups removed is shown in (a) and the monomer moiety is shown in (b). Selected bond lengths (Å) and angles (°): P–N(2), 1.608(3); Sc–N(1), 2.155(3); Sc–N(2), 2.170(3); Sc–C(1), 2.322(4); Sc–C(1′), 2.365(3); Sc–C(42), 2.307(4); P–C(25), 1.777(3); N(1)–C(26), 1.393(4); N(1)–Sc–N(2), 89.3(1); N(1)–C(26)–C(25)–P, 4.4(4); C(26)–C(25)–P–N(2), 50.2(3); P–C(37)–C(42)–Sc, 25.6(3).

by filtration. The $^1H$ NMR spectrum of a $C_7D_8$ solution of **5c** suggests a complete loss of symmetry in the molecule as all of the isopropyl methyl signals become diastereotopic and a new signal arises at 0.52 ppm for the Sc–Me group

which integrates to 3H. An upfield shift in the $^{31}P$ NMR experiment is observed as a new resonance appears at 27.7 ppm. X-ray quality crystals of **5c** were grown from a layered solution of toluene and hexane at −35 °C and the molecular structure is shown in Fig. 9.

The solid state structural analysis of **5c** shows that it adopts a dimeric conformation which is structurally akin to **5d**, with a pair of bridging methyl groups linking the two scandium atoms. As in the *P*-methyl ligand supported system, an axial phenyl group on phosphorus assumes a non-innocent role [14] and an *ortho*-C–H bond engages in a σ-bond metathesis reaction with a putative scandium hydride **4c′** (Scheme 4). Thus, dihydrogen serves as a catalyst for the metalation of **4c** to give dimer **5c**. The Sc–C(42) distance of 2.307(4) Å is slightly shorter than the Sc–C(1) at 2.322(4) Å and Sc–C(1′) at 2.365(3) Å. There is also a large torque observed for the metalated phenyl group with a P–C(37)–C(42)–Sc torsion angle of 25.6(3)°.

## 3. Conclusions

An optimized synthesis of a versatile anilido-phosphinimine ligand is reported; these ligands can be readily affixed to scandium using standard salt metathesis protocols. While the ligand is a competent donor to scandium, it is susceptible to ligand deactivation either under thermal conditions for **4a**,**d** or in the presence of dihydrogen, **4c**. The rapid conversion of the intermediate hydride **4c′**, is suggestive of a highly reactive hydride species and efforts are currently underway to capture this system by developing more metalatively robust ligand scaffolds.

## 4. Experimental

### 4.1. General methods

All manipulations were performed either in an Innovative Technologies System One inert atmosphere glovebox or on greaseless vacuum lines equipped with Teflon needle valves (Kontes) using swivel-frit type glassware. Toluene, THF and hexanes were dried and purified using the Grubbs/Dow purification system, [23] and stored in evacuated bombs. Bromobenzene and bromobenzene-$d_5$ were predried over $CaH_2$, and hexamethyldisiloxane, THF-$d_8$ Benzene-$d_6$ and toluene-$d_8$ were dried and stored over sodium/benzophenone. All were distilled prior to use.

The following reagents were synthesized using literature protocols: mesityl azide [24], 2-isopropylphenyl azide [25] and 2,6-diisopropylphenyl azide [25]. Lithio ligands **2b–d** were prepared according to the protocol developed in this lab for **2a** [13]. Phosphine reagents were obtained from Strem and all other materials were obtained from Aldrich and used as received.

Samples were analyzed by NMR spectroscopy on Bruker AMX-300 and DRX-400 spectrometers at room temperature unless otherwise specified. $^1H$ and $^{13}C$ were referenced to $Si(CH_3)_4$ through the residual peaks of the employed solvent, $^2H$ to external $Si(CD_3)_4$ at 0.0 ppm, $^{11}B$ spectra to external $BF_3 \cdot OEt_2$ at 0.0 ppm and $^{19}F$ spectra to $CFCl_3$ using an external standard of hexafluorobenzene ($\delta$ −163.0 ppm) in $C_6D_6$. NMR data are provided in ppm; $^{13}C$ resonances for the $C_6F_5$ groups are not reported. The coupling constants (*i.e.* $^3J_{H-H}$) for the isopropyl groups on the ligand range between 6.4 and 7.2 Hz, and thus, are not reported in the NMR analysis of the compounds. Elemental analyses were performed by Mrs. Roxanna Smith and Mrs. Dorothy Fox in the microanalytical laboratory at the University of Calgary. Complexes containing scandium (*i.e.* **3–5**) were consistently low in carbon; possibly a result of metal-catalyzed silicon carbide formation leading to incomplete combustion [26]. X-ray data were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer [27] using Mo Kα radiation at −80 °C.

### 4.2. Syntheses of complexes

#### 4.2.1. General procedure for 1-F-2-$PR_2C_6H_4$

The following is a modification to a published procedure [15]. A solution of 1-bromo-2-fluorobenzene (6.77 mL, 62 mmol) in 200 mL was cooled to −78 °C and *n*BuLi (2.5 M, 24.8 mL, 62 mmol) was added via syringe is stirred for 15 min. A solution of $Me_2PCl$ (4.9 mL, 62 mmol) in 25 mL of THF was then added via cannula and the solution was stirred for 4 h at −78 °C, then slowly warmed to room temperature overnight. The red solution was quenched with 100 mL of 1 M HCl and extracted with ether, washed twice with 100 mL of water, then with 50 mL of brine. Combined organic fractions were dried over $MgSO_4$, filtered, and volatiles removed *in vacuo* to afford a pale yellow oil (1-F-2-$PMe_2C_6H_4$). Yield: 6.62 g (69%).

#### 4.2.2. General procedure for 1-F-2-($PR_2$=$NAr$)$C_6H_4$

A solution of 1-F-2-$PMe_2C_6H_4$ (6.55 g, 42 mmol) in 50 mL of $Et_2O$ was added to a solution of $DippN_3$ (8.54 g, 42 mmol) in 50 mL of $Et_2O$ and stirred at room temperature for 2 h, or until $N_2$ effervescence is complete. Volatiles were removed *in vacuo* to afford a pale yellow oil which was recrystallized from refluxing hexane (1-F-2-($PMe_2$=NDipp)$C_6H_4$). Yield: 13.26 g (95%).

#### 4.2.3. Characterization of 1-(NHDipp)-2-($PPh_2$=NMipp)$C_6H_4$ (**1b**)

Yield: 41%. $^1H$ NMR ($C_6D_6$): $\delta$ 9.03 (s, 1H, N*H*), 7.87 (m, 4H, *m*-P-($C_6H_5$)$_2$), 7.31 (m, 1H, $PNC_6H_4$), 7.12–7.09 (m, 3H, $NC_6H_3$), 7.02–6.87 (m, 10H, *o*,*p*-P($C_6H_5$)$_2$, $PNC_6H_4$, $PC_6H_4N$), 6.44 (m, 1H, $PC_6H_4N$), 6.27 (m, 1H, $PC_6H_4N$), 4.13 (sp, 1H, C*H*$Me_2$), 3.00 (sp, 2H, C*H*$Me_2$), 1.35 (d, 6H, CH(C$H_3$)$_2$), 0.99 (d, 6H, CH(C$H_3$)$_2$), 0.84 (d, 6H, CH(C$H_3$)$_2$). $^{13}C$ NMR ($C_6D_6$): $\delta$ 153.6, 148.9 (2 quaternary aromatic), 148.1 (1Ph), 142.4 (1 quaternary aromatic), 134.8 (1Ph), 133.7 (1 quaternary aromatic), 133.3, 132.7, 132.6, 131.5 (4Ph), 131.3 (1 quaternary

aromatic), 128.6, 126.1, 125.8, 124.1, 121.1, 118.9, 116.0, 113.3 (8Ph), 112.1, 110.8 (2 quaternary aromatic) 28.6 (*C*HMe$_2$), 28.4 (*C*HMe$_2$), 24.3 (CH(*C*H$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 6.8. Anal. Calc. for $C_{39}H_{43}N_2P$: C, 82.07; H, 7.59; N, 4.91. Found C, 82.13; H, 7.47, N, 4.99%.

#### 4.2.4. Characterization of 1-(NHDipp)-2-($PPh_2$=NDipp)$C_6H_4$ (**1c**)

Yield: 45%. $^1$H NMR ($C_6D_6$): $\delta$ 9.06 (s, 1H, N*H*), 7.73 (m, 4H, *m*-P-(C$_6$*H*$_5$)$_2$), 7.19–7.15 (m, 6H, PNC$_6$*H*$_4$, NC$_6$*H*$_3$), 7.02–6.97 (m, 8H, NC$_6$*H*$_3$, *o*,*p*-P(C$_6$*H*$_5$)$_2$, NC$_6$*H*$_3$, PC$_6$*H*$_4$N), 6.4 (m, 2H, PC$_6$*H*$_4$N), 3.77 (sp, 2H, C*H*Me$_2$), 3.13 (sp, 2H, C*H*Me$_2$), 1.11 (d, 6H, CH(C*H*$_3$)$_2$), 1.03 (d, 12H, CH(C*H*$_3$)$_2$), 0.95 (d, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 154.4 (1 quaternary aromatic), 148.0 (1Ph), 144.2 (1 quaternary aromatic), 143.2 (1Ph), 135.7, 135.2, 134.7, 133.9, 133.3 (5 quaternary aromatic), 133.1, 132.9, 131.5, 128.9, 124.7, 124.1, 120.9, 116.5, 114.6 (9Ph), 112.0 (1 quaternary aromatic) 29.7 (*C*HMe$_2$), 28.8 (*C*HMe$_2$), 25.0 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 1.2. Anal. Calc. for $C_{42}H_{49}N_2P$: C, 82.32; H, 8.06; N, 4.57. Found C, 82.26; H, 8.46, N, 4.61%.

#### 4.2.5. Characterization of 1-(NHDipp)-2-($PMe_2$=NDipp)-$C_6H_4$ (**1d**)

Yield: 37%. $^1$H NMR ($C_6D_6$): $\delta$ 10.35 (s, 1H, N*H*), 7.20 (m, 5H, NC$_6$*H*$_3$), 7.06 (m, 1H, PC$_6$*H*$_4$N), 6.96 (t, 1H, NC$_6$*H*$_3$), 6.81 (m, 1H, PC$_6$*H*$_4$N), 6.52 (m, 1H, PC$_6$*H*$_4$N), 6.38 (m, 1H, PC$_6$*H*$_4$N), 3.78 (sp, 2H, C*H*Me$_2$), 3.45 (sp, 2H, C*H*Me$_2$), 1.29 (d, $^2J_{H-P} = 14$ Hz 6H, P(C*H*$_3$)$_2$), 1.23 (d, 12H, CH(C*H*$_3$)$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 153.7, (1 quaternary aromatic), 147.5 (1Ph), 144.3 (1 quaternary aromatic), 143.9 (1Ph), 136.3, 133.1 (2 quaternary aromatic), 130.0, 127.7, 124.6, 123.6 (4Ph), 121.4 (1 quaternary aromatic), 116.6, 113.6 (2Ph), 113.3 (1 quaternary aromatic) 29.1 (*C*HMe$_2$), 28.8 (*C*HMe$_2$), 25.3 (CH(*C*H$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 16.9 (P(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 8.6. Anal. Calc. for $C_{34}H_{51}N_2P$: C, 78.72; H, 9.91; N, 5.40. Found C, 79.04; H, 10.11, N, 5.33%.

#### 4.2.6. Characterization of 1-(NLiDipp)-2-($PPh_2$=NMipp)-$C_6H_4$ (**2b**)

Yield: 98%. $^1$H NMR ($C_6D_6$): $\delta$ 7.61 (m, 4H, *m*-P-(C$_6$*H*$_5$)$_2$), 7.24–7.19 (m, 5H, PNC$_6$*H*$_4$, NC$_6$*H*$_3$), 7.07–6.88 (m, 10H, *o*,*p*-P(C$_6$*H*$_5$)$_2$, PNC$_6$*H*$_4$, PC$_6$*H*$_4$N), 6.21 (m, 1H, PC$_6$*H*$_4$N), 6.27 (m, 1H, PC$_6$*H*$_4$N), 3.26 (sp, 1H, C*H*Me$_2$), 2.92 (sp, 2H, C*H*Me$_2$), 1.18 (d, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, 6H, CH(C*H*$_3$)$_2$), 0.96 (d, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 149.6, 147.7 (2 quaternary aromatic), 144.3 (1Ph), 142.9 (1 quaternary aromatic), 135.4 (1Ph), 133.7 (1 quaternary aromatic), 133.1, 132.4, 131.5, 131.1 (4Ph), 129.6 (1 quaternary aromatic), 128.5, 126.6, 125.8, 124.9, 123.8, 122.9, 121.0, (7Ph), 115.6, 108.1 (2 quaternary aromatic) 28.4 (*C*HMe$_2$), 27.8 (*C*HMe$_2$), 25.7 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 21.6. Anal. Calc. for $C_{39}H_{42}LiN_2P$: C, 81.23; H, 7.34; N, 4.86. Found C, 81.44; H, 7.12, N, 4.60%.

#### 4.2.7. Characterization of 1-(NLiDipp)-2-($PPh_2$=NDipp)-$C_6H_4$ (**2c**)

Yield: 94%. $^1$H NMR ($C_6D_6$): $\delta$ 7.47 (m, 4H, *m*-P-(C$_6$*H*$_5$)$_2$), 7.28-7.25 (m, 4H, PNC$_6$*H*$_4$, NC$_6$*H*$_3$), 7.09–6.97 (m, 7H, NC$_6$*H*$_3$, *o*,*p*-P(C$_6$*H*$_5$)$_2$, PNC$_6$*H*$_3$, PC$_6$*H*$_4$N), 6.83 (m, 1H, NC$_6$*H*$_3$), 6.08 (m, 1H, PC$_6$*H*$_4$N), 5.99 (m, 1H, PC$_6$*H*$_4$N), 3.34 (sp, 2H, C*H*Me$_2$), 2.62 (sp, 2H, C*H*Me$_2$), 1.31 (d, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, 6H, CH(C*H*$_3$)$_2$), 1.06 (d, 6H CH(*CH*$_3$)$_2$) 0.85 (d, 6H, CH(C*H*$_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 162.9, 150.6 (2 quaternary aromatic), 145.1, 144.9, 144.8 (3Ph), 134.5 (1 quaternary aromatic), 133.7 (1Ph), 133.2 (1 quaternary aromatic), 131.8 (1Ph), 130.7 (1 quaternary aromatic), 128.5, 124.4, 124.1, 123.5 (4Ph), 122.6, 117.2, 110.8 (3 quaternary aromatic), 108.0 (1Ph) 29.4 (*C*HMe$_2$), 27.9 (*C*HMe$_2$), 26.9 (CH(*C*H$_3$)$_2$), 24.9 (CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 19.4. Anal. Calc. for $C_{42}H_{48}LiN_2P$: C, 81.53; H, 7.82; N, 4.53. Found C, 81.22; H, 7.95, N, 4.36%.

#### 4.2.8. Characterization of 1-(NLiDipp)-2-($PMe_2$=NDipp)-$C_6H_4$ (**2d**)

Yield: 91%. $^1$H NMR ($C_6D_6$): $\delta$ 7.31 (m, 2H, NC$_6$*H*$_3$), 7.19 (m, 3H, NC$_6$*H*$_3$, PC$_6$*H*$_4$N), 7.04 (m, 1H, PC$_6$*H*$_4$N), 6.97 (t, 1H NC$_6$*H*$_3$) 6.76 (m, 1H, PC$_6$*H*$_4$N), 6.22 (m, 2H, PC$_6$*H*$_4$N), 3.51 (sp, 2H, C*H*Me$_2$), 3.29 (sp, 2H, C*H*Me$_2$), 1.39 (d, $^2J_{H-P} = 14$ Hz 6H, P(C*H*$_3$)$_2$), 1.30 (d, 6H, CH(C*H*$_3$)$_2$), 1.21 (m, 18H, CH(C*H*$_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 161.3, 150.1, 145.6 (3 quaternary aromatic), 144.9, 144.0, 132.8 (3Ph), 129.0 (1 quaternary aromatic), 124.0, 123.6, 122.7, 122.4 (4Ph), 115.3, 110.8 (2 quaternary aromatic), 108.3 (1Ph), 28.3 (*C*HMe$_2$), 28.2 (*C*HMe$_2$), 25.2 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 13.6 (P(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 19.2. Anal. Calc. for $C_{34}H_{50}LiN_2P$: C, 77.83; H, 9.61; N, 5.34. Found C, 77.97; H, 9.52, N, 5.30%.

#### 4.2.9. Synthesis of [1-(NDipp)-2-($PPh_2$=NMes)$C_6H_4$]-$ScCl_2$ (**3a**)

The following is a representative procedure for **3a**–**d**. A 50 mL bomb was charged with **2a** (2.26 g, 3.9 mmol) and $ScCl_3THF_3$ (1.43 g, 3.9 mmol) and 25 mL of toluene was condensed. The mixture was stirred overnight at 110 °C and upon cooling to room temperature, was transferred to a swivel frit apparatus and filtered. Removal of toluene *in vacuo* followed by sonication in hexanes and filtration afforded a white powder. Yield: 2.55 g (95%). $^1$H NMR ($C_7D_8$): $\delta$ 7.58 (m, 4H, *m*-P-(C$_6$*H*$_5$)$_2$), 7.24 (m, 3H, PC$_6$*H*$_4$N, NC$_6$*H*$_3$), 7.10 (m, 4H, *o*-P(C$_6$*H*$_5$)$_2$), 7.01–6.92 (m, 5H, *p*-P(C$_6$*H*$_5$)$_2$, NC$_6$*H*$_3$, PC$_6$*H*$_4$N) 6.55 (s, 2H, PNC$_6$*H*$_2$), 6.23 (m, 2H, PC$_6$*H*$_4$N), 3.32 (sp, 2H, C*H*Me$_2$), 2.23 (s, 6H, NC$_6$H$_2$*Me*-2,6), 1.99 (s, 3H, NC$_6$H$_2$*Me*-*4*)

1.42 (d, 6H, CH(C$H_3$)$_2$), 1.02 (d, 6H, CH(C$H_3$)$_2$). $^{13}$C NMR ($C_7D_8$): $\delta$ 147.8 (1 quaternary aromatic), 137.2 (1Ph), 137.1, 135.8, 135.3 (3 quaternary aromatic), 134.9, 134.8 (2Ph), 134.5 (1 quaternary aromatic), 133.2, 130.7, 129.0, 128.7 (4Ph), 127.9 (1 quaternary aromatic), 125.8 (1Ph), 119.2, 115.8 (2 quaternary aromatic) 29.1 (*C*HMe$_2$), 26.9 (CH(*C*H$_3$)$_2$), 25.1 (CH(*C*H$_3$)$_2$), 21.3 ($C_6H_2$*Me-2,6*), 21.1 ($C_6H_2$*Me*-4). $^{31}$P{$^1$H} NMR ($C_7D_8$): $\delta$ 29.4. Anal. Calc. for $C_{39}H_{42}Cl_2N_2PSc$: C, 68.32; H, 6.17; N, 4.09. Found C, 67.62; H, 6.35, N, 3.67%.

#### 4.2.10. Characterization of [1-(NDipp)-2-($PPh_2$=NMipp)-$C_6H_4$]$ScCl_2$ (**3b**)

Yield: 70%. $^1$H NMR ($C_6D_6$): $\delta$ 7.63 (m, 4H, *m*-P-($C_6H_5$)$_2$), 7.32–7.29 (m, 4H, PNC$_6H_4$, NC$_6H_3$), 7.13–6.81 (m, 11H, *o*,*p*-P($C_6H_5$)$_2$, PNC$_6H_4$, PC$_6H_4$N), 6.32 (m, 1H, PC$_6H_4$N), 6.24 (m, 1H, PC$_6H_4$N), 3.73 (sp, 1H, C*H*Me$_2$), 3.5 (br s, 2H, C*H*Me$_2$), 1.49 (br s, 6H, CH(C$H_3$)$_2$), 1.16 (br s, 12H, CH(C$H_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 159.4, 148.1 (2 quaternary aromatic), 148.0 (1Ph), 138.3, 134.2 (2 quaternary aromatic), 135.4, 134.7, 134.3, 134.2 (4Ph), 133.3, 129.7 (2 quaternary aromatic), 128.6, 128.5, 127.1, 126.5, 125.6 (5Ph), 117.9 (1 quaternary aromatic), 116.2 (1Ph), 28.9 (*C*HMe$_2$), 28.2 (*C*HMe$_2$), 26.4 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 32.6. Anal. Calc. for $C_{39}H_{42}Cl_2N_2PSc$: C, 68.32; H, 6.17; N, 4.09. Found C, 67.97; H, 6.32, N, 4.22%.

#### 4.2.11. Characterization of [1-(NDipp)-2-($PPh_2$=NDipp)-$C_6H_4$]$ScCl_2$ (**3c**)

Yield: 76%. $^1$H NMR ($C_6D_6$): $\delta$ 7.51 (m, 4H, *m*-P-($C_6H_5$)$_2$), 7.30–7.26 (m, 3H, PNC$_6H_4$, NC$_6H_3$), 7.06–6.91 (m, 9H, NC$_6H_3$, *o*,*p*-P($C_6H_5$)$_2$, PNC$_6H_3$), 6.80 (m, 2H, PC$_6H_4$N), 6.24 (m, 1H, PC$_6H_4$N), 6.16 (m, 1H, PC$_6H_4$N), 3.77 (sp, 2H, C*H*Me$_2$), 3.07 (sp, 2H, C*H*Me$_2$), 1.60 (d, 6H, CH(C$H_3$)$_2$), 1.38 (d, 6H, CH(C$H_3$)$_2$), 1.00 (d, 6H CH(*CH*$_3$)$_2$) 0.83 (d, 6H, CH(C$H_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 158.1 (1 quaternary aromatic), 149.4, 146.2 (2Ph), 139.7 (1 quaternary aromatic), 128.7, 128.5, 128.3 (3Ph), 126.5 (1 quaternary aromatic), 125.7 (1Ph), 124.5 (1 quaternary aromatic), 118.1, 118.0, 115.7, 115.5 (4Ph), 110.4 (1 quaternary aromatic) 29.4 (*C*HMe$_2$), 28.6 (*C*HMe$_2$), 26.9 (CH(*C*H$_3$)$_2$), 25.6 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 33.6. Anal. Calc. for $C_{42}H_{48}Cl_2N_2PSc$: C, 69.32; H, 6.65; N, 3.85. Found C, 70.44; H, 6.80, N, 3.43%.

#### 4.2.12. Characterization of [1-(NDipp)-2-($PMe_2$=NDipp)-$C_6H_4$]$ScCl_2$ (**3d**)

Yield: 74% $^1$H NMR ($C_6D_6$): $\delta$ 7.32–7.29 (m, 3H, NC$_6H_3$, PC$_6H_4$N), 7.06 (m, 3H, NC$_6H_3$), 7.04 (m, 1H, PC$_6H_4$N), 6.78 (t, 1H, NC$_6H_3$) 6.49 (m, 1H, PC$_6H_4$N), 6.31 (m, 1H, PC$_6H_4$N), 6.03 (m, 1H, PC$_6H_4$N), 3.58 (sp, 4H, C*H*Me$_2$), 1.62 (d, 6H, CH(C$H_3$)$_2$), 1.47 (d, 6H, CH(C$H_3$)$_2$), 1.36 (d, $^2J_{H-P}$ = 12 Hz 6H, P(C$H_3$)$_2$), 1.09 (d, 6H, CH(C$H_3$)$_2$), 1.03 (d, 6H, CH(C$H_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 156.6 (1 quaternary aromatic), 149.8 (1Ph), 145.8, 133.8, 133.6 (3 quaternary aromatic), 129.4, 128.1, 127.9 (3Ph), 126.7 (1 quaternary aromatic), 126.2, 124.6, 117.2, 116.1 (4Ph), 111.5 (1 quaternary aromatic) 29.5 (*C*HMe$_2$), 29.0 (*C*HMe$_2$), 26.7 (CH(*C*H$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 24.1 (CH(*C*H$_3$)$_2$), 13.1 (P(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 34.2. Anal. Calc. for $C_{32}H_{44}Cl_2N_2PSc$: C, 63.68; H, 7.35; N, 4.64. Found C, 62.96; H, 7.08, N, 4.79%.

#### 4.2.13. Synthesis of [1-(NDipp)-2-($PPh_2$=NMes)$C_6H_4$]-$ScMe_2$ (**4a**)

The following is a representative synthesis of **4a**–**d**. A 50 mL flask was charged with **3a** (200 mg, 0.29 mmol) and 20 mL of toluene was condensed. The solution was cooled to 0 °C and *n*BuLi (1.6 M, 0.36 mL, 0.58 mmol) was introduced dropwise via syringe. The reaction was warmed to room temperature and stirred for one hour, then the LiCl was removed by filtration and the toluene removed to afford a pale yellow solid. Yield 160 mg (85%). $^1$H NMR ($C_7D_8$): $\delta$ 7.53 (m, 4H, *m*-P-($C_6H_5$)$_2$), 7.27 (m, 3H, PC$_6H_4$N, NC$_6H_3$), 7.10–7.06 (m, 4H, *o*-P($C_6H_5$)$_2$), 7.02–6.93 (m, 5H, *p*-P($C_6H_5$)$_2$, NC$_6H_3$, PC$_6H_4$N) 6.64 (s, 2H, PNC$_6H_2$), 6.16 (m, 2H, PC$_6H_4$N), 3.13 (sp, 2H, C*H*Me$_2$), 2.18 (s, 6H, NC$_6$H$_2$*Me*-2,6), 2.03 (s, 3H, NC$_6$H$_2$*Me*-4) 1.22 (d, 6H, CH(C$H_3$)$_2$), 0.99 (d, 6H, CH(C$H_3$)$_2$) −0.26 (s, 6H, Sc(C$H_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_7D_8$): $\delta$ 28.2. $^{13}$C NMR resonances were not assigned due to metalative decomposition during acquisition.

#### 4.2.14. Characterization of [1-(NDipp)-2-($PPh_2$=NMipp)-$C_6H_4$]$ScMe_2$ (**4b**)

Yield: 86%. $^1$H NMR ($C_6D_6$): $\delta$ 7.81–7.30 (m, 8H, *m*-P-($C_6H_5$)$_2$, PNC$_6H_4$, NC$_6H_3$), 7.17–7.14 (m, 3H, NC$_6H_3$, PNC$_6H_4$) 7.05–6.95 (m, 8H, *o*,*p*-P($C_6H_5$)$_2$, PNC$_6H_4$, PC$_6H_4$N), 7.72 (m, 1H, PC$_6H_4$N), 6.31 (m, 1H, PC$_6H_4$N), 6.22 (m, 1H, PC$_6H_4$N), 3.95 (sp, 1H, C*H*Me$_2$), 3.36 (br s, 2H, C*H*Me$_2$), 1.29 (br s, 6H, CH(C$H_3$)$_2$), 1.15 (br s, 12H, CH(C$H_3$)$_2$), −0.38 (s, 6H Sc(C$H_3$)$_2$). $^{13}$C NMR ($C_6D_6$): $\delta$ 160.2 (1 quaternary aromatic), 148.9 (1Ph), 148.0, 138.6, 137.6 (3 quaternary aromatic), 137.5, 135.0, 134.5 (3Ph), 134.0, 133.2 (2 quaternary aromatic), 129.3.6, 128.8, 128.5, 127.4 (4Ph), 126.6, 126.2 (2 quaternary aromatic), 125.6, 125.4, 117.6, 113.9 (4Ph), 106.4 (1 quaternary aromatic) 28.9 (*C*HMe$_2$), 28.4 (*C*HMe$_2$), 26.5 (CH(*C*H$_3$)$_2$), 23.9 (Sc(*C*H$_3$)$_2$) 23.3 (CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 28.2. Anal. Calc. for $C_{41}H_{48}N_2PSc$: C, 76.38; H, 7.50; N, 4.34. Found C, 75.48; H, 7.41, N, 4.65%.

#### 4.2.15. Characterization of [1-(NDipp)-2-($PPh_2$=NDipp)-$C_6H_4$]$ScMe_2$ (**4c**)

Yield: 72%. $^1$H NMR ($C_6D_6$): $\delta$ 7.48 (m, 4H, *m*-P-($C_6H_5$)$_2$), 7.36–7.31 (m, 3H, PNC$_6H_4$, NC$_6H_3$), 7.09–6.75 (m, 11H, NC$_6H_3$, *o*,*p*-P($C_6H_5$)$_2$, PNC$_6H_3$, PC$_6H_4$N), 6.18 (m, 2H, PC$_6H_4$N), 3.80 (sp, 2H, C*H*Me$_2$), 3.12 (sp, 2H, C*H*Me$_2$), 1.53 (d, 6H, CH(C$H_3$)$_2$), 1.24 (d, 6H, CH(C$H_3$)$_2$), 1.06 (d, 6H CH(*CH*$_3$)$_2$) 0.90 (d, 6H, CH(C$H_3$)$_2$), −0.01 (s, 6H, Sc(C$H_3$)$_2$). $^{13}$C NMR ($C_6D_6$):

$\delta$ 158.8 (1 quaternary aromatic), 148.7, 146.2 (2Ph), 139.6, 137.8 (2 quaternary aromatic), 134.0 (1Ph), 133.5, 133.4, 133.3 (3 quaternary aromatic), 132.5, 128.3 (2Ph), 125.6 (1 quaternary aromatic), 125.1, 124.2, 117.8, 113.2 (4Ph), 110.1 (1 quaternary aromatic) 29.0 ($CHMe_2$), 28.2 ($CHMe_2$), 26.6 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 24.7 ($Sc(CH_3)_2$) 23.9 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 29.7. Anal. Calc. for $C_{44}H_{54}N_2PSc$: C, 76.94; H, 7.92; N, 4.08. Found C, 75.84; H, 7.47, N, 3.84%.

Table 3
Summary of data collection and structure refinement details for **1b**,**c**, **3a**,**c**

| | **1b** | **1c** | **3a** | **3c** |
|---|---|---|---|---|
| Color | Colorless | Colorless | Colorless | Colorless |
| Habit | Prismatic | Block | Block | Prismatic |
| Size ($mm^3$) | $.22\times.20\times.18$ | $.24\times.16\times.11$ | $.20\times.20\times.18$ | $.26\times.12\times.12$ |
| Formula | $C_{39}H_{43}N_2P$ | $C_{42}H_{49}N_2P$ | $C_{78}H_{84}Cl_4P_2Sc_2$ | $C_{42}H_{48}Cl_2N_2PSc$ |
| Molecular weight | 570.72 | 612.80 | 1371.14 | 739.71 |
| $a$ (Å) | 10.762(3) | 11.494(2) | 18.776(4) | 10.1450(10) |
| $b$ (Å) | 21.353(5) | 12.772(2) | 21.772(5) | 13.417(2) |
| $c$ (Å) | 14.131(3) | 14.673(3) | 25.481(6) | 18.882(4) |
| $\alpha$ (°) | 90 | 64.625(10) | | 84.210(5) |
| $\beta$ (°) | 90.776(14) | 82.333(10) | 101.028(19) | 83.171(5) |
| $\gamma$ (°) | 90 | 66.033(8) | | 73.196(9) |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $C2/c$ | $P\bar{1}$ |
| $Z$ | 4 | 2 | 8 | 2 |
| $V$ (Å$^3$) | 3247.0(14) | 1776.2(6) | 10244(4) | 2436.9(7) |
| $T$ (K) | 273(2) | 173(2) | 173 (2) | 173(2) |
| $\mu$ ($mm^{-1}$) | 0.114 | 0.11 | 0.315 | 0.33 |
| Transmission factors | .9798–.9754 | .988–.974 | .945–.940 | .961–.919 |
| $\theta$ Range (°) | 2.4–27.5 | 3.6–27.5 | 3.0–25.0 | 3.2–27.3 |
| Data/restraints/parameters | 7413/0/385 | 8072/0/406 | 8974/0/531 | 10885/0/541 |
| GoF | 1.01 | 1.00 | 1.03 | 1.01 |
| $R_1$ ($I>2\sigma(I)$) | 0.053 | 0.048 | 0.098 | 0.044 |
| $wR_2$ (all data) | 0.117 | 0.123 | 0.255 | 0.103 |

Table 4
Summary of data collection and structure refinement details for **4b**,**c**, and **5c**,**d**

| | **4b** | **4c** | **5c** | **5d** |
|---|---|---|---|---|
| Color | Colorless | Colorless | Yellow | Colorless |
| Habit | Block | Prismatic | Prismatic | Needle |
| Size ($mm^3$) | $.20\times.16\times.08$ | $.16\times.15\times.10$ | $.12\times.08\times.07$ | $.12\times.08\times.06$ |
| Formula | $C_{48}H_{56}N_2PSc$ | $C_{44}H_{54}N_2PSc$ | $C_{49}H_{64}N_2PSc$ | $C_{72}H_{102}N_4P_2Sc_2$ |
| Molecular weight | 736.88 | 686.82 | 756.95 | 1175.44 |
| $a$ (Å) | 10.266(3) | 19.364(2) | 17.779(3) | 46.690(2) |
| $b$ (Å) | 13.478(6) | 18.661(4) | 20.047(4) | 12.035(4) |
| $c$ (Å) | 16.188(8) | 21.813(3) | 24.459(7) | 27.799(4) |
| $\alpha$ (°) | 73.84(2) | | | |
| $\beta$ (°) | 84.07(3) | | 94.162(7) | 118.945(7) |
| $\gamma$ (°) | 79.50(3) | | | |
| Crystal system | Triclinic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $Pbca$ | $C2/c$ | $C2/c$ |
| $Z$ | 2 | 8 | 8 | 16 |
| $V$ (Å$^3$) | 2112.0(15) | 7882(2) | 8695(3) | 13669(5) |
| $T$ (K) | 173(2) | 173(2) | 173(2) | 173(2) |
| $\mu$ ($mm^{-1}$) | 0.246 | 0.259 | 0.240 | 0.287 |
| Transmission factors | .981–.953 | .975–.960 | .983–.972 | .983–.966 |
| $\theta$ Range (°) | 2.9–25.1 | 3.2–27.6 | 1.5–25.0 | 1.9–25.1 |
| Data/restraints/parameters | 7415/0/466 | 8951/0/443 | 7619/0/478 | 12047/0/739 |
| GoF | 1.06 | 1.04 | 1.00 | 1.03 |
| $R_1$ ($I>2\sigma(I)$) | 0.074 | 0.046 | 0.058 | 0.052 |
| $wR_2$ (all data) | 0.186 | 0.106 | 0.145 | 0.127 |

#### 4.2.16. Synthesis of {[κ³-1-(NDipp)-2-(PPh(C₆H₄)=NDipp)C₆H₄]ScMe}₂ (5c)

A 50 mL bomb was charged with **4c** (200 mg, 0.29 mmol) and 15 mL of hexane was condensed. The flask was evacuated and hydrogen (4 atm) was condensed. The flask was sealed and the yellow solution was stirred at room temperature at which point a white precipitate was observed. The mixture was transferred to a swivel frit apparatus and the solid collected by filtration. Yield: 138 mg (71%). $^1$H NMR ($C_6D_6$): δ 7.45–6.48 (m, 17H, *m*-P($C_6H_5$)$_2$, PNC$_6H_4$, NC$_6H_3$), *o*,*p*-P($C_6H_5$)$_2$, PC$_6H_4$N, 6.30 (m, 1H, PC$_6H_4$N), 5.94 (m, 1H, PC$_6H_4$N), 3.88 (ov sp, 2H, C*H*Me$_2$), 3.52 (sp, 1H, C*H*Me$_2$), 3.16 (sp, 1H, C*H*Me$_2$), 1.70–0.65 (br m, 18H, CH(C$H_3$)$_2$), 0.52 (s, 3H, Sc(C$H_3$)$_2$) 0.25 (d, 6H, CH(C$H_3$)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$): δ 27.7. Anal. Calc. for $C_{43}H_{50}N_2PSc$: C, 76.99; H, 7.51; N, 4.18. Found C, 76.71; H, 7.77, N, 4.45%.

#### 4.2.17. Synthesis of {[κ³-1-(NDipp)-2-(PMe(CH₂)=NDipp)C₆H₄]ScMe}₂ (5d)

A 5 mm J-Young tube was charged with **4d** (20 mg, 36 μmol) and dissolved in $C_6D_6$. The sample was heated in an oil bath at 65 °C for 4 h and analyzed by $^1$H and $^{31}$P NMR. Slow evaporation of the benzene afforded single crystals which were analyzed by X-ray analysis. $^1$H NMR ($C_6D_6$): δ 7.28–7.13 (m, 3H, NC$_6H_3$, PC$_6H_4$N), 7.02 (m, 3H, NC$_6H_3$), 6.84 (m, 3H NC$_6H_3$, PC$_6H_4$N) 6.45 (m, 1H, PC$_6H_4$N), 6.02 (m, 1H, PC$_6H_4$N), 3.82 (sp, 1H, C*H*Me$_2$), 3.33 (sp, 2H, C*H*Me$_2$), 3.22 (sp, 1H, C*H*Me$_2$), 1.57 (d, 3H, CH(C$H_3$)$_2$), 1.45 (d, 3H, CH(C$H_3$)$_2$), 1.24 (m, 9H, CH(C$H_3$)$_2$, P(C$H_3$)(C$H_2$)), 1.15 (d, 3H, CH(C$H_3$)$_2$), 0.99 (d, 3H, CH(C$H_3$)$_2$), 0.82 (d, 3H, CH(C$H_3$)$_2$), 0.67 (d, 3H, CH(C$H_3$)$_2$), 0.60 (d, 3H, CH(C$H_3$)$_2$), 0.50 (s, 3H, Sc(C$H_3$)). $^{31}$P{$^1$H} NMR ($C_6D_6$): δ 29.7. Anal. Calc. for $C_{34}H_{50}N_2PSc$: C, 72.57; H, 8.96; N, 4.98. Found C, 62.96; H, 7.08, N, 4.79%.

### 4.3. X-ray crystallographic studies

Crystals of **1b**,**c**, **3a**,**c**, **4b**,**c**, and **5c**,**d** were coated with Paratone 8277 oil and mounted on a glass fiber. Measurements were made on a Nonius Kappa CCD diffractometer (University of Calgary) using graphite-monochromated Mo Kα radiation with a wavelength of 0.71073 Å for all measurements. Tables 3 and 4 give further details and the crystallographic information files are available as Supplementary material.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.037.

## References

[1] (a) W.E. Piers, D.J.H. Emslie, Coord. Chem. Rev. 233–234 (2002) 131;
(b) P. Mountford, B.D. Ward, Chem. Commun. (2003) 1797.
[2] (a) P.M. Zeimentz, S. Arndt, B.R. Elvidge, J. Okuda, Chem. Rev. 106 (2006) 2404;
(b) S. Arndt, J. Okuda, Adv. Synth. Catal. 347 (2005) 339;
(c) S. Bambirra, H. Tsurugi, D. van Leusen, B. Hessen, Dalton Trans. (2006) 1157;
(d) S.C. Lawrence, B.D. Ward, S.R. Dubberley, C.M. Kozak, P. Mountford, Chem. Commun. (2003) 2880.
[3] For a review on early-metal hydrides see: (a) A.J. Hoskin, D.W. Stephan, Coord. Chem. Rev. 233 (2002) 107;
(b) J.R. Hagadorn, J. Arnold, Organometallics 15 (1996) 984;
(c) G.C. Bazan, W.P. Shaefer, J.E. Bercaw, Organometallics 12 (1993) 2126.
[4] (a) G.R. Giesbrecht, J.C. Gordon, Dalton Trans. (2004) 2387;
(b) D.J. Beetstra, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 22 (2003) 4372.
[5] L. Bouget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.
[6] (a) D.S. Laitar, C.J.N. Mathison, W.M. Davis, J.P. Sadighi, Inorg. Chem. 42 (2003) 7354;
(b) G.W. Coates, M. Cheng, PCT Int. Appl., WO 0008088, 2000; Chem Abstr. 132 (2000) 152332;
(c) D.J.E. Spencer, A.M. Reynolds, P.L. Hollad, B.A. Jazdzewski, C. Duboc-Toia, L. LePape, S. Yokota, Y. Tachi, S. Itoh, W.B. Tolman, Inorg. Chem. 41 (2002) 6307.
[7] (a) S.G. McGeachin, Can. J. Chem. 46 (1968) 1903;
(b) P.H.M. Budzelaar, A.B. van Oort, A.G. Orpen, Eur. J. Inorg. Chem. (1998) 1485.
[8] P.G. Hayes, W.E. Piers, L.W.M. Lee, L.K. Knight, M. Parvez, M.R.J. Elsegood, W. Clegg, Organometallics 20 (2001) 2533.
[9] (a) P.G. Hayes, W.E. Piers, R. McDonald, J. Am. Chem. Soc. 124 (2002) 2132;
(b) P.G. Hayes, W.E. Piers, M. Parvez, J. Am. Chem. Soc. 125 (2003) 5622;
(c) L.W.M. Lee, W.E. Piers, M.R.J. Elsegood, W. Clegg, M. Parvez, Organometallic 18 (1999) 2949.
[10] W.E. Piers, P.G. Hayes, A.L. Kenward, J.A. Ross, K.D. Conroy, M. Parvez, Abs. Pap. Am. Chem. Soc. 230 (2005) INOR-238.
[11] P.G. Hayes, G.C. Welch, D.J.H. Emslie, C.L. Noack, W.E. Piers, M. Parvez, Organometallics 22 (2003) 1577.
[12] (a) D.W. Stephan, J.C. Stewart, F. Guerin, R.E.v.H. Spence, D.G. Harrison, Organometallics 18 (1999) 1116;
(b) R.G. Cavell, K. Babu, K.J. Aparna, J. Organomet. Chem. 617–618 (2001) 158;
(c) L. Orzechowski, S. Harder, Organometallics 26 (2007) 2144;
(d) M. Demange, L. Boubekeur, A. Auffrant, N. Mezailles, L. Ricard, X. Le Goff, P. Le Floch, New J. Chem. 30 (2006) 1745;
(e) A.E. Diaz-Alvarez, P. Crochet, M. Zablocka, V. Cadierno, C. Duhayon, J. Gimeno, J.-P. Majoral, New. J. Chem. 30 (2006) 1295;
(f) S.A. Ahmed, M.S. Hill, P.B. Hitchcock, Organometallics 25 (2006) 394;
(g) Y. Smurnyy, C. Bibal, M. Pink, K.G. Caulton, Organometallics 24 (2005) 3849;

(h) M.S. Hill, P.B. Hitchcock, J. Organomet. Chem. 689 (2004) 3163;
(i) M.S. Hill, P.B. Hitchcock, S.M.A. Karagouni, J. Organomet. Chem. 689 (2004) 722;
(j) M.S. Hill, P.B. Hitchcock, J. Chem. Soc., Dalton Trans. (2002) 4694;
(k) S. Al-Benna, M.J. Sarsfield, M.J. Thornton-Pett, D.L. Ormsby, P.J. Maddox, P. Bres, M. Bochmann, J. Chem. Soc., Dalton Trans. (2000) 4247;
(l) L. Boubekeur, L. Ricard, N. Mezailles, M. Demange, A. Auffrant, P. Le Floch, Organometallics 25 (2006) 3091;
(m) L.R. Falvello, S. Fernandez, M.M. Garcia, R. Navarro, E.P. Urriolabeitia, J. Chem. Soc., Dalton Trans. (1998) 3745;
(n) M.T. Gamer, S. Dehnen, P.W. Roesky, Organometallics 20 (2001) 4230;
(o) A. Zulys, T.K. Panda, M.T. Gamer, P.W. Roesky, Organometallics 24 (2005) 2197;
(p) M.T. Gamer, P.W. Roesky, M. Rastatter, A. Steffens, M. Glanz, Chem. Eur. J. 11 (2005) 3165;
(q) M. Rastatter, A. Zulys, P.W. Roesky, Chem. Eur. J. 13 (2007) 3606;
(r) M.J. Sarsfield, M. Thornton-Pett, M. Bochmann, J. Chem. Soc., Dalton Trans. (1999) 3329;
(s) M.J. Sarsfield, M. Said, M. Thornton-Pett, L.A. Gerrard, M. Bochmann, J. Chem. Soc. (2001) 822;
(t) M. Said, M. Thornton-Pett, M. Bochmann, J. Chem. Soc., Dalton Trans. (2001) 2844;
(u) M. Said, M. Thornton-Pett, D.L. Hughes, M. Bochmann, Inorg. Chim. Acta 360 (2007) 1354.

[13] G.C. Welch, W.E. Piers, M. Parvez, R. McDonald, Organometallics 23 (2004) 1811.

[14] B. Lui, D. Cui, J. Ma, X. Chen, X. Jing, Chem. Eur. J. 13 (2007) 834.

[15] E.W. McEwen, A.B. Janes, J.W. Knapczyk, V.L. Kyllingstad, W. Shiau, S. Shore, J. Smith, J. Am. Chem. Soc. 100 (1978) 7304.

[16] (a) J. Meyer, H. Staudinger, Helv. Chim. Acta 2 (1919) 635;
(b) M. Alajarin, C.L. Leonardo, P.L. Lorente, D. Bautista, Synthesis 14 (2000) 2085.

[17] (a) Y. Ren, X. Lui, W. Gao, H. Xia, L. Ye, Y. Mu, Eur. J. Inorg. Chem. 13 (2007) 1808;
(b) S.M. Kloek, K.I. Goldberg, J. Am. Chem. Soc. 129 (2007) 3460;
(c) T. Bok, H. Yun, B.Y. Lee, Inorg. Chem. 45 (2006) 4228;
(d) X. Liu, H. Xia, G. Hong, L. Ye, Y. Mu, Q. Su, Y. Ren, Eur. J. Inorg. Chem. 6 (2006) 1216;
(e) H.-Y. Wang, X. Meng, G.-X. Guo, Dalton Trans. (2006) 2579;
(f) A.M. Reynolds, B.F. Gherman, C.J. Cramer, W.B. Tolman, Inorg. Chem. 44 (2005) 6989;
(g) X. Liu, W. Gao, Y. Mu, G. Li, L. Ye, H. Xia, Y. Ren, S. Feng, Organometallics 24 (2005) 1614;
(h) B.Y. Lee, H.Y. Kwon, S.Y. Lee, S.J. Na, S. Han, H. Yun, H. Lee, Y.-W. Park, J. Am. Chem. Soc. 127 (2005) 3031.

[18] (a) Y. Mu, W.E. Piers, D.C. MacQuarrie, M.J. Zaworotko, V.G. Young, Organometallics 15 (1996) 2720;
(b) M.A. Putzer, J.S. Rogers, G.C. Bazan, J. Am. Chem. Soc. 121 (1999) 8112;
(c) C.J. Schaverien, N. Meijboom, A.G. Orpen, J. Chem. Soc., Chem. Commun. (1992) 124;
(d) D.J.H. Emslie, W.E. Piers, M. Parvez, R. McDonald, Organometallics 21 (2002) 4226;
(e) D.J.H. Emslie, W.E. Piers, M. Parvez, Dalton Trans. (2003) 2615.

[19] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203.

[20] (a) S. Bambirra, M.W. Bouwkamp, A. Meetsma, B. Hessen, J. Am. Chem. Soc. 126 (2004) 9182;
(b) S. Ge, S. Bambirra, A. Meetsma, B. Hessen, Chem. Commun. (2006) 3320;
(c) P.M. Zeimentz, S. Arndt, B.R. Elvidge, J. Okuda, Chem. Rev. 106 (2006) 2404;
(d) S.C. Marinescu, T. Agapie, M.W. Day, J.E. Bercaw, Organometallics 26 (2007) 1178.

[21] (a) A.D. Sadow, T.D. Tilley, Angew. Chem., Int. Ed. 42 (2003) 803;
(b) A.D. Sadow, T.D. Tilley, J. Am. Chem. Soc. 125 (2003) 7971;
(c) A.D. Sadow, T.D. Tilley, J. Am. Chem. Soc. 127 (2005) 643.

[22] M.E. Thompson, J.E. Bercaw, Pure Appl. Chem. 56 (1984) 1.

[23] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Organometallics 15 (1996) 1518.

[24] S. Abe, S. Murata, H. Tomioka, J. Org. Chem. 62 (1997) 3055.

[25] L.P. Spencer, R. Altwer, P. Wei, L. Gelmini, J. Gauld, D.W. Stephan, Organometallics 22 (2003) 3841.

[26] M.D. Fryzuk, G. Giesbrecht, S.J. Rettig, Organometallics 15 (1996) 3329.

[27] Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.