

Synthesis, characterization and reactivity of tetramethylphospholyl complexes of scandium

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Abstract

Reaction of 2 equiv. of $(C_4Me_4P)Li(tmeda)$ ($tmeda$ = tetraethylenediamine) with 1 equiv. of $ScCl_3(THF)_3$ gave the new compound $(\eta^5-C_4Me_4P)_2ScCl_2Li(tmeda)$ (**1**), which was characterized by X-ray crystallography. A phospholyl moiety in **1** is labile, as demonstrated by reactions of **1** with $LiCH(SiMe_3)_2$ and Cp^*Li ($Cp^* = C_5Me_5$) to afford, respectively, $(\eta^5-Me_4C_4P)Sc[CH(SiMe_3)_2]Cl_2Li(tmeda)$ (**4**) and $(\eta^5-Me_4C_4P)Cp^*ScCl_2Li(tmeda)$ (**5**). Attempts to generate alkyl derivatives of the general type $(\eta^5-C_4Me_4P)_2ScR$ (R = alkyl) were unsuccessful.

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1. Introduction

Early transition metal cyclopentadienyl complexes are being investigated for a variety of catalytic transformations, including olefin polymerization [1] and C–H bond activation processes [2]. It has been observed that for many such complexes, simple modifications of ligand sets may induce major changes in reactivity. This is illustrated, for example, by the recent work of Chirik et al. which demonstrates that the $(\eta^5-C_5HMe_4)_2Zr(II)$ group [3] exhibits nitrogen activation chemistry that is distinctly different from that of a comparable $(\eta^5-C_5Me_5)_2Zr(II)$ species [4]. Interestingly, the influence of ancillary ligand structure on the σ -bond metathesis chemistry of early metal complexes has received little attention [4,5]. However, in general it seems that soft donor ligands based on cyclic π -systems (e.g., cyclopentadienyl derivatives) give rise to the most active complexes for σ -bond metathesis conversions with silanes [2a,2b,5b,5c,5d,5f,5g] and alkanes [2b,2d,2e,2f,2g,2h,2i,5b–7].

Recent investigations in our laboratory have sought to identify catalytic processes for transformations of alkanes via concerted, σ -bond metathesis steps. These efforts have identified the 14-electron complex Cp_2^*ScMe as a slow, short-lived catalyst for the hydromethylation of propene, presumably by a mechanism involving insertion of propene, followed by a σ -bond metathesis reaction of the resulting isobutyl complex with methane [6]. While this observation establishes the feasibility of a new catalytic process for methane under mild conditions, it raises a number of questions regarding strategies for the control of activity and selectivity for such transformations. Ideally, such strategies would be based on a detailed knowledge of the influence of electronic and steric factors for ancillary ligands in d^0 complexes on σ -bond metathesis reactivity. Early results suggest that catalysis via σ -bond metathesis may be greatly influenced by such factors. Thus, compared to Cp_2^*ScMe , the *ansa* complex $Me_2Si(\eta^5-C_5Me_4)_2ScMe$ exhibits higher reactivity toward 1,1-disubstituted olefins [7]. This complex is a catalyst for the hydromethylation of isobutene and related terminal secondary olefins, whereas Cp_2^*ScMe is not. In further investigations of the influence of ancillary ligands on this chemistry, scandium

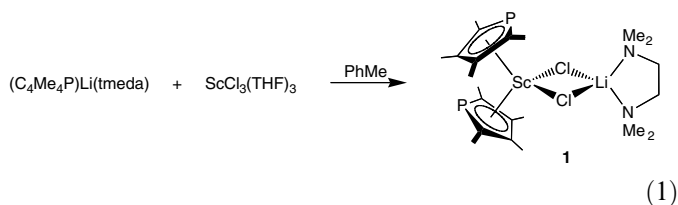
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complexes of the phospholyl ligand $\text{Me}_4\text{C}_4\text{P}^-$ were targeted.

The $\text{Me}_4\text{C}_4\text{P}^-$ ligand is expected to express an electronic influence similar to that of C_5Me_5^- , while being somewhat softer and slightly less hindered [8]. A number of group 4 phospholyl complexes have been synthesized [9], but analogous group 3 derivatives are limited to the yttrium complex ($\eta^5\text{-C}_4\text{Me}_4\text{P}_2\text{YCl}_2\text{Li}(\text{DME})_2$) [10]. While no scandium–phospholyl derivatives are known, related 1,2,4-triphosphacyclopentadienyl complexes of scandium(II) have been reported [11]. Here we describe initial attempts to explore the coordination chemistry of the phospholyl ligand $\text{Me}_4\text{C}_4\text{P}^-$ with scandium, and to develop synthetic routes to ($\eta^5\text{-Me}_4\text{C}_4\text{P}$) $_2\text{Sc}$ - complexes.

2. Results and discussion

Addition of 2 equiv. of off-white $(\text{C}_4\text{Me}_4\text{P})\text{Li}(\text{tmeda})$ [12] to a suspension of $\text{ScCl}_3(\text{THF})_3$ in toluene produced a bright yellow solution. Filtration, concentration and cooling of this solution provided crystalline, yellow ($\eta^5\text{-C}_4\text{Me}_4\text{P}$) $_2\text{ScCl}_2\text{Li}(\text{tmeda})$ (**1**) in 71% yield (Eq. (1)). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **1** in benzene- d_6 exhibits a single resonance at 99.8 ppm, which is downfield relative to the resonances for $(\text{C}_4\text{Me}_4\text{P})\text{Li}(\text{tmeda})$ (66.3 ppm) [12] and ($\eta^5\text{-C}_4\text{Me}_4\text{P}_2\text{YCl}_2\text{Li}(\text{dme})_2$) (84.0 ppm) [10]. The ^1H NMR spectrum of **1** contains two methyl resonances at 2.15 and 2.46 ppm, and the downfield signal exhibits a $^3J_{\text{PH}}$ coupling constant of 8 Hz which is characteristic of phospholyl $\alpha\text{-Me}$ groups [9b,9f]. Integration of this spectrum established a 2:1 ratio for the phospholyl and tmeda groups.



The molecular structure of **1**, which crystallizes with half a molecule of toluene per scandium complex, is depicted in Fig. 1. The scandium atom is coordinated to two chloride and two phospholyl ligands in a pseudo-tetrahedral fashion. The rather acute $\text{Cl}(1)\text{-Sc-Cl}(2)$ bond angle of $89.15(6)^\circ$ presumably results from constraints of the ScCl_2Li four-membered ring. The phospholyl rings are coordinated to the scandium in a η^5 fashion, with the phosphorous atoms *anti* to one another. The phospholyl centroid–scandium distance of $2.29(2)$ Å is longer than all related distances measured for Cp^*Sc complexes, the longest of which is $2.2134(7)$ Å for $\text{Cp}^*\text{ScCH}_2\text{CMe}_3$ [6]. Furthermore, the $\text{Sc}-(\text{C}_4\text{Me}_4\text{P})_{\text{centroid}}$ distance in **1** is as long as the longest such distance reported for a transition metal complex, which is 2.296 Å for the zirconacyclopentadiene ($\eta^5\text{-C}_4\text{Me}_4\text{P}$) $_2\text{Zr}(\text{C}_4\text{Me}_4)$ [9f]. The long $\text{Sc}-(\text{C}_4\text{Me}_4\text{P})_{\text{centroid}}$ bond in **1** suggests the presence of a relatively weak metal–

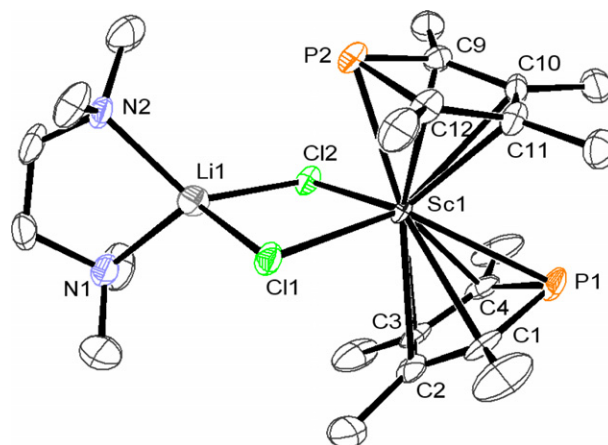


Fig. 1. ORTEP diagram of **1**. The hydrogens and the disordered toluene have been removed for clarity. Selected bond distances (Å): $\text{Sc}(1)\text{-Cl}(1)$ 2.512(2), $\text{Sc}(1)\text{-Cl}(2)$ 2.510(2), $\text{Sc}(1)\text{-P}(1)$ 2.694(2), $\text{Sc}(1)\text{-C}(1)$ 2.582(6), $\text{Sc}(1)\text{-C}(2)$ 2.658(6), $\text{Sc}(1)\text{-C}(3)$ 2.647(6), $\text{Sc}(1)\text{-C}(4)$ 2.563(6), $\text{Sc}(1)\text{-P}(2)$ 2.718(2), $\text{Sc}(1)\text{-C}(9)$ 2.611(6), $\text{Sc}(1)\text{-C}(10)$ 2.656(6), $\text{Sc}(1)\text{-C}(11)$ 2.633(6), $\text{Sc}(1)\text{-C}(12)$ 2.588(6).

ligand bonding interaction. This observation is consistent with related reports which suggest that phospholyls are poor donors relative to Cp^* [13].

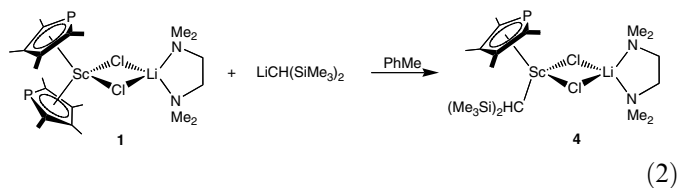
For investigations of σ -bond metathesis activity in scandium complexes of the phospholyl ligand, and for comparisons with the “benchmark” Cp^*ScR system, species of the type ($\eta^5\text{-C}_4\text{Me}_4\text{P}$) $_2\text{Sc-R}$ ($\text{R} = \text{alkyl}$) were desired [6,7]. Addition of 1 equiv. of solid MeLi to a solution of **1** in C_6D_6 gave partial conversion to two new species. The major product (**2**) exhibits a resonance at 88.1 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, and the minor one (**3**) resonates at 82.9 ppm. Addition of a second equiv. of MeLi to this reaction mixture resulted in complete consumption of **1** and most of **2**, and **3** became the dominant product. Both **2** and **3** exhibit similar ^1H NMR spectra, which contain resonances for coordinated tmeda and $\eta^5\text{-Me}_4\text{C}_4\text{P}$ groups. The major difference between the spectra of the two products is apparent in upfield resonances at -0.74 and -1.10 ppm, respectively, for **2** and **3**. The same experiment on a larger scale in toluene at -78 °C also afforded a mixture of **2** and **3**. The residual solid, resulting from the removal of the volatiles under reduced pressure, was extracted in pentane, but the separation of both species by selective recrystallization was unsuccessful. Flame tests for the isolated mixture of compounds indicated, however, the presence of Li. These observations suggest that **2** and **3** may be formulated as ($\eta^5\text{-C}_4\text{Me}_4\text{P}$) $_2\text{ScCl}(\text{Me})\text{Li}(\text{tmeda})$ and ($\eta^5\text{-C}_4\text{Me}_4\text{P}$) $_2\text{ScMe}_2\text{Li}(\text{tmeda})$, respectively, which is in accord with the known chemistry of $\text{Cp}^*\text{MCl}_2\text{Li}$ complexes ($\text{M} = \text{Y}$, lanthanide) [14].

The results described above highlight a key difference between the chemistry of the Cp^*Sc - and ($\eta^5\text{-C}_4\text{Me}_4\text{P}$) $_2\text{Sc}$ -fragments. Whereas addition of 2 equivs of Cp^*Li to $\text{ScCl}_3(\text{THF})_3$ results in formation of the neutral, monochloride Cp^*ScCl [2i], the analogous reaction of

(C₄Me₄P)Li with ScCl₃(THF)₃ gives the ate complex **1**. Whereas methylations of the latter compound also produce ate complexes, Cp₂*ScMe appears to be quite stable in the presence of small donors [2i]. This difference in behavior could be attributed to the longer bond length associated with the scandium–phospholyl interaction, or to the fact that C₄Me₄P is less sterically demanding than Cp*.

In numerous studies of Sc complexes, it has been shown that addition of a donor ligand L can help the formation of “neutral” Cp₂*ScR(L) species [15]. Unfortunately, addition of 2 equiv. of PMe₃ to a solution of **3** in C₆D₆ did not produce new products, as determined by NMR spectroscopy. Attempts to promote conversion by increasing both the reaction time and the temperature gave only intractable scandium species and elimination of the phospholyl ligand, as indicated in the ³¹P{¹H} NMR spectrum by the appearance of resonances for both (Me₄C₄P)Li(tmeda) and (Me₄C₄HP)₂ [12].

Given the expected difficulty in converting ate complexes such as **2** and **3** to the 14 electron (Me₄C₄P)₂ScMe, our attention turned to incorporation of bulkier alkyl groups which might stabilize a lower coordination number for scandium. Initial efforts with Me₃CCH₂Li and PhCH₂MgCl produced complex reaction mixtures. In contrast, LiCH(SiMe₃)₂ reacted cleanly with a solution of **1** in pentane to give a colorless solution. The white product, isolated in 54% yield from the reaction mixture, exhibits a resonance at 119.2 ppm in the ³¹P{¹H} NMR spectrum. The ¹H NMR spectrum contains resonances for CH(SiMe₃)₂, tmeda and Me₄C₄P groups. The NMR spectra and combustion analyses



are consistent with the formula (Me₄C₄P)Sc[CH(SiMe₃)₂]Cl₂Li(tmeda) (**4**; Eq. (2)). Thus, compound **4** forms via a ligand displacement of Me₄C₄P[−], which may be driven by the lability of the latter group, as well as the relatively insoluble nature of Me₄C₄PLi. In addition, the interaction of lithium with the lone pair on phosphorous could facilitate the exchange of ligands.

Crystals obtained by recrystallization of **4** from pentane at −80 °C were suitable for an X-ray diffraction study, and the molecular structure is shown in Fig. 2. Two independent molecules were found in the monoclinic unit cell, and these differ slightly in the orientation of the phospholyl rings. The average Sc-(Me₄C₄P)_{centroid} distance (2.220(3) Å) is shorter than that in **1** (2.29(1) Å), as might be expected for the lower coordination number of the scandium center of **4**. In light of the coordinatively unsaturated metal center in **4**, the existence of an α-agostic interaction for the methyne proton of the CH(SiMe₃)₂ ligand might be expected [16]. However, the rather long Sc...H distances (average of 2.60 Å) and the

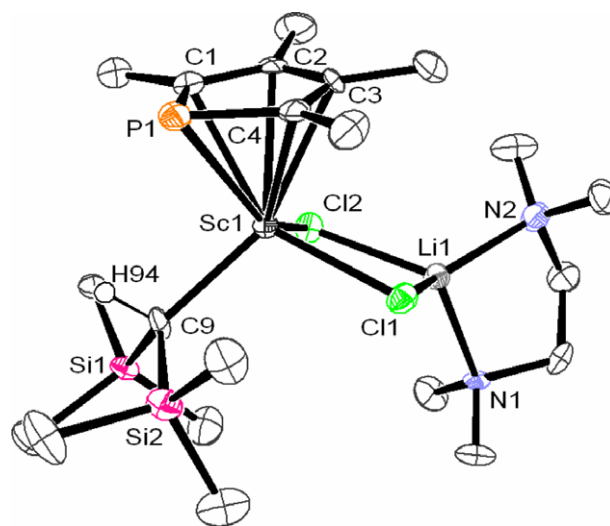


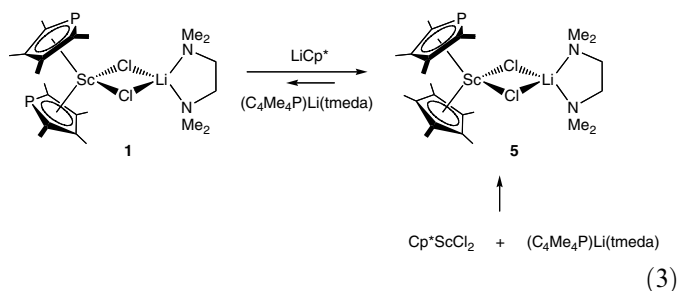
Fig. 2. ORTEP diagram for one of the molecules in the asymmetric unit of **4**. The hydrogens have been removed for clarity. Selected bond distances (Å): Sc(1)–Cl(1) 2.445(3), Sc(1)–Cl(2) 2.444(3), Sc(1)–P(1) 2.712(2), Sc(1)–C(1) 2.509(9), Sc(1)–C(2) 2.545(9), Sc(1)–C(3) 2.552(9), Sc(1)–C(4) 2.570(9), Sc(1)–C(9) 2.233(9).

Sc–C–H angles of 102° do not support the presence of such an interaction. Furthermore, the ¹J_{C–H} coupling constant for the methyne C–H bond is 96 Hz, indicating that any such interaction should be relatively weak [17]. The absence of an α-agostic interaction in **4** is consistent with the presence of strongly π-donating chloride ligands, which is also reflected in Sc–Cl bond lengths (2.44 Å) that are short relative to those in **1** (2.51 Å). Similar bonding patterns appear to exist for the related complex Cp*Lu[CH(SiMe₃)₂]Cl₂Li(tmeda) [18].

Attempts to introduce carbon-based ligands via reaction of **4** with various alkyllithium and Grignard reagents were unsuccessful. For example, addition of one or more equiv. of Cp*Li, (Me₄C₄P)Li(tmeda) or LiCH(SiMe₃)₂ to **4** did not result in the displacement of LiCl(tmeda), even after heating at 60 °C for five days. Given these results, an alternate strategy for the exploration of scandium phospholyl complexes was pursued.

Given the lability of one of the phospholyl ligands of **1**, it seemed that it might be possible to prepare potentially more stable complexes of the type (η⁵-C₄Me₄P)Cp*ScR (Cp* = a cyclopentadienyl ligand). The addition of 1 equiv. of Cp*Li to a solution of **1** in C₆D₆ at 110 °C led to the formation of a new complex, which exhibits a ³¹P{¹H} NMR chemical shift that is quite similar to that for **1**, at 100.2 ppm. The ¹H NMR spectrum also indicates the emergence of a new species that may be formulated as (η⁵-C₄Me₄P)Cp*ScCl₂Li(tmeda) (**5**). However, this reaction did not go to completion, even after 30 days, and resulted in the elimination of (Me₄C₄P)Li(tmeda) (ca. 20%, Eq. (3)). Thus, after 20 days, the ratio of **5** to **1** was approximately 4:1. Longer reaction times, even with a slight excess of Cp*Li, led to the same ratio of complexes. Attempts to selectively crystallize **5** were unsuccessful, and afforded

mixtures of **5** and **1**. A second attempt to obtain **5** in pure form involved reaction of the tetramethylphospholyl salt with Cp^*ScCl_2 [19]. However, even with a substoichiometric amount of the phospholyl lithium reagent, the reaction gave a mixture of **5** and **1** after stirring for 30 min at 25 °C. These results are consistent with the facile exchange of ligands between scandium centers, which has some precedent in cyclopentadienyl ligand exchange reactions of lanthanide complexes [20].



The chemistry described above indicates that the binding of lithium chloride by scandium phospholyl complexes represents a potential problem in the synthesis of alkyl derivatives of the type $(\eta^5\text{-C}_4\text{Me}_4\text{P})_2\text{ScR}$. Thus, an attempt was made to exchange the chlorides in **1** for the more labile triflate anion. Addition of 1 equiv. of Me_3SiOTf to a C_6D_6 solution of **1** resulted in instantaneous bleaching of the yellow solution and appearance of a white precipitate. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this reaction solution contains a new signal at -33.4 ppm (**6**), which is significantly upfield with respect to shifts for the other η^5 -phospholyl scandium complexes, and another small peak at 104.0 ppm. In the ^1H NMR spectrum, a resonance for the α -Me protons for the phospholyl group is observed at 2.05 ppm ($^3J_{\text{P-H}}$ of 10 Hz), and one major SiMe_3 resonance appears at 0.02 ppm, which is also coupled to phosphorous ($^4J_{\text{P-H}} = 4$ Hz). A $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum with selective decoupling of the -33.4 ppm resonance indicates that both couplings are associated with the same phosphorous atom. The integration and the chemical shifts of the signals indicate that **6** does not contain a η^5 -phospholyl ligand, but is instead the phosphine $\text{Me}_4\text{C}_4\text{P}(\text{SiMe}_3)$. The observed $^{31}\text{P}\{^1\text{H}\}$ chemical shift is close to that for *P*-trimethylsilyl-2,5-bis-(*tert*-butyl)phosphole, at -41.3 ppm [21]. A related procedure involving the addition of 1.05 equiv. of silver triflate to a solution of **1** in C_6D_6 or toluene produced an insoluble new species, which could not be isolated in pure form.

3. Conclusions

The synthesis of phospholyl complexes of scandium has been achieved. For the initially isolated chloride precursor **1**, η^5 -coordination of both phospholyl ligands was observed. However, structural data and observed reaction chemistry are consistent with weak binding of the phospholyl groups. Indeed, reactions of the transmetallation

reagents $\text{LiCH}(\text{SiMe}_3)_2$ and Cp^*Li result in displacement of a phospholyl ligand, with formation of **4** and **5**, respectively. Further attempts to functionalize **4** were unsuccessful. For complex **5**, there is an equilibrium with **1** that precludes its isolation.

An apparent problem with the use of **1** as a starting material concerns the nonlabile nature of the $\text{Cl}_2\text{Li}(\text{tmeda})$ group bound to scandium. Attempts to employ chemical reagents for abstraction of chloride or lithium have so far not provided a pathway to neutral $(\text{Me}_4\text{C}_4\text{P})_2\text{ScX}$ complexes. A difficulty with the synthesis of such complexes is lability of the phospholyl ligands, which may be associated with the stability of a η^1 -coordination mode for the phospholyl ligand. Thus, it appears that further attempts to develop the chemistry of scandium phospholyl complexes should focus on phospholyl ligands with different substitution patterns.

4. Experimental

All manipulations were conducted under an atmosphere of nitrogen using standard Schlenk techniques or a glovebox. Dry, deoxygenated solvents were employed for all manipulations. All solvents were distilled from Na/benzophenone ketyl, except benzene- d_6 , which was purified by vacuum distillation from Na/K alloy. $(\text{C}_4\text{Me}_4\text{P})\text{Li}(\text{tmeda})$ [12], $\text{ScCl}_3(\text{THF})_3$ [22] and $\text{LiCH}(\text{SiMe}_3)_2$ [23] were prepared according to literature procedures. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory, U.C. Berkeley. NMR spectra were recorded at 25 °C on either a Bruker AMX-300 spectrometer at 300 MHz (^1H) and 75.5 MHz (^{13}C) or on a Bruker AMX-400 spectrometer at 400 MHz (^1H), 100 MHz (^{13}C), and 161.9 MHz (^{31}P).

4.1. Crystallographic structural determinations

Crystallographic data are collected in Table 1. Crystals of both **1** and **4** were immersed in paratone N oil, and mounted on a glass fiber and examined on a Siemens SMART diffractometer with graphite monochromated Mo $\text{K}\alpha$ radiation. The frame data were integrated using the program SAINT [24]. Empirical absorption corrections were made using SADABS [25]. Structures were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the teXsan crystallographic software package.

4.2. $(\text{C}_4\text{Me}_4\text{P})_2\text{ScCl}_2\text{Li}(\text{tmeda})$ (**1**)

Toluene (30 mL) was added to a mixture of $\text{C}_4\text{Me}_4\text{PLi}(\text{tmeda})$ (0.580 g, 2.21 mmol) and $\text{ScCl}_3(\text{THF})_3$ (0.406 g, 1.105 mmol). The resulting yellow solution was stirred for 3 h and filtered. The resulting solution was then concentrated to 10 mL and stored for 16 h at -80 °C. Yellow crystals of **1** were isolated and dried under dynamic vacuum for

Table 1
Crystallographic data for compounds **1** and **4**

	1	4
Formula	C _{25.5} H ₄₄ N ₂ LiP ₂ Cl ₂ Sc	C ₂₁ H ₄₇ LiN ₂ Si ₂ PCL ₂ Sc
FW	563.39	537.56
Size (mm)	0.18 × 0.26 × 0.14	0.20 × 0.18 × 0.08
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> ₂ <i>1</i> / <i>a</i>
<i>a</i> (Å)	8.6175(8)	22.181(2)
<i>b</i> (Å)	10.437(1)	12.420(1)
<i>c</i> (Å)	18.654(2)	23.179(2)
α, β, γ (°)	76.753(2), 76.753(2), 69.521(2)	90, 104.858(1), 90
<i>V</i> (Å ³)	1508.7(2)	6172.1(8)
<i>Z</i>	2	8
<i>D</i> _{calc} (g cm ⁻³)	1.240	1.157
<i>F</i> ₀₀₀	598.00	2304.00
Temperature (°C)	-149	-146
Number of unique/total reflections	4839/7614	7282/21037
<i>R</i> _{int}	0.046	0.093
<i>T</i> _{max} / <i>T</i> _{min}	1.00/0.45	1.00/0.49
Number of variables	286	537
Reflection/parameter ratio	9.76	6.10
$R = \sum F_o - F_c / \sum F_o $	0.058	0.045
$R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$	0.069	0.053
Goodness-of-fit ($[\sum w(F_o - F_c)^2 / (N_o - N_v)]^{1/2}$)	1.72	1.22
Maximum and minimum peaks in final difference map (e ⁻ Å ³)	0.53/-0.67	0.34/-0.50

4 h, affording the product in 71% yield (0.571 g, 0.784 mmol). ¹H NMR (benzene-*d*₆): δ 2.46 (d, 12H, ³*J*_{PH} = 8 Hz, α -Me), 2.15 (s, 12H, β -Me), 1.97 (s, 12H, -NMe₂), 1.65 (s, 4H, -CH₂N). ¹³C{¹H} NMR (benzene-*d*₆): δ 144.4 (d, ¹*J*_{PC} = 55 Hz), 140.1 (d, ²*J*_{PC} = 4 Hz), 56.3 (s), 45.6 (s), 17.2 (d, ²*J*_{PC} = 29 Hz), 15.5 (s). ³¹P{¹H} NMR (benzene-*d*₆): δ 99.8. Anal. Calc. for C_{22.5}H₄₄Cl₂LiN₂P₂Sc (**1** · $\frac{1}{2}$ PhMe): C, 54.36; H, 7.87; N, 4.97. Found: C, 54.51; H, 8.17; N, 4.83%.

4.3. Generation of (C₄Me₄P)₂ScMeXLi(*tmeda*) (*X* = Cl (**2**) and Me (**3**))

To a solution of **1** (0.0100 g, 0.019 mmol) in C₆D₆ (0.35 mL) was added 1 equiv. of MeLi (0.0004 g, 0.019 mmol). The reaction mixture was added to an NMR tube and shaken for 5 min to yield predominantly **2** and a considerable amount of **1** and **3** (by ¹H NMR spectroscopy). To the same solution was added another equiv. of MeLi (0.004 g, 0.019 mmol) to afford a mixture comprised predominantly of **3**, with a small amount of **2**. For **2**: δ ¹H NMR (benzene-*d*₆): 2.27 (s, β -Me), 2.25 (d, ³*J*_{PH} = 10 Hz, α -Me), 1.95 (s, -NMe₂), -0.74 (s, Sc-Me). ³¹P{¹H} NMR (benzene-*d*₆): δ 87.8 ppm. For **3**: ¹H NMR (benzene-*d*₆): δ 2.26 (s, β -Me), 2.18 (d, ³*J*_{PH} = 10 Hz, α -Me), 1.95 (s, -NMe₂), 1.64 (s, -CH₂N), -1.07 (s, Sc-Me) ³¹P{¹H} NMR δ (benzene-*d*₆): 82.5 ppm.

4.4. (C₄Me₄P)[(Me₃Si)₂CH]ScCl₂Li(*tmeda*) (**4**)

Toluene (10 mL) was added to a mixture of **1** (0.117 g, 0.226 mmol) and LiCH(SiMe₃)₂ (0.041 g, 0.248 mmol).

After 2 min, the solution changed from deep yellow to colorless with a white precipitate. The reaction vessel was covered with aluminium foil and the solution was stirred for 12 h. The solvent was then removed under dynamic vacuum and the resulting white solid was extracted with four portions of pentane (10 mL). The combined, colorless extracts were concentrated to 20 mL and cooled to -80 °C for 3 d. The crystalline product was isolated by decanting the supernatant. The later solution was concentrated by half and cooled again to -80 °C to yield more colorless crystals for a cumulative yield of 54% (0.065 g, 0.122 mmol). ¹H NMR (benzene-*d*₆): δ 2.52 (d, 6H, ³*J*_{PH} = 13 Hz, α -Me), 2.13 (s, 6H, β -Me), 1.86 (s, 12 H, -NMe₂), 1.55 (s, 4H, -CH₂N), 1.04 (s, 18H, -SiMe₃), 0.52 (s, 1H, -CH(SiMe₃)₂). ¹³C{¹H} NMR (benzene-*d*₆): δ 147.6 (d, ²*J*_{PC} = 50 Hz), 138.4 (d, ²*J*_{PC} = 3.8 Hz), 56.2 (s), 54.5 (s, ¹*J*_{HC} = 96 Hz), 45.5 (s), 17.2 (d, ³*J*_{PC} = 25 Hz), 15.1 (s). ³¹P{¹H} NMR (benzene-*d*₆): δ 119.2. Anal. Calc. for C₂₁H₄₇Cl₂LiN₂PScSi₂: C, 46.91; H, 8.82; N, 5.21. Found: C, 46.87; H, 8.75; N, 5.14%.

4.5. Generation of (C₄Me₄P)(Cp*)ScCl₂Li(*tmeda*) (**5**)

A solution of **1** (0.010 g, 0.019 mmol) and Cp*Li (0.0028 g, 0.019 mmol) in benzene-*d*₆ (0.35 mL) was prepared in an NMR tube. The reaction was heated to 110 °C and monitored for 30 days. The evolution of **5** and (Me₄C₄P)Li(*tmeda*) was observed, and after 20 days, a 4:1 equilibrium mixture of **5**:**1** was established. ¹H NMR (benzene-*d*₆): δ 2.26 (s, Cp*), 2.22 (d, ³*J*_{PH} = 10 Hz, α -Me), 2.10 (s, β -Me), 1.88 (s, -NMe₂), 1.56 (s, -CH₂N). ³¹P{¹H} NMR (benzene-*d*₆): δ 100.2.

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Appendix A. Supplementary informations available

Crystallographic data have been deposited with CCDC (CCDC No. 606632 for compound **1** and CCDC No. 606633 for compound **4**). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the internet at www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.06.042](https://doi.org/10.1016/j.jorganchem.2006.06.042).

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