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Synthesis and characterization of mono-(pentamethylcyclopentadienyl)alkoxyscandium alkyl derivatives, $(\eta^5\text{-}C_5Me_5)(OR)ScR'$

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Abstract

Strategies for the syntheses of the title compounds are described. $Cp^*Sc(acac)_2$ ($Cp^* = (\eta^5\text{-}C_5Me_5)$; acac = acetylacetonate) is prepared by treatment of $Sc(acac)_3$ with $Cp^*MgCl\cdot THF$. Oligomeric $[Cp^*ScCl_2]_n$ is prepared by treatment of $Cp^*Sc(acac)_2$ with two equivalents of $AlCl_3$. $Cp^*(OR)ScCl$ ($R = 2,4,6\text{-}C_6H_2(CMe_3)_3$, $3,5\text{-}C_6H_3(CMe_3)_2$) are obtained as their THF adducts via treatment of $[Cp^*ScCl_2]_n$ with LiOR in THF or as their lithium chloride adducts via treatment of $[Cp^*ScCl_2]_n$ with LiOR in toluene in the presence of PMe_3. Whereas the alkylation of $Cp^*\{O\text{-}2,4,6\text{-}C_6H_2(CMe_3)_3\}ScCl$ yields unstable products which appear to readily undergo metalation of an *ortho* tert-butyl group with loss of alkane, treatment of $Cp^*\{O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}ScCl$ with methyllithium yields an unreactive scandium methyl derivative, which is likely dimeric $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$. This methyl derivative proved to be unexpectedly inert toward olefins, 2-butyne and even Lewis bases such as pyridine and THF.

Introduction

Organoscandium derivatives have proven to be convenient subjects for our investigations of the scope and mechanism of a variety of transformations characteristic of organometallic compounds of the early transition metals and lanthanide elements [1]. Recently we focused our attention on scandocene alkyls and hydrides as Ziegler–Natta olefin polymerization catalysts [2]. Since the 14-electron Cp^*_2ScR ($Cp^* = (\eta^5\text{-}C_5Me_5)$) complexes are isoelectronic with $[Cp_2MR]^+$ ($Cp = (\eta^5\text{-}C_5H_5)$; M = Ti, Zr, Hf), the presumed active species for catalysts based on group 4 metallocenes [3], they have provided excellent models with which to probe the mechanisms of this poorly understood process. Moreover, these organoscandium

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catalysts may exhibit useful features which derive from the unique properties of scandium.

As we have reported, permethylscandocene alkyls may catalyze the living polymerization of ethylene at low temperatures [2a]. Unfortunately, the living nature of this system could not be exploited, since ethylene is the only substrate for which the catalyst is active. Theorizing that the sterically imposing Cp^* ligands are largely responsible for this limitation, we have begun to explore ways to decrease the steric bulk about the scandium center. This process of fine-tuning was aimed at opening up the reactive metal center enough to allow access by higher olefins, while at the same time maintaining sufficient bulk to keep the complexes monomeric in solution. By tying the two cyclopentadienyl ligands back with a dimethylsilane-diyl linking group, e.g. $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}ScR$ and $\{(\eta^5\text{-}C_5H_3CMe_3)_2SiMe_2\}ScR$, we observe catalytic dimerization of α olefins; however, under no circumstances have we observed α olefin polymerization with these bis(cyclopentadienyl)scandium derivatives. Replacement of one cyclopentadienyl group with an amide ligand, e.g. with $\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}ScR$ ("$Cp^*SiNRScR$"), results in catalysts which effect the oligomerization of α olefins [2b]. Buoyed by this success, we envisioned a similar series of catalysts which incorporated an alkoxide donor in place of the amide donor. We anticipated that the target compounds $Cp^*(OR)ScR'$ would be electronically more similar to the Cp^*_2ScR analogs, since [RO] like $(\eta^5\text{-}C_5Me_5)$ may formally donate 5 electrons (using the "neutral ligand" method of electron counting) to the scandium center [4]. Herein we report the syntheses of some representative $Cp^*(OR)ScR'$ derivatives, together with an initial survey of their reaction chemistry. It appears that this chemistry is dominated by the formation of strong alkoxide bridges, which give these compounds tremendous stability, both in the solid state and in solution.

Results

Unlike the linked Cp^*-amide ligand, e.g. $\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}$, synthesis of an appropriate linked Cp^*-alkoxide chelating ligand was not easily effected [5]. We thus set as targets complexes of the general formula $Cp^*(OR)ScR'$, incorporating monodentate alkoxide donors. We chose the butylated aryloxy ligands, 2,4,6-tri-tert-butylphenoxide and 3,5-di-tert-butylphenoxide both because of their ready availability and prior utility as ancillary ligands in early transition metal chemistry [6].

Early transition metal or lanthanide alkoxide derivatives typically are prepared via reaction of suitable metal halide precursor with lithium alkoxide or alkane elimination in the reaction of an alcohol with a metal alkyl. The requisite Cp^*ScCl_2 starting material is not readily obtained by the most obvious route, reaction of $ScCl_3(THF)_3$ with one equivalent of Cp^*Li, however. A complex mixture of ill defined products results, likely due to the presence of THF. The high yield synthesis shown in equations 1 and 2 exploits the relationship between scandium and aluminum:

$$Sc(acac)_3 + Cp^*MgCl \cdot THF \xrightarrow{\text{toluene}} Cp^*Sc(acac)_2 + MgCl(acac)(THF) \qquad (1)$$

$$Cp^*Sc(acac)_2 + 2\ AlCl_3 \xrightarrow{\text{toluene}} [Cp^*ScCl_2]_n + 2\ AlCl_2(acac) \qquad (2)$$

Only one Cp* ligand is transferred to scandium in the reaction with $Cp^*MgCl \cdot THF$ with one equivalent of anhydrous scandium tris(acetylacetonate). Cp^*Li may be substituted for $Cp^*MgCl \cdot THF$ with only a slight reduction in yield. The canary yellow, air-stable product $Cp^*Sc(acac)_2$ is subsequently treated with two equivalents of aluminum chloride in a reaction which transfers acetylacetonate from scandium to the (even more!) oxophilic aluminum. The oligomeric, base-free $[Cp^*ScCl_2]_n$ precipitates from the reaction medium in 72% overall yield based on $Sc(acac)_3$. This material is insoluble in aliphatic solvents, but it dissolves readily in THF, likely forming THF adduct(s) of lower nuclearity.

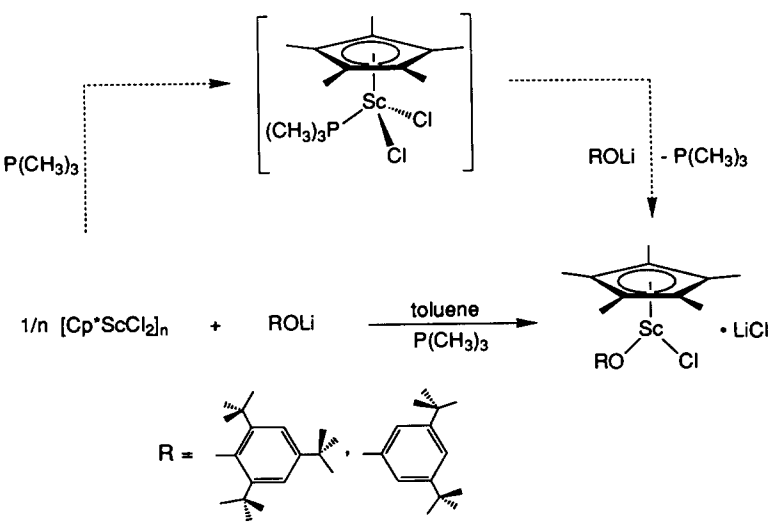
Reaction of $[Cp^*ScCl_2]_n$ with one equivalent of ROLi (R = 2,4,6-tri-tert-butylphenoxide) in toluene leads to a 1:1 mixture of starting dichloride and a compound which exhibits an NMR spectrum consistent with the formulation $[Cp^*Sc(OR)_2]_n$ [7 *]. Presumably, the oligomeric dichloride is solubilized as the first alkoxide is introduced such that the reaction with a second equivalent of ROLi is much more rapid than with the suspended oligomer. A single alkoxide ligand can, however, be added by carrying out the reaction in THF (eq. 3).

$$1/n\left[Cp^*ScCl_2\right]_n \xrightarrow[THF]{LiOR,\ -\ LiCl} Cp^*(OR)ScCl(THF) \qquad (3)$$

$(R = 2,4,6\text{-}C_6H_2(CMe_3)_3)$

The product is isolated as a THF adduct of the desired, base-free alkoxychloride, in which the THF is held very tightly by the scandium center. Heating the solid to 120 °C under high vacuum did not effect its removal, and its presence proved to be detrimental to subsequent reactivity with alkyllithium reagents.

The desired alkoxychloride was obtained by slow addition of one equivalent of ROLi to a toluene suspension of the dichloride in the presence of the softer Lewis base, trimethylphosphine (Scheme 1). Although PMe_3 does not totally solublize the

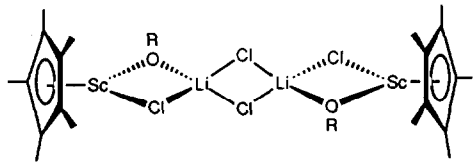


Scheme 1.

* Reference number with asterisk indicates a note in the list of references.

oligomer, ^{31}P NMR evidence indicates that some PMe_3 is bound to scandium in solution, suggesting that an equilibrium between a soluble PMe_3 adduct of low nuclearity and insoluble oligomeric materials exists. It is likely that reaction occurs between this PMe_3 adduct and the alkoxy lithium reagent, which is added very slowly. Upon completion of addition and isolation of the product, the phosphine is removed completely under high vacuum. The lability of the PMe_3 for this putative adduct contrasts with the trimethylphosphine adducts of $\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}Sc(PMe_3)R$, two of which have been isolated and crystallographically characterized [26,8].

Although PMe_3-free, the alkoxychlorides, $Cp^*\{O\text{-}2,4,6\text{-}C_6H_2(CMe_3)_3\}ScCl$ and $Cp^*\{O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}ScCl$, are isolated as lithium chloride adducts, as determined by microanalytical data. The ^1H NMR spectra are straightforward and establish clearly the presence of one alkoxide ligand per $[Cp^*Sc]$ unit, based on relative integrals of the tert-butyl vs. the $(\eta^5\text{-}C_5Me_5)$ methyl resonances. The nuclearity of the complexes in solution has not been established; however, a dimeric arrangement such as that shown below appears most likely.



The apparent symmetry and relatively high solubility in aromatic solvents suggest that structures of higher nuclearity are unlikely.

The synthetic protocol generally followed for preparing hydrides of scandium involves hydrogenation of alkyl derivatives, which are, in turn, normally prepared by metathesis reactions of the analogous chloride and alkyllithium reagent. We thus began to explore the alkylation reactions with $Cp^*\{O\text{-}2,4,6\text{-}C_6H_2(CMe_3)_3\}ScCl$ and $Cp^*\{O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}ScCl$. Alkylations of $Cp^*\{O\text{-}2,4,6\text{-}C_6H_2(CMe_3)_3\}ScCl$ with the bulky alkyllithium reagents $LiCH_2SiMe_3$ and $LiCH(SiMe_3)_2$ in toluene, benzene or petroleum ether solvents proceed slowly at room temperature to produce thermally unstable alkoxy-alkyl derivatives. Rate-limiting displacement of LiCl from the starting lithium chloride adduct is probably responsible for the sluggish rate, a situation exacerbated by the bulky properties of the alkyl groups employed. The alkyl derivatives undergo subsequent slow decomposition to a mixture of products, including RH ($R = CH_2SiMe_3$ and $CH(SiMe_3)_2$). The organometallic products were not fully characterized, but the initial step appears to be metalation (intramolecular σ bond metathesis) with one of the ortho-tert-butyl groups of the alkoxide ligand. An analogous process was originally reported by Rothwell [9]. This decomposition was slow enough to allow isolation of $Cp^*\{O\text{-}2,4,6\text{-}C_6H_2(CMe_3)_3\}ScCH(SiMe_3)_2$ as a white powder, albeit in poor yield. Reaction of this compound with dihydrogen is not clean; evidently the corresponding hydride is also unstable in solution. The apparent instability of these alkyl and hydride derivatives did not augur well for olefin polymerization, indicating that chain transfer and termination reactions would almost certainly be facile. Derivatives with the alkoxide ligand $\{O\text{-}2,4,6\text{-}C_6H_2(CMe_3)_3\}$ therefore were not explored further.

Alkyl substitution at the more remote 3 and 5 positions appeared to be a possible solution to the above mentioned problem. Indeed, alkylation of $Cp^*\{O\text{-}3,5\text{-}$

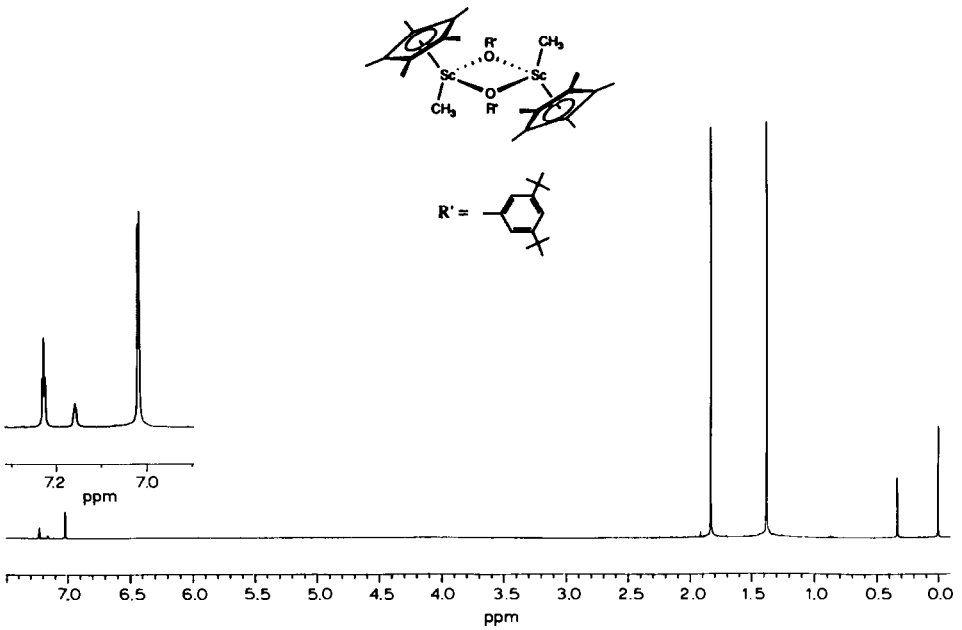


Fig. 1. ^{1}H NMR spectrum (500 MHz, benzene-d_6) for $[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2$.

$C_6H_3(CMe_3)_2\}ScCl$ proceeds smoothly and rapidly at room temperature to yield what is likely an alkoxide-bridged dimer, $[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2$ (eq. 4).

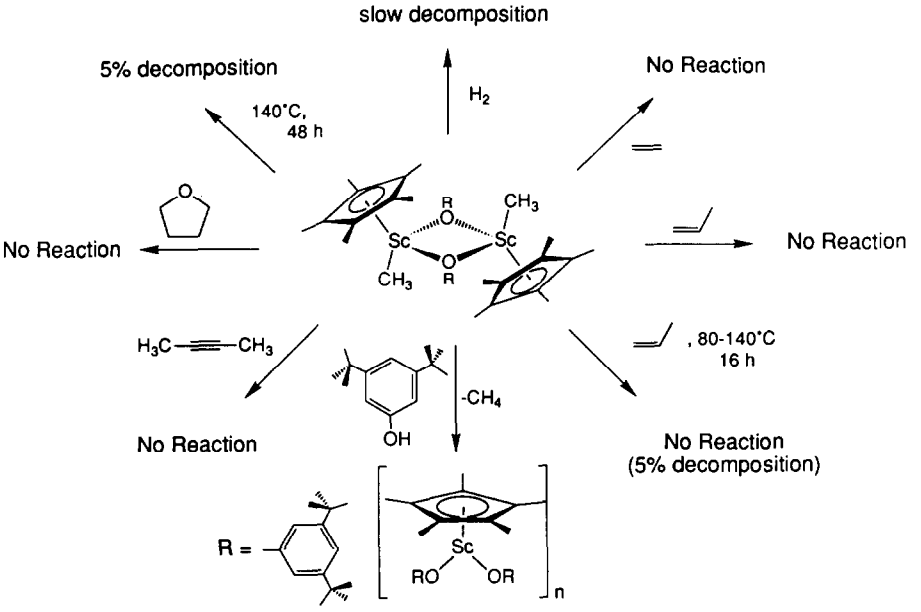
$$2\ Cp^*\{\text{O-3,5-}C_6H_3(CMe_3)_2\}ScCl + 2\ CH_3Li \xrightarrow{Et_2O} [Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2 + 2\ LiCl \quad (4)$$

$[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2$ is obtained in 85% isolated yield, and its ^{1}H NMR spectrum is given in Fig. 1. Microanalytical data confirm that no LiCl remains coordinated, and although X-ray quality crystals were not obtained, a dimeric structure is likely. Unfortunately, decomposition occurs in solution, so that a molecular weight determination by ebulliometry was inconclusive. The analogous CH_2SiMe_3 complex, prepared similarly, has been identified only on the basis of its ^{1}H NMR spectrum, but is likely isostructural to $[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2$.

An alternate procedure for the preparation of $[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2]_2$ may also be used (eq. 5):

$$2/x\ [Cp^*Sc(CH_3)_2]_x + 2\ HO\text{-3,5-}C_6H_3(CMe_3)_2 \rightarrow [Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2 + 2\ CH_4 \quad (5)$$

With slightly less than one equivalent of di-tert-butylphenol, $[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2$ may be obtained in greater than 90% yield (^{1}H NMR), along with one equivalent of CH_4. The high yield of $[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2$ suggests that reaction of the phenol with insoluble $[Cp^*Sc(CH_3)_2]_x$ is much faster than subsequent reaction with the product, which does occur at a modest rate (*vide infra*).



Scheme 2.

The requisite dimethyl oligomer $[Cp^*Sc(CH_3)_2]_x$ is prepared from $[Cp^*ScCl_2]_x$ and methyllithium and obtained as a flocculent off-white powder as described in the Experimental section. It is only sparingly soluble in aromatic solvents and decomposes upon heating in benzene-d_6. Two signals associated with $[ScCH_3]$ are observed in the ^1H NMR spectrum (benzene-d_6, 25 °C), suggesting an oligomeric structure with both terminal and bridging methyl ligands. On the other hand, in THF-d_8 a single scandium methyl resonance is observed, suggesting a simple THF-stabilized monomer with a three-legged piano stool type structure. While stable for short periods of time in THF, it does decompose at a modest rate to a variety of products, one of which appears to be a butoxy/methyl derivative similar to $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ described above. This complex is thus highly susceptible to σ bond metathesis reactions with a variety of solvents.

Since $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ was available pure and in high yield, we first concentrated on its reaction chemistry prior to complete characterization of the other alkyl cogeners. Those reactions which were studied are shown in Scheme 2. Reaction with dihydrogen proceeded surprisingly slowly, yielding after 4 days a complex mixture of Cp*-containing products. Methane evolution accompanies this reaction, but no ^1H NMR resonances attributable to a hydride could be identified. In the reaction of $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ with olefins under a variety of conditions escalating in severity, no indications of insertion chemistry were observed. Indeed, the methyl complex remained largely intact even at 140 °C in the presence of 2–3 equivalents of propene! No reaction occurs with 2-butyne at room temperature. Even relatively potent Lewis bases such as pyridine and THF, which normally bind quite tightly to scandium, failed to break the strong alkoxide bridges of $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$. Only reaction with

3,5-di-tert-butylphenol produced a clean product, $Cp^*\{O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}_2Sc$, along with an equivalent of methane.

The unpredicted, remarkably low reactivity of $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ led us to reconsider the use of complexes of the general formula $Cp^*(OR)ScR'$ as olefin polymerization catalysts. The formation of dimers or higher oligomers with robust alkoxide bridges appears to dominate their chemistry. This propensity may be alleviated by using very bulky alkoxide ligands; however, it is likely that an alkoxide of sufficient bulk to prevent cluster formation will also restrict access of olefin to the scandium center. Moreover, as was found for the unstable derivatives $Cp^*\{O\text{-}2,4,6\text{-}C_6H_2(CMe_3)_3\}ScR$, sterically bulky substituents may also present C–H bonds in close proximity to Sc–R. Facile σ bond metathesis with loss of RH and metalation of the ligand system thus ensues.

Experimental

General considerations

All manipulations were performed using glove box and high vacuum techniques as described previously [10]. Toluene was predried over sodium, distilled from sodium benzophenone ketyl and stored over titanocene [11]. Petroleum ether was predried over sodium, distilled from CaH_2 and stored over titanocene. Tetrahydrofuran (THF) was distilled from and stored over sodium benzophenone ketyl. Benzene-d_6 was dried over 4 Å molecular sieves. Argon and dihydrogen were purified by passage over MnO on Vermiculite [12] and activated 4 Å molecular sieves. Routine ^1H NMR spectra were recorded on a Bruker WM-500 instrument or a Varian EM-390 90 MHz machine.

Butylated phenols were purchased from Aldrich Chemicals and used as received to make the alkoxide ligands employed by deprotonation with n-butyllithium in hexanes and isolation by filtration. Alkyllithium reagents RLi ($R = CH_3$, CH_2SiMe_3, $CH_2CH_2CH_2CH_3$) were purchased from Aldrich Chemicals. The bulky alkyllithium reagent $LiCH(SiMe_3)_2$ [13], and $Cp^*MgCl \cdot THF$ [14] were prepared as described previously. Ethylene and propene were purchased from Matheson and used by vacuum transferring from a cold (−78°C) trap. 2-Butyne was purchased from Aldrich and dried over molecular sieves prior to degassing with two freeze–pump–thaw cycles.

(1) Preparation of Sc(acac)$_3$. The procedure used is a modification of that described earlier [15]. Sc_2O_3 (10 g) was suspended in distilled water (100 mL), and concentrated HCl (6.0 mL) was added. The mixture was heated gently until all of the solid had dissolved (1–2 h). The solution was diluted with distilled water to one liter and 2,4-pentadione (45 mL) was added. With swirling, pyridine (36 mL) was added dropwise over a 15 min period. The flocculent white precipitate which began to appear after about half of the pyridine had been added was isolated by suction filtration, washed with 3×100 mL portions of water and dried *in vacuo* for 12 h. Yield 85%.

*(2) Preparation of Cp*Sc(acac)$_2$.* A 250 mL round bottom flask was charged with $Sc(acac)_3$ (7.5 g; 21.9 mmol) and $Cp^*MgCl \cdot THF$ (6.0 g; 22.5 mmol) and equipped with a 180° needle valve. Dry toluene (80 mL) was transferred into the vessel by cannula, and the suspension stirred for 3 h at room temperature, during which time the suspension took on a canary yellow color. The toluene was then

removed under reduced pressure, and excess $Cp^*MgCl \cdot THF$ was quenched with 30 mL of methanol. Subsequent operations were carried out in air. The methanol suspension was stirred for 10 min after which the yellow solid was isolated by suction filtration and washed with 3×30 mL portions of methanol. The microcrystalline yellow solid (7.2 g, 87%) was dried *in vacuo*. The product so obtained may be used directly, or it may be recrystallized from hot toluene. The procedure described above may be scaled up to prepare at least 20 g. ^1H NMR (90 MHz, benzene-d_6) $CH_3COCHCOCH_3$ 1.8 δ (s 12 H); $[C_5(CH_3)_5]$ 2.1 δ (s 15 H); $CH_3COCHCOCH_3$ 5.2 δ (s 2 H). Anal. Found: C, 63.27; H, 7.52. $C_{20}H_{29}ScO_4$ calcd.: C, 63.48; H, 7.72%.

(3) Preparation of $[Cp^*ScCl_2]_x$. In a glove box a 100 mL round bottom flask was charged with $Cp^*Sc(acac)_2$ (5.0 g; 13.4 mmol) and aluminum chloride (3.5 g; 26.6 mmol) and attached to a swivel frit assembly equipped with medium porosity frit. Dry toluene (50 mL) was transferred into the flask by cannula, and the mixture stirred at room temperature for 3 h. The suspension was then heated to boiling, and the cream colored solid isolated by filtration. After washing once with toluene and twice with hexanes, the product (2.8 g, 83%) was dried *in vacuo*. ^1H NMR (90 MHz, THF-d_8): $[C_5(CH_3)_5]$ 2.1 δ (s). Anal. Found: C, 47.32; H, 5.73. $C_{10}H_{15}ScCl_2$ calcd.: C, 47.83; H, 6.02%.

(4) Preparation of $Cp^*Sc(OR)Cl \cdot LiCl$ *(OR =* O-2,4,6-$C_6H_2(CMe_3)_3$, O-3,5-$C_6H_3(CMe_3)_2$*).* A 250 mL three-necked round bottom flask was charged with $[Cp^*ScCl_2]_x$ (5.0 g, 20 mmol) and equipped with swivel frit assembly (medium porosity frit, side port) and a pressure equalizing solid addition funnel containing ROLi (0.95 equiv., 19 mmol R = 2,4,6-$C_6H_2(CMe_3)_3$, 5.1 g; R = 3,5-$C_6H_3(CMe_3)_2$, 4.0 g). The assembly was attached to a vacuum line via a 90° needle valve and carefully evacuated to prevent the alkoxide from being sucked into the reaction flask. Dry toluene (ca. 150 mL) was vacuum transferred into the vessel at −78°C; trimethylphosphine (4.1 mL, 40 mmol) was then vacuum transferred into the vessel to partially dissolve the oligomeric dichloride. Argon was admitted to a pressure of one atmosphere, and the suspension allowed to warm to room temperature before addition of ROLi was started. Incremental addition of the alkoxide was carried out over a period of 45 min, during which the mixture cleared somewhat and became slightly yellow in color. After stirring for an additional hour the mixture was reduced in volume to ca. 70 mL, and the white solid isolated by filtration. The product was washed twice with hexanes and dried *in vacuo*. A second crop was taken by re-suspending the residue from the filtrate in hexanes, triturating the mixture and filtering off the white solid thus suspended. Combined yield 5.2 g (51%), R = 2,4,6-$C_6H_2(CMe_3)_3$; 6.2 g (67%), R = 3,5-$C_6H_3(CMe_3)_2$. ^1H NMR for $Cp^*Sc(OR)Cl \cdot LiCl$ (OR = O-2,4,6-$C_6H_2(CMe_3)_3$) (500 MHz, benzene-d_6): *p*-$C(CH_3)_3$, 1.38 δ (s, 9H); *o*-$C(CH_3)_3$, 1.66 δ (s, 18H); $[C_5(CH_3)_5]$, 1.92 δ (s, 15 H); 2,4,6-$C_6H_2(CMe_3)_3$, 7.46 δ (s, 2H). Anal. Found: C, 65.02; H, 8.29. $C_{28}H_{44}ScCl_2OLiC$ (calcd.): C, 64.74; H, 7.56%. ^1H NMR for $Cp^*Sc(OR)Cl \cdot LiCl$ (OR = O-3,5-$C_6H_3(CMe_3)_2$) (500 MHz, benzene-d_6): *m*-$C(CH_3)_3$, 1.40 δ (s, 18H); $[C_5(CH_3)_5]$, 1.85 δ (s, 15 H); $C_6HH_2(CMe_3)_2$, 7.29 δ (s, 1H); $C_6HH_2(CMe_3)_2$, 7.38 δ (s, 2H).

(5) Preparation of $[Cp^*Sc(CH_3)_2]_x$. $[Cp^*ScCl_2]_x$ (0.89 g, 3.5 mmol) was loaded into a 100 mL round bottom flask and attached to a swivel frit assembly. The apparatus was evacuated and dry Et_2O (40 mL) was vacuum transferred into the

vessel. The suspension was cooled to −78 °C, and $CH_3Li \cdot LiBr$ (5.2 mL of a 1.5 *M* solution in Et_2O, 2.1 equiv.) was added in one portion against a counterflow of argon. The mixture was gradually warmed to room temperature and stirred for a total of 2 h. The Et_2O was removed under reduced pressure, and toluene (50 mL) and PMe_3 (2 mL) were vacuum transferred into the vessel. The suspension was stirred vigorously for 30 min and filtered. The volatiles were removed in vacuo, during which time a flocculent off-white precipitate appeared. The product (0.503 g, 67%) was isolated by suspending the residue in hexanes and filtering. ^1H NMR (90 MHz, benzene-d_6): Sc-CH_3, −0.5 δ (s, 3H); Sc-CH_3, −0.4 δ (s, 3H); [$C_5(CH_3)_5$], 2.1 δ (s, 15H). ^1H NMR (90 MHz, THF-d_8): Sc-CH_3, −1.15 δ (s, 6H); [$C_5(CH_3)_5$], 1.92 δ (s, 15H).

(6) Preparation of [Cp(CH$_3$)Sc{μ-O-3,5-C$_6$H$_3$(CMe$_3$)$_2$}]$_2$. Method A.* A 50 mL round bottom flask was charged with $Cp^*Sc(O\text{-}3,5\text{-}C_6H_3(CMe_3)_2)Cl \cdot LiCl$ (1.3 g, 2.8 mmol) and attached to a swivel frit assembly equipped with a fine porosity frit. The apparatus was evacuated and Et_2O (ca. 30 mL) was condensed into the vessel. At 0 °C a solution of methyllithium/lithium bromide complex (2.0 mL of a 1.5 *M* solution in Et_2O, 3.1 mmol) was added via a syringe against a flow of argon. The reaction mixture was stirred at 0 °C for 30 min before allowing the mixture to warm to room temperature. Et_2O was removed *in vacuo* and ca. 50 mL of dry toluene vacuum transferred onto the residue. The resulting suspension was heated to 70 °C, and the lithium halides removed by filtration. The toluene was then removed *in vacuo*, the white residue re-suspended in hexanes and the product (0.95 g, 85%) isolated by filtration. ^1H NMR (500 MHz, benzene-d_6): Sc-CH_3, 0.33 δ (s, 3H); *m*-C(CH_3)$_3$, 1.38 δ (s, 18H); [$C_5(CH_3)_5$], 1.83 δ (s, 15H); *o*-C*H*, 7.01 δ (d, ^4J(HH) = 1.7 Hz; 2H); *p*-C*H*, 7.23 δ (t, 1H). Anal. Found: C, 73.76; H, 9.50. $C_{25}H_{39}ScO$ calcd.: C, 74.95; H, 9.83%.

Method B. $[Cp^*Sc(CH_3)_2]_x$ (35 mg, 0.16 mmol) and 3,5-di-tert-butylphenol (34 mg, 0.16 mmol) were mixed in sealable 5 mm NMR tube equipped with a 180° needle valve. The tube was evacuated, and ca. 0.5 mL of benzene-d_6 vacuum transferred into the tube. The tube was sealed with a torch and allowed to thaw with mixing. ^1H NMR analysis indicated the production of CH_4 (0.15 δ) and $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ (> 90%) as the major products.

(7) Reaction of [Cp(CH$_3$)Sc{μ-O-3,5-C$_6$H$_3$(CMe$_3$)$_2$}]$_2$ with olefins, alkynes, dihydrogen, pyridine and 3,5-di-tert-butylphenol.* A sealable 5 mm NMR tube equipped with a 180° needle valve was loaded with $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ (20–25 mg) and ca. 0.5 mL of benzene-d_6. The solution was degassed by two freeze–pump–thaw cycles, and 2–3 equivalents of substrate (ethylene, propene or 2-butyne) were vacuum transferred by way of a calibrated bulb and sealed with a torch under 0.9 atm of argon. In the reaction with dihydrogen, H_2 was admitted to 0.95 atm while cooling as much of the NMR tube as possible with liquid nitrogen, and the tube sealed with a torch. In the reaction with pyridine or 3,5-di-tert-butylphenol, a solution containing approximately one equivalent of substrate in benzene-d_6 was added to the sample of $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ at −78 °C against a counterflow of argon and sealed as before.

(8) Reaction of [Cp(CH$_3$)Sc{μ-O-3,5-C$_6$H$_3$(CMe$_3$)$_2$}]$_2$ with THF.* A 10 mL round bottom flask equipped with a 180° needle valve was loaded with $[Cp^*(CH_3)Sc\{\mu\text{-}O\text{-}3,5\text{-}C_6H_3(CMe_3)_2\}]_2$ (20 mg) and attached to a vacuum line. After evacuation THF (5 mL) was vacuum transferred into the vessel at −78 °C. The

reaction mixture was warmed until a clear solution was obtained and stirred for 1 h at room temperature. The THF was pumped away, and the residue was examined by ^{1}H NMR spectroscopy. The resulting spectrum was entirely unchanged from that for $[Cp^*(CH_3)Sc\{\mu\text{-O-3,5-}C_6H_3(CMe_3)_2\}]_2$.

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