

5. SCANDIUM TRICHLORIDE TRIS(TETRAHYDROFURAN) AND β -DIKETIMINATE-SUPPORTED SCANDIUM CHLORIDE COMPLEXES

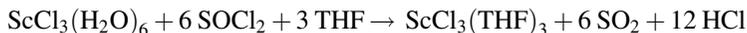
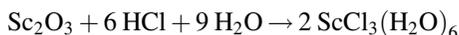
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General Procedures

All manipulations were performed either in an inert atmosphere glovebox or on a double manifold high-vacuum line equipped with Teflon needle valves.¹ Toluene and hexanes were dried and purified using the Grubbs/Dow purification system² and stored in evacuated bombs. Diethyl ether and benzene-*d*₆ were dried and stored over sodium/benzophenone ketyl. Compounds [L^{Me,*i*Pr2}Li]_x³⁻⁵ (L^{Me,*i*Pr2} = [ArNC(Me)]₂CH⁻, Ar = 2,6-*i*Pr₂C₆H₃) and [L^{*t*Bu,*i*Pr2}Li]_x⁵ (L^{*t*Bu,*i*Pr2} = [ArNC(*t*Bu)]₂CH⁻, Ar = 2,6-*i*Pr₂C₆H₃) were prepared according to literature procedures. ¹H and ¹³C NMR spectra were referenced to SiMe₄ through the residual solvent signals.

A. SCANDIUM TRICHLORIDE TRIS(TETRAHYDROFURAN), ScCl₃(THF)₃*



Procedures

■ **Caution.** *This reaction is extremely exothermic, so the SOCl₂/THF solution should be added carefully.*

ScCl₃(THF)₃ is prepared by a modified literature procedure.⁶ A 1-L round-bottomed flask equipped with a condenser is charged with Sc₂O₃ (20.3 g,

§ The checkers converted commercially available ScCl₃(H₂O)₆ (Strem Chemicals) to ScCl₃(THF)₃ using the protocol in Ref. 6. It should be noted that the checkers did not use a swivel frit, but rather, conducted manipulations inside a glovebox using a commercially available microporous frit (medium porosity).

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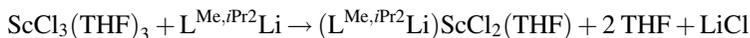
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0.147 mol) and 6 M HCl (300 mL). The reaction mixture is heated at reflux for 3 h during which period the mixture changes from a cloudy white suspension to a clear yellow solution. The solvent is removed by rotary evaporation to give $\text{ScCl}_3(\text{H}_2\text{O})_6$ as a thick yellow oil. A solution of SOCl_2 (350 mL) in THF (250 mL) is added dropwise to the oil over 2 h, during which time a large quantity of gas (HCl and SO_2) evolves. Precipitation of a white solid, followed by a gradual change to a clear yellow solution, also occurs during this period. The reaction mixture is then heated at 86°C for 18 h, and the solvent is removed by rotary evaporation to afford an oily yellow solid. The moisture-sensitive mixture is quickly attached to a swivel-frit¹ apparatus and evacuated. Et_2O (200 mL) is added to the residue, which is then stirred for 20 min and filtered. The fine white powder is washed with Et_2O (4×50 mL) and the solvent is removed *in vacuo*. Yield: 100.8 g, 0.274 mol, 93%. IR (neat):⁶ 1004 (s), 846 (s) cm^{-1} .

Properties

The product is a fine white powder that must be stored under an inert atmosphere as it rapidly absorbs moisture from air.

B. SCANDIUM 2,4-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)PENTYL DICHLORIDE TETRAHYDROFURAN, ($\text{L}^{\text{Me},i\text{Pr}_2}$) $\text{ScCl}_2(\text{THF})$



A 250-mL round-bottomed flask is attached to a swivel-frit¹ assembly and charged with $[\text{L}^{\text{Me},i\text{Pr}_2}\text{Li}]_x$ (5.00 g, 11.8 mmol) and $\text{ScCl}_3(\text{THF})_3$ (5.00 g, 13.6 mmol).^{*} Toluene (90 mL) is vacuum distilled into the evacuated flask at -78°C , and the mixture is heated with stirring at reflux for 16 h. During this period, the solution gradually changes from almost colorless to pale yellow. The reaction mixture is hot filtered to remove LiCl and excess $\text{ScCl}_3(\text{THF})_3$, and the toluene is removed from the filtrate *in vacuo*. The residue is sonicated for 10 min in hexanes (60 mL), followed by cold (-78°C) filtration.^{**} After exposure to vacuum for 6 h, ($\text{L}^{\text{Me},i\text{Pr}_2}$) $\text{ScCl}_2(\text{THF})$ is isolated in 94% yield (6.72 g, 11.1 mmol).

Anal. Calcd. for $\text{C}_{33}\text{H}_{49}\text{N}_2\text{Cl}_2\text{OSc}$: C, 65.44; H, 8.15; N, 4.63. Found: C, 65.35; H, 8.61; N, 4.61. ¹H NMR (benzene- d_6): δ 7.21 (m, 6H, C_6H_3), 5.32 (s, 1H, CH), 3.56 (sp, 4H, CHMe_2 , $J_{\text{HH}} = 6.8$ Hz), 3.48 (m, 4H, OCH_2CH_2), 1.65 (s, 6H, NCMe), 1.48

^{*} The checkers performed the same reaction inside an N_2 filled glovebox equipped with a cold well. Similar yields were obtained as long as the glassware is oven dried and the N_2 atmosphere contains <1 ppm of O_2 and is virtually free of moisture

^{**} The checkers performed an alternative method to sonication by vigorously stirring the mixture for 5–6 hours in 80–100 mL of hexanes. Similar yields were obtained.

(m, 4H, OCH₂CH₂), 1.39 (d, 12H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz), 1.17 (d, 12H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz). ¹³C{¹H} NMR (benzene-*d*₆): δ 162.3 (NCMe), 143.3 (C_{ipso}), 143.3, 126.6, 124.2 (C₆H₃), 99.8 (CH), 28.6 (CHMe₂), 25.0, 24.7 (CHMe₂), 24.4 (Me).

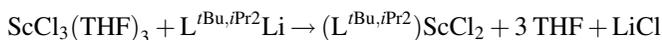
Properties

Complex (L^{Me,*i*Pr₂})ScCl₂(THF) is an off-white solid that is soluble in most organic solvents, such as diethyl ether, THF, hexanes (slightly), toluene, and bromobenzene; however, prolonged exposure to chlorinated solvents such as dichloromethane or chloroform results in decomposition. Although (L^{Me,*i*Pr₂})ScCl₂(THF) rapidly decomposes upon exposure to even trace air or moisture, samples can be stored indefinitely under an inert atmosphere.

Related Compounds

Complex (L^{Me,*i*Pr₂})ScCl₂(THF) can be alkylated by reaction with lithium or potassium reagents. With LiMe, the resulting complex retains one THF molecule (L^{Me,*i*Pr₂})ScMe₂(THF), but larger groups (e.g., LiCH₂EMe₃ (E = C, Si), KCH₂Ph) afford THF-free complexes.⁷ It is also possible to remove THF directly from (L^{Me,*i*Pr₂})ScCl₂(THF) via heating to 130°C under dynamic vacuum (10⁻⁴ Torr) for 18 h. The resultant chloride-bridged dimer, [(L^{Me,*i*Pr₂})ScCl₂]₂, is largely insoluble in alkane solvents, although reaction with LiMe to yield the methyl-bridged complex [(L^{Me,*i*Pr₂})ScMe₂]₂ proceeds in toluene.⁸

C. SCANDIUM 2,2,6,6-TETRAMETHYL-3,5-BIS-(2,6-DIISOPROPYLPHENYLIMIDO)HEPTYL DICHLORIDE, (L^{*t*Bu,*i*Pr₂})ScCl₂



Method A: A thick-walled round-bottomed pressure vessel (Fig. 1) equipped with a Teflon valve¹ is charged with [L^{*t*Bu,*i*Pr₂}Li]_x (11.1 g, 21.9 mmol) and ScCl₃(THF)₃ (9.38 g, 25.7 mmol) and evacuated.* Toluene (400 mL) is condensed into the vessel, which is then sealed and heated at 110°C for 3 days. It is necessary that the mixture be constantly stirred. Quiescent mixtures generally require an additional 3–4 days. During this time, the color changes from pale to deep yellow.** The

* The checkers performed the same reaction inside an N₂ filled glovebox equipped with a heating stir plate and obtained similar yields.

** Minute quantities of water (usually from inadequately dried ScCl₃(THF)₃) will cause a black or dark green color during early stages of the reaction. Such colors are generally supplanted by the usual deep yellow as time progresses. If dark colors are observed during (or persist throughout) the reaction, the normal workup protocol outlined above will still give the desired product, albeit in somewhat lower yields.



Figure 1. Heavy-walled reactor used in this procedure.

reaction mixture is transferred via cannula into a 500 mL round-bottomed flask, which is attached to a swivel-frit¹ apparatus. A hot filtration is performed to remove LiCl, and excess $\text{ScCl}_3(\text{THF})_3$, followed by removal of toluene under reduced pressure.* The bright yellow residue is sonicated for 10 min in hexanes (100 mL) and cooled to -78°C , and the slurry is filtered. The resultant yellow solid is dried under vacuum for 12 h to afford $(\text{L}^{\text{iBu},\text{iPr}_2})\text{ScCl}_2$ in 86% yield (11.7 g, 18.9 mmol).

Method B: The above method is used with the exception that the reaction mixture is heated at 180°C for approximately 30 min and $(\text{L}^{\text{iBu},\text{iPr}_2})\text{ScCl}_2$ is obtained in 68% yield.

Anal. Calcd. for $\text{C}_{35}\text{H}_{53}\text{N}_2\text{Cl}_2\text{Sc}$: C, 68.06; H, 8.65; N, 4.54. Found: C, 68.54; H, 7.98; N, 4.92. ^1H NMR (benzene- d_6): δ 7.05 (m, 6H, C_6H_3), 6.01 (s, 1H, CH), 3.10 (sp, 4H, CHMe_2 , $J_{\text{HH}} = 6.8$ Hz), 1.43 (d, 12H, CHMe_2 , $J_{\text{HH}} = 6.8$ Hz), 1.26 (d, 12H, CHMe_2 , $J_{\text{HH}} = 6.8$ Hz), 1.17 (s, 18H, NCCMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6): δ 174.3 (NCCMe_3), 142.8 (C_{ipso}), 141.1, 127.0, 124.3 (C_6H_3), 90.8 (CH), 44.7 (CMe_3), 32.3 (CMe_3), 29.9 (CHMe_2), 26.9, 24.4 (CHMe_2).

Properties

Complex $(\text{L}^{\text{iBu},\text{iPr}_2})\text{ScCl}_2$ is a pale yellow solid that is soluble in most organic solvents, such as diethyl ether, THF, hexanes (slightly), toluene, and bromobenzene. Unlike $(\text{L}^{\text{Me},\text{iPr}_2})\text{ScCl}_2(\text{THF})$, $(\text{L}^{\text{iBu},\text{iPr}_2})\text{ScCl}_2$ does not retain THF, although it does share a similar sensitivity toward air and moisture.

* The checkers performed the reaction inside an N_2 filled glovebox equipped with a cold well and filtered the product using an oven dried medium porosity filter frit. Similar yields were obtained.

Related Compounds

Complex $(L^{tBu,iPr2})ScCl_2$ can be dialkylated using a wide array of Grignard and lithium reagents.⁶ Substitution of only one chloride group can be accomplished by reaction with $LiCH_2SiMe_3$ at $-78^\circ C$ to afford $(L^{tBu,iPr2})ScCl(CH_2SiMe_3)$.⁷ Alternatively, it is possible to prepare $(L^{tBu,iPr2})ScCl(Me)$ by the ligand redistribution of $(L^{tBu,iPr2})ScCl_2$ and $(L^{tBu,iPr2})ScMe_2$. Upon reaction with methylalumoxane (MAO) or $B(C_6F_5)_3$, $(L^{tBu,iPr2})ScMe_2$ is an active ethylene polymerization catalyst.⁹ If activated with MAO, complex $(L^{tBu,iPr2})ScCl_2$ is also catalytically active; however, larger polydispersities and lower activity, in comparison to the dimethyl analogue, are observed.⁹

Acknowledgments

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