Synthetic and Mechanistic Studies of Organoscandium Compounds. Dimerization and Branching of Alkenes Catalyzed by Scandocene Hydrides.

Thesis by

Emilio E. Bunel

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To all my women :

Maria Jose, Paula and Susana

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ABSTRACT

Mixed-ring scandocene alkyl and hydride derivatives of structure $Cp^*CpSc(CH_3)(PMe_3)$, $Cp^*CpSc(\eta^1\text{-}\eta^5\text{-}C_5H_4)Cp^*Sc(H)$, $Cp^*(\eta^5\text{-}1,3,4\text{-}C_5Me_3H_2)Sc(CH_3)(PMe_3)$ and $Cp^*(\eta^5\text{-}1,3,4\text{-}C_5Me_3H_2)Sc(H)(PMe_3)$ were prepared ($Cp^* = \eta^5\text{-}C_5Me_5$, $Cp = \eta^5\text{-}C_5H_5$). Dimethylsilicon bridged scandocene alkyl and hydride derivatives $Me_2Si(\eta^5\text{-}C_5Me_4)_2ScCH(SiMe_3)_2$, $Me_2Si(\eta^5\text{-}C_5Me_4)_2Sc(H)(PMe_3)$, *meso*-$Me_2Si(\eta^5\text{-}t\text{-butyl}C_5H_3)_2ScCH_2SiMe_3$ and (*meso*-$Me_2Si(\eta^5\text{-}t\text{-butyl}C_5H_3)_2Sc(H))_2$ were also prepared. The activation energy for phosphine dissociation in $Cp^*CpSc(CH_3)(PMe_3)$ and $Cp^*(\eta^5\text{-}1,3,4\text{-}C_5Me_3H_2)Sc(H)(PMe_3)$ were measured. The crystal structures of $Me_2Si(\eta^5\text{-}C_5Me_4)_2ScCH(SiMe_3)_2$ and $Me_2Si(\eta^5\text{-}C_5Me_4)_2Sc(H)(PMe_3)$ were determined.

The hydride derivatives, $Me_2Si(\eta^5\text{-}C_5Me_4)_2Sc(H)(PMe_3)$ and (*meso*-$Me_2Si(\eta^5\text{-}t\text{-butyl}C_5H_3)_2Sc(H))_2$ catalyze the following carbon-carbon bond forming reactions: (1) The catalytic dimerization of α-olefins to head-to-tail dimers, (2) The catalytic cyclization of α,ω-diolefins to methylenecycloalkanes with ring sizes between 5 and 9 carbon atoms, (3) The catalytic formation of six-membered ring nitrogen and sulfur heterocycles by catalytic cyclization of bisallyl amines and bisallyl sulfides respectively and (4) The catalytic formation of the spiro hydrocarbons 2-methylene spiro[4.4] nonane and 2-methylene dispiro [4.1.4.2] tridecane by catalytic cyclization of 5-methylene-1,8-nonadiene and 5,8-dimethylene-1,11-dodecadiene.

(*meso*-$Me_2Si(\eta^5\text{-}t\text{-butyl}C_5H_3)_2Sc(H))_2$ catalyzes the ring opening reaction of methylenecyclopropane to butadiene and methylenecyclobutane to 1,4-pentadiene. Labelling experiments show that intramolecular olefin insertion in ω-alkenyl scandium complexes and β-alkyl elimination in cycloalkylmethyl scandium complexes is reversible when rings containing 3 or 4 carbon atoms are involved. The hydride derivative (*meso*-$Me_2Si(\eta^5\text{-}t\text{-butyl}C_5H_3)_2Sc(H))_2$ also catalyzes the isomerization of 1,4-pentadiene to isoprene and 2-methyl-1,4-pentadiene to 2,3-dimethylbutadiene and the isomerization of 3-methyl-1,4-pentadiene to 1,5-hexadiene, which is then cyclized to methylenecyclopentane.

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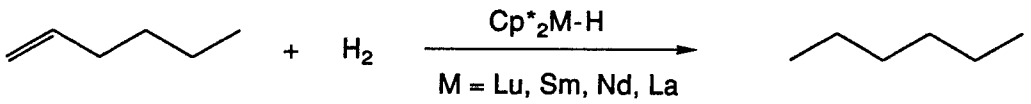
INTRODUCTION

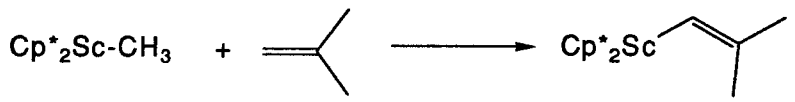
The formation of carbon-carbon bonds and the reverse process, the cleavage of carbon-carbon bonds, are crucial steps in the elaboration of hydrocarbons. The search for catalysts to perform both processes is an important field of investigation. A wide variety of organometallic compounds effect the formation of carbon-carbon bonds, but few have been reported to perform carbon-carbon bond breaking reactions.[1] Some of the most fascinating in this regard are organometallic derivatives of the lanthanides and related group 3 transition metals. Permethylmetallocene derivatives of these metals are of current interest because of their simple and interesting reactivity patterns toward small hydrocarbons. These metal complexes,[2] of general structure $Cp^*_2MR(L)$ ($Cp^* = \eta^5\text{-}C_5Me_5$; M = Sc, Y, La,...Lu; R = H, alkyl, aryl; L = two electron donor), with d^0 or d^0f^n metal centers and 14 or 16 electron counts are highly Lewis acidic, properties which greatly influence their ability to promote carbon-carbon bond forming or breaking processes for simple hydrocarbons. These derivatives are active as olefin polymerization catalysts (Equation 1) [3] and olefin hydrogenation catalysts (Equation 2).[4] They also react with the C-H bonds of arenes (Equation 3), olefins (Equation 4) and alkanes (Equation 5).[1a]

$$Cp^*_2LuCH_3 + n\ CH_2{=}CH_2 \longrightarrow Cp^*_2Lu\text{-}(CH_2\text{-}CH_2)_n\text{-}CH_3 \qquad \text{Eq. 1}$$



Eq. 2

$$Cp^*_2Sc\text{-}CH_3 + C_6H_6 \longrightarrow Cp^*_2Sc\text{-}C_6H_5 + CH_4 \qquad \text{Eq. 3}$$



Eq. 4

$$Cp^*_2Sc\text{-}CH_3 + {}^{13}CH_4 \longrightarrow Cp^*_2Sc\text{-}{}^{13}CH_3 + CH_4 \qquad \text{Eq. 5}$$

The olefin chemistry of the Cp^*_2M-H derivatives is rather simple. Olefin insertion across the M-H bond and subsequent insertion of a second equivalent of olefin into the resulting M-alkyl bond represent the initiation and propagation steps in the polymerization of ethylene. With these complexes, ethylene is the only olefin which has been successfully polymerized; propylene and higher α-olefins are only oligomerized and the catalyst lifetimes are rather limited.[3] The metal-alkyl bond can undergo β-hydrogen or β-alkyl elimination giving M-H or M-R with the simultaneous extrusion of olefin.[5]

Scandium is the smallest member of the group 3 transition metals and the lanthanides. Thus, the steric constraints imposed by the ligands should be most severe with scandium. It is the purpose of the present work to describe the olefin chemistry of modified cyclopentadienyl scandocene derivatives as an extension of the chemistry previously observed in the bis(pentamethylcyclopentadienyl) scandium system.[6]

The first chapter of this thesis presents both the synthesis and characterization of mixed ring scandocene hydrides and dimethylsilicon-bridged cyclopentadienyl scandocene hydrides. It is found that rather modest changes in the ligands around scandium cause major changes in chemical reactivity. For example, as described in the second chapter, α-olefins are catalytically dimerized in a head to tail fashion in contrast with the $[Cp^*_2Sc]$ system, which reacts only stoichiometrically with α-olefins to yield the alkenyl derivatives. Further applications of the α-olefin dimerization are found in the catalytic cyclization of α,ω-diolefins to methylenecycloalkanes as well as in the cyclization of bisallyl methyl amine and bisallyl sulfide to 3-methylene N-methyl piperidine and 3-methylene perhydro-thiane. The third chapter describes the carbon-carbon bond activation chemistry of these complexes exemplified in the isomerization of 1,4-pentadienes. 1,4-Pentadiene, 2-methyl-1,4-pentadiene and 3-methyl-1,4-pentadiene are catalytically converted to isoprene, 2,3-dimethylbutadiene and methylenecyclopentane respectively. The key steps in these transformations are reversible olefin insertion and β-alkyl elimination.

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2. (a) Thompson, M.E,; Bercaw, J.E. *Pure and Appl. Chem.* **1984**, *58*, 1. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P.N.; Schumann, H.; Marks, T.J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (c) Watson, P.L.; Herskovitz, T. Am. Chem. Symp. Series **1983**, *212*, 459.
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5. Watson, P.L.; Roe, D.C. *J. Am. Chem. Soc.* 1982, 104, 6471.
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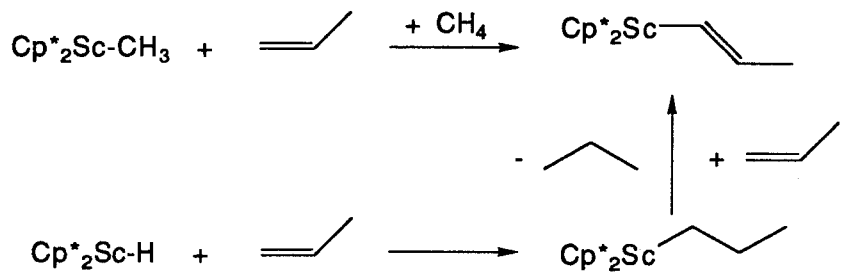
CHAPTER 1

THE SYNTHESIS AND CHARACTERIZATION OF SCANDIUM ALKYL AND HYDRIDE DERIVATIVES.

INTRODUCTION

The chemistry of Cp^*_2Sc-R (R = alkyl, aryl, H) is rich in stoichiometric reactions, but the catalytic activity towards small molecules such as α-olefins remains restricted essentially to ethylene polymerization and hydrogenation of some olefins.[1] Unfortunately, Cp^*_2Sc-R (R= H, alkyl) complexes do not react with α-olefins in the same way they do with ethylene. The reactivity of Cp^*_2Sc-R with α-olefins differs from that with ethylene in that only stoichiometric reactions (insertion of one molecule of α-olefin) have been observed in the case of scandium. The reason for the low reactivity toward insertion of more than one α-olefin is likely steric in origin. With more bulky olefins than ethylene, reaction at the vinylic C-H bond of the olefin, (σ-bond metathesis), is preferred over a second insertion giving scandium vinyl complexes and free alkane.[1b]



This pathway minimizes the steric constraints by orienting the alkyl substituents of the α-olefin away from the Cp* rings.

This chapter describes several new compounds designed to help elucidate the importance of steric effects in the bis(cyclopentadienyl)scandium system in relation to the insertion of α-olefins. To accomplish this goal, several $Cp^*Cp'ScR(PMe_3)$ ($Cp' = \eta^5$-$C_5H_5 \equiv Cp$, η^5-1,3,4-$Me_3C_5H_2 \equiv Cp^0$), $Me_2SiCp'_2ScR$ ($Cp' = \eta^5$-C_5Me_4, η^5-*t*-butylC_5H_3) and $Me_2SiCp'Cp''ScR$ ($Cp' = \eta^5$-C_5Me_4, $Cp'' = \eta^5$-*t*-butylC_5H_3, (-)-2-methylbutyl–η^5-C_5H_3, (+)-menthyl–η^5-C_5H_3) derivatives were synthesized.

RESULTS AND DISCUSSION

Synthesis of Mixed Rings Scandocene Derivatives

To decrease the steric hindrance at the scandium center in the [Cp^*_2Sc] system, a cyclopentadienyl ring less sterically demanding has been replaced for one pentamethylcyclopentadienyl ring. We found that $Sc(acac)_3$ (acac = acetylacetonate) reacts with $Cp^*MgCl \cdot THF$ in toluene giving cleanly $Cp^*Sc(acac)_2$ (**1**) as a yellow crystalline, air stable material, in good yield. Reaction of **1** with aluminum trichloride provides $(Cp^*ScCl_2)_n$ (**2**), a convenient starting material for the synthesis of mixed-ring scandocenes. **2** is completely insoluble in toluene and is easily isolated from the reaction mixture. The ^1H NMR spectrum in THF-d_8 shows only a singlet at 2.07 ppm, assigned to the Cp* ring.

$$Sc(acac)_3 + Cp^*MgCl\text{-}THF \xrightarrow{\text{Toluene, } 25^0C} Cp^*Sc(acac)_2 + (acac)MgCl$$

1

$$Cp^*Sc(acac)_2 + 2\ AlCl_3 \xrightarrow{\text{Toluene, } 25^0C} 1/n(Cp^*ScCl_2)_n + Cl_2Al(acac)$$

2

$$Cp^*ScCl_2 + \dot{Cp}Li \xrightarrow{\text{Toluene, } 80^0C} Cp^*\dot{Cp}ScCl + LiCl$$

3 : $\dot{Cp} = Cp^*$
4 : $\dot{Cp} = Cp$
5 : $\dot{Cp} = 1,3,4\text{-}Me_3C_5H_2$

Reaction of **2** with one equivalent of Cp*Li, CpLi or Cp^0Li cleanly yields Cp^*_2ScCl (**3**), Cp*CpScCl (**4**) or Cp^*Cp^0ScCl(**5**) respectively. Cp^*_2ScCl had been previously reported.[1b] **4** is sparingly soluble in benzene suggesting a dimeric structure similar to that reported for $(Cp_2ScCl)_2$.[2] The ^1H NMR spectrum (400 MHz) at room temperature shows two broad resonances: one at 2.1 ppm ($\nu_{1/2}$ = 3 Hz), assigned to the Cp* ring, and another at 6.4 ppm ($\nu_{1/2}$

= 7.5 Hz), assigned to the Cp ring. When the sample is heated to 80°C, the ^{1}H NMR (400 MHz) spectrum shows sharp singlets at 2.0 and 6.3 ppm. These NMR data suggest that an equilibrium between monomer and dimer exists. Compound **5** is quite similar to **4** in regard to solubility, and is probably a dimer. Low solubility of **4** and **5** in benzene precluded measurement of the molecular weight.

Reaction of **4** or **5** with methyllithium in diethyl ether in the presence of PMe_3, followed by extraction with petroleum ether cleanly gives $Cp^*Cp'Sc(CH_3)(PMe_3)$ (**6**) or $Cp^*Cp^0Sc(CH_3)(PMe_3)$ (**7**). Attempts to generate the methyl complexes in the absence of PMe_3 gave only intractable materials.

$$Cp^*Cp'ScCl + CH_3Li + PMe_3 \xrightarrow{Et_2O} Cp^*Cp'Sc(CH_3)(PMe_3) + LiCl$$

6 : $Cp' = Cp$
7 : $Cp' = 1,3,4\text{-}Me_3C_5H_2$

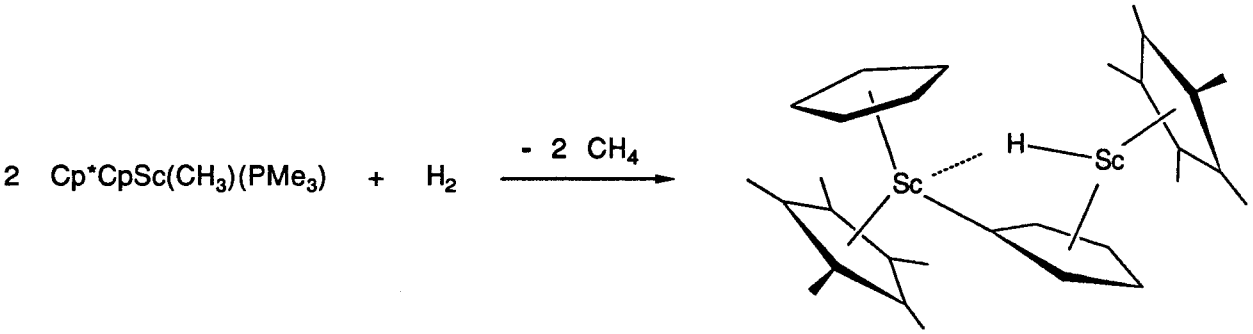
^{1}H NMR spectra (25°C, 400 MHz, C_6D_6) of both **6** and **7** show the methyl protons as singlets. This lack of coupling of the hydrogens of the methyl groups to the phosphorus of the PMe_3 suggests a rapid equilibrium between phosphine-complexed and uncomplexed forms. In the low temperature ^{1}H NMR (400 MHz, -80°C, C_7D_8) spectrum of **6** the methyl group (-0.6 ppm, J_{HP} = 2.9 Hz) appears as a doublet due to splitting by the phosphorus.

$$Cp^*Cp'Sc(CH_3)(PMe_3) \rightleftharpoons Cp^*Cp'Sc\text{-}CH_3 + PMe_3$$

Loss of coupling of the methyl group to the phosphine occurs at -70°C. At -80° C, the spectrum of **7** shows one singlet at 2.01 ppm assigned to the Cp* ring and three singlets at 1.73, 1.86, and 2.33 ppm assigned to the three different methyl groups of the Cp^0 ring. The hydrogens of the Cp^0 ring are coupled to each other (J = 2.3 Hz) and one set is coupled to the phosphorus of the phosphine. Upon irradiation of the non-phosphorus coupled signal the other signal collapses to a doublet (J_{HP} = 6 Hz). Coalescence of the two hydrogens of the Cp^0 ring occurs at -29°C,

yielding a rate constant for phosphine exchange of $k_{(-28\,^\circ C)} = 218\ sec^{-1}$ and an activation energy of $\Delta G^{\ddagger} = 11.5\ kcal\text{-}mol^{-1}$.

Hydrogenolysis of alkyl complexes Cp*CpSc(CH_3)(PMe_3) (**6**) and Cp*Cp^{0}Sc(CH_3)(PMe_3) (**7**) provides a convenient entry to hydride complexes. Hydrogenolysis of Cp*CpSc(CH_3)(PMe_3) gives Cp*CpSc-(η^1-η^5-C_5H_4)Cp*Sc-H (**8**), rather than the expected product.



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The ^{1}H NMR (400 MHz, C_6D_6) spectrum shows two different Cp* rings at 1.93 and 2.17 ppm, a singlet from one Cp ring at 5.93 ppm, and four multiplets from the η^1,η^5-C_5H_4 ring centered at 6.13, 6.26, 6.38, and 6.63 ppm. There is no evidence in the ^{1}H NMR spectrum (400 MHz, C_7D_8) for the hydride resonance even at -80°C. Excessive broadening of the hydride resonance is attributed to the quadrupole moment of ^{45}Sc. The formation of product **8** can be explained according to Scheme 1.

The reversibility of the last step can be observed in the reaction of **6** with D_2; in this case the product isolated is Cp* (η^5-C_5D_5)Sc-(η^1-η^5-C_5D_4)Cp*Sc-D. Hydrogenolysis of **6** in THF-d_8 (as monitored by ^{1}H NMR) yields Cp*CpSc(H)(THF), analogous to the previously reported Cp*$_2$Sc(H)(THF) complex.[1b] The ^{1}H NMR spectrum of Cp*CpSc(H)(THF) shows a singlet at 2.0 ppm assignable to the Cp* ring and another singlet at 5.95 ppm assignable to the Cp ring. If the overpressure of H_2 is eliminated, Cp*CpSc(H)(THF) cleanly decomposes to **8**. A compound similar to **8** was recently reported in the thermolysis of Cp*$_2$Y(H)(THF).[3]

Hydrogenolysis of **7** gave the expected product, $Cp^*Cp^0Sc(H)(PMe_3)$ (**9**). The ^1H NMR spectrum (-80°C, 400 MHz, C_7D_8) of **9** shows a similar pattern as for **7**. There is a broad peak ($\nu_{1/2}$ = 33.7 Hz) at 4.55 ppm that is assigned to the hydride, broadened due to the quadruple moment of scandium. Coalescence was obtained for the hydrogens of the Cp^0 ring at -29°C yielding $k_{(-29°C)} = 90.6\ sec^{-1}$ and $\Delta G^{\ddagger} = 12\ kcal\text{-}mol^{-1}$.

$$Cp^*Cp^0Sc(CH_3)(PMe_3) + H_2 \longrightarrow Cp^*Cp^0Sc(CH_3)(PMe_3) + CH_4$$

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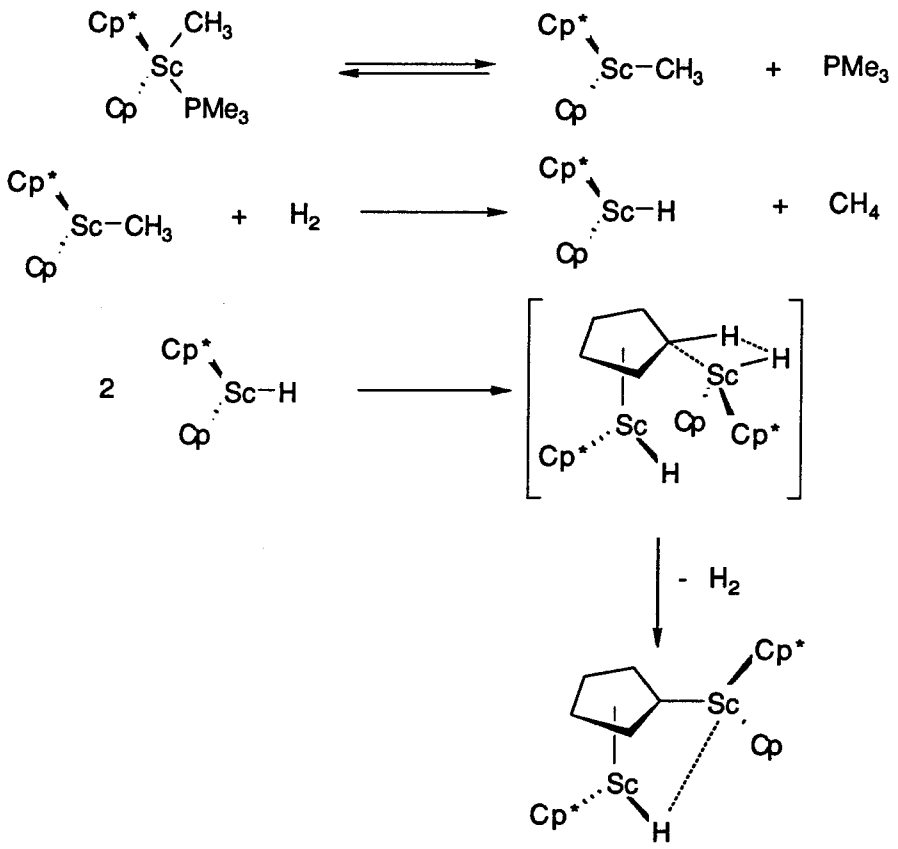
Comparison of the rates of phosphine exchange for **7** and **9** shows that this process is faster for the methyl derivative. This behavior can be explained by steric arguments since the phosphine would presumably have more room to bind to the hydride derivative than to the methyl derivative.

Scheme 1



Synthesis of Scandocene Derivatives with $SiMe_2$ Bridging the Cyclopentadienyl Rings.

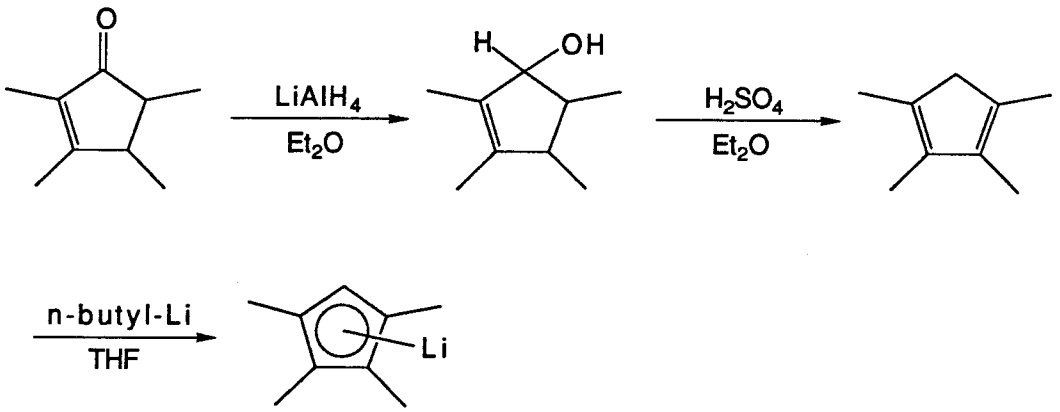
Rather than altering ring substituents, another way to decrease the steric hindrance at the scandium center is to "tie" the rings together with a dimethylsilyl bridge. This approach was developed first by Marks[4] in an effort to obtain more reactive uranium and thorium derivatives (relative to the analogous $Cp^*_2MR_2$, M = Th, U). This linkage produces a smaller ring centroid-metal-ring centroid angle, thus opening the coordination sphere of the metal center.

The $Me_2Si(C_5Me_4H_2)_2$ ligand is prepared as shown in Scheme 2. The key starting material for the synthesis of this ligand is 1,2,3,4-tetramethylcyclopentadiene. Reduction of the commercially available 2,3,4,5-tetramethyl-2-cyclopentenone with $LiAlH_4$ provides 2,3,4,5-tetramethyl-2-cyclopentenol in excellent yield; dehydration of the alcohol provides the desired 1,2,3,4-tetramethylcyclopentadiene in moderate yield. A seemingly trivial, but important modification was found to be the isolation of the lithium salt of 1,2,3,4-tetramethylcyclopentadiene prior to the reaction with dichlorodimethylsilane. $Me_2Si(C_5Me_4H_2)_2$ is isolated as a non-volatile oil which requires no further purification. The dilithium salt $Me_2Si(C_5Me_4)_2Li_2$ (**10**) is prepared *via* deprotonation of the ligand with *n*-butyllithium.

Similarly, $Me_2Si(t\text{-butyl}C_5H_4)_2$ is prepared according to the following "one-pot" synthesis (Scheme 3). Treatment of *t*-butylcyclopentadienyl lithium with dichlorodimethylsilane provides $Me_2Si(t\text{-butyl}CpH)_2$, which is isolated as an oil and converted without further purification to the dilithium salt, $Me_2Si(t\text{-butyl}Cp)_2Li_2$ (**11**), by reaction with *n*-butyllithium. Metallocenes derived from **11** could conceiveably provide a mixture of *meso* and racemic isomers depending on the relative positions of the *t*-butyl groups in the metallocene. Curiously, only the meso compound is formed (*vide infra*).

Treatment of tetramethylcyclopentadienyllithium with dichlorodimethylsilane in a 1:1 molar ratio provides $(C_5Me_4H)SiMe_2Cl$ (**12**) in high yield. This compound is isolated as an oil

Scheme 2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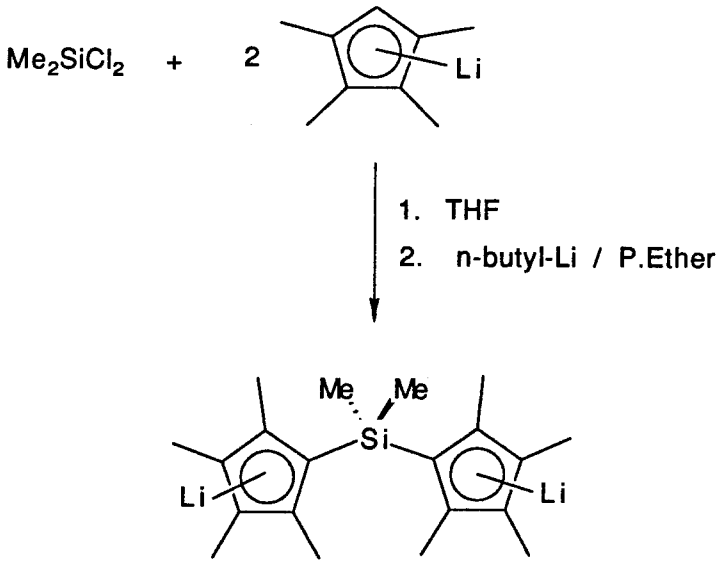
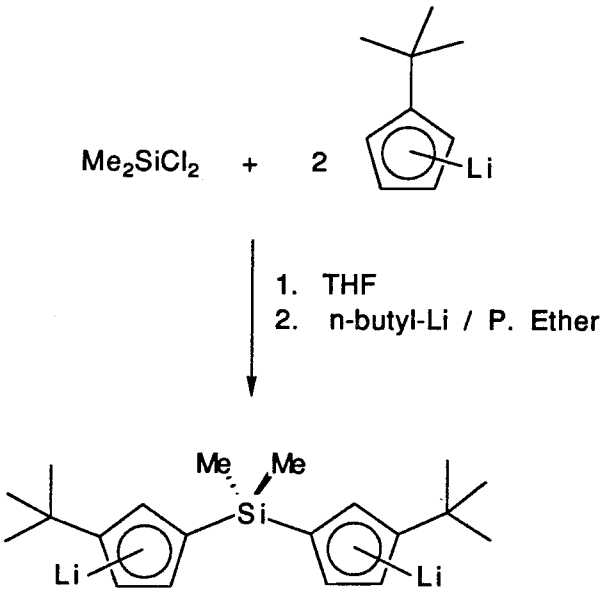
Et2O
H
OH
H2SO4
Et2O
n-butyl-Li
THF
Li


Me2SiCl2
+
2
Li
1. THF
2. n-butyl-Li / P.Ether
Me
Me
Si
Li
Li

14

which solidifies at -40°C. From $(C_5Me_4H)SiMe_2Cl$ as the starting material, another variety of silicon bridged ligands bearing only one tetramethylcyclopentadienyl ring is obtained (Scheme 4). Treatment of **12** with *t*-butylC_5H_4Li, (-)-2-methyl butylC_5H_4Li or (+)-menthylC_5H_4Li provides respectively $Me_2Si(C_5Me_4H)$(*t*-butylC_5H_4), $Me_2Si(C_5Me_4H)$((-)-2-methylbutylC_5H_4), or $Me_2Si(C_5Me_4H)$((+)-menthylC_5H_4) which were converted to their respective dilithium salts *via* deprotonation with *n*-butyllithium. The (-)-2-methylbutyl and (+)-menthyl groups were used as ancillary ligands to induce the preferential formation of one optically active metallocene.

Scheme 3



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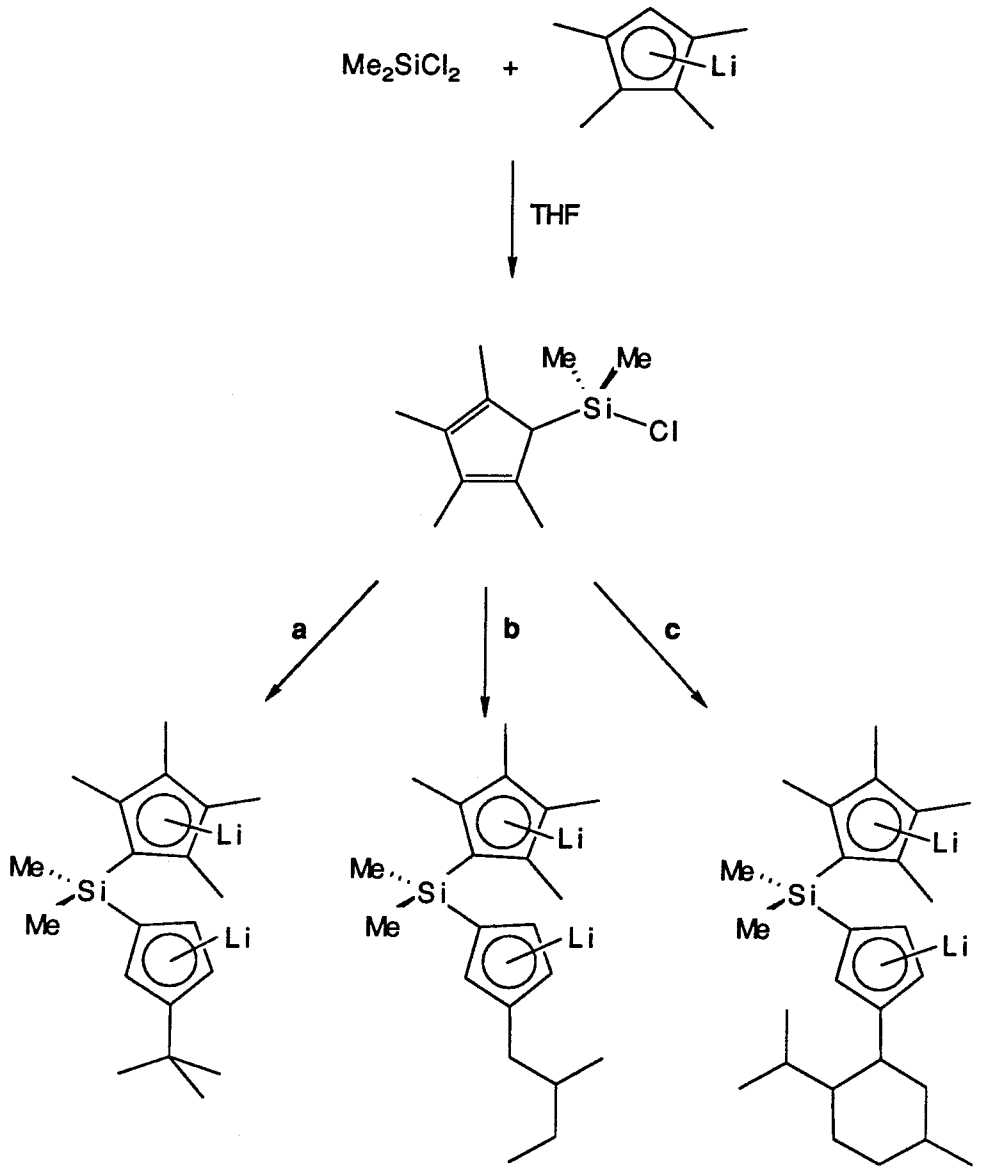
Scheme 4

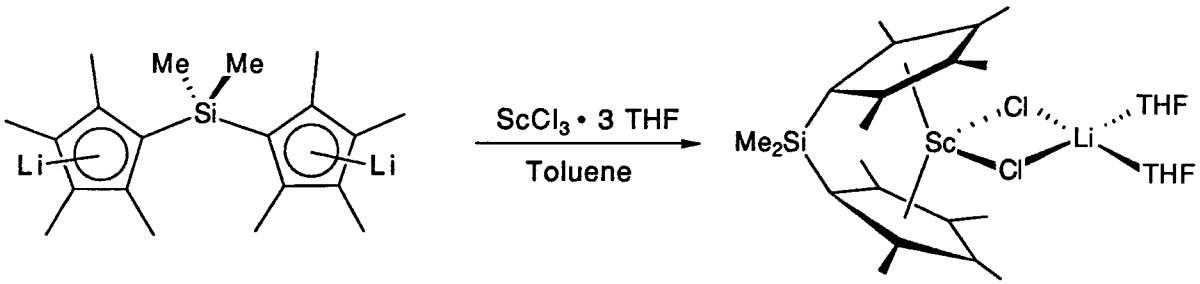


a : 1. t-butylCpLi / THF
2. n-butyl-Li / Et_2O

b : 1. (-)-2-methylbutylCpLi / THF
2. n-butyl-Li / Et_2O

c : 1. (+)-menthylCpLi / THF
2. n-butyl-Li / Et_2O

Scheme 5



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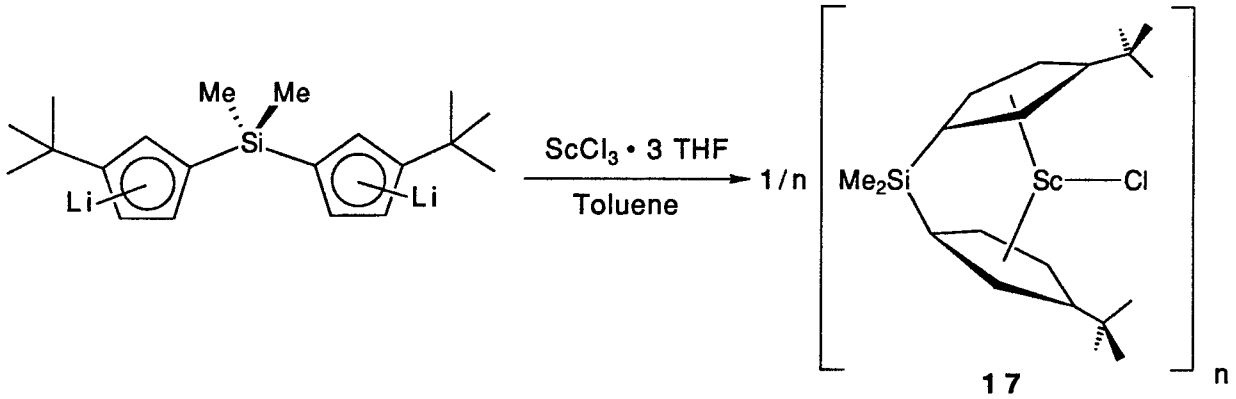

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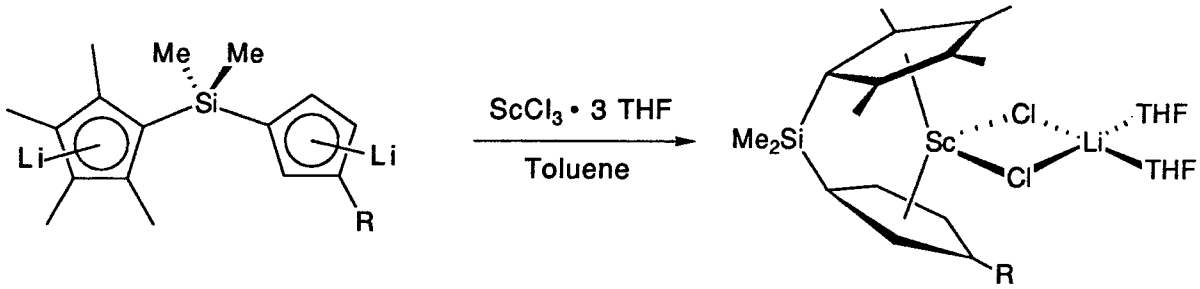
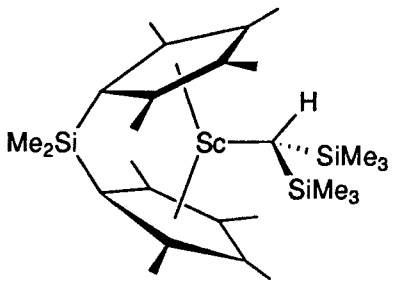


18 : R = t-butyl
19 : R = (-)-2-methylbutyl
20 : R = (+)-menthyl

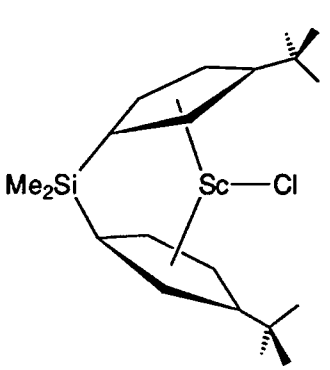
The silicon-bridged metallocenes, **16-20**, shown in Scheme 5 are obtained by treating $ScCl_3 \cdot 3THF$ with the dilithium salts of the ligands. Metathesis of the bridged scandocene chlorides with bulky lithium alkyls such as Me_3SiCH_2Li or $(Me_3Si)_2CHLi$ yields the product without coordinated solvent (i.e. tetrahydrofuran or diethylether).

$Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$ (**21**) is obtained as a bright yellow, highly crystalline material from the reaction of $Me_2Si(C_5Me_4)_2ScCl \cdot LiCl \cdot (Et_2O)_2$ (**16**) with $(Me_3Si)_2CHLi$. The ^1H NMR spectrum (400 MHz) at room temperature shows four singlets assigned to the methyl groups of the C_5Me_4 ring, suggesting that rotation around the scandium-carbon σ bond is restricted. The spectrum does not change upon heating the sample to 100°C, which implies a large barrier ($\geq$ 20 kcal-mol^{-1}).

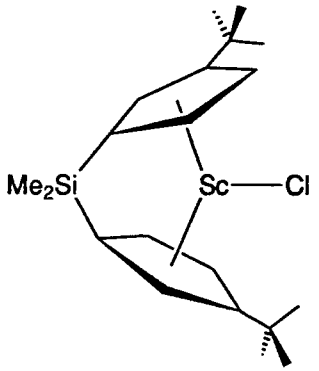


21

Treatment of $ScCl_3 \cdot 3THF$ with $Me_2Si(t\text{-butyl}C_5H_3)_2Li_2$ affords *meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2ScCl$ (**17**). The low solubility of **17** in benzene precludes the determination of the molecular weight. The ^1H NMR spectrum in CD_2Cl_2 shows one singlet at 1.22 ppm assigned to the *t*-butyl groups, two singlets at 0.54 and 0.87 ppm assigned to the methyl groups of the bridge and three triplets at 6.33, 6.54 and 6.70 ppm assigned to the hydrogens of the equivalent Cp rings. These NMR data suggest that of the two possible isomers,**17a** and **17b**, only **17a** actually forms. In structure **17a**, the methyl groups of the silicon bridge are equivalent, whereas in structure **17b** they are inequivalent. The NMR spectra for all the [$Me_2Si(t\text{-butyl}C_5H_3)_2Sc$] derivatives are similar. Metathesis of *meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2ScCl$ with Me_3SiCH_2Li cleanly gives *meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2Sc\text{-}CH_2SiMe_3$ (**22**).



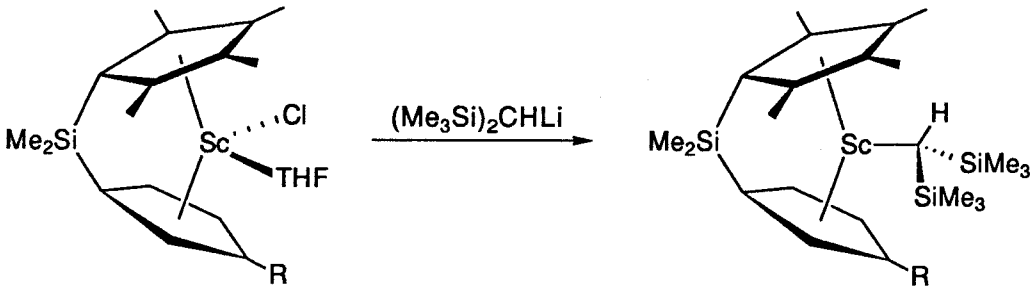
17a



17b

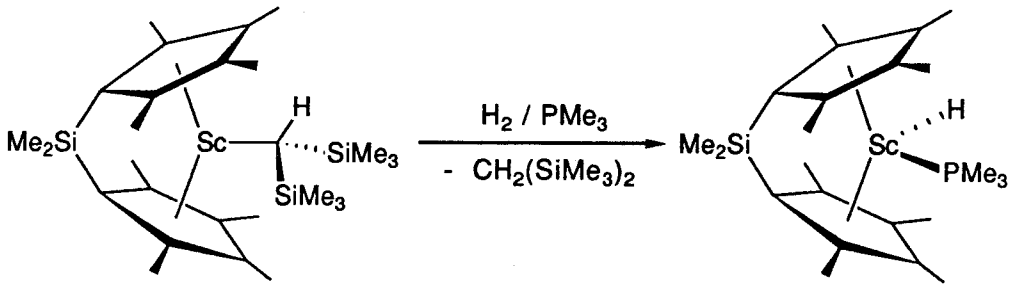
For all the other scandocene chlorides, treatment with $(Me_3Si)_2CHLi$ provides the Sc-$CH(SiMe_3)_2$ derivatives as shown in Scheme 6. The presence of optically active groups, (-)-2-methylbutyl in **14** and (+)-menthyl in **15** could lead to the preferential formation of one of two possible diastereomers. The ^1H NMR spectrum of **23** shows that the $SiMe_3$ groups in the Sc-$CH(SiMe_3)_2$ moiety are inequivalent. There are 4 resonances due to the $SiMe_3$ groups in the case of **24** and **25**, two of them per diastereomer. Integration of these resonances provides a simple way to determine the enantiomeric excess. The diastereomers of **24** are formed in equal proportion, but in the case of **25** there is a slight excess of one isomer (8 % ee).

Scheme 6



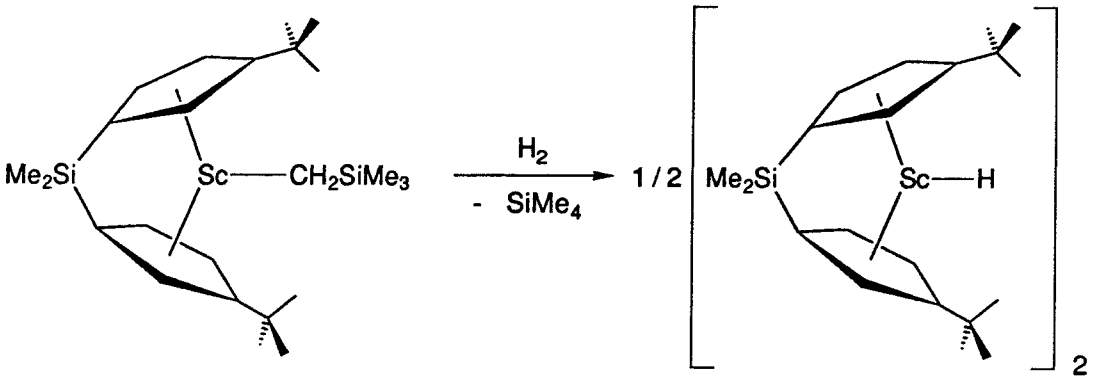
23 : R = t-butyl
24 : R = (-)-2-methylbutyl
25 : R = (+)-menthyl

The bulky alkyl derivative $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$ reacts with dihydrogen in petroleum ether to yield $(Me_2Si(C_5Me_4)_2ScH)_x$ as a yellow precipitate. Unfortunately, $(Me_2Si(C_5Me_4)_2ScH)_x$ decomposes in tetrahydrofuran or benzene solution, precluding the observation of its NMR spectrum. However, when the hydrogenation is performed in the presence of one equivalent of trimethylphosphine, $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$ (**26**) may be isolated. The X-ray structure of **26** (*vide infra*) confirms the structure in the solid state.



26

Reaction of *meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2Sc\text{-}CH_2SiMe_3$ with dihydrogen in petroleum ether gives the hydride, *meso*-$(Me_2Si(t\text{-butyl}C_5H_3)_2Sc\text{-}H)_2$ (**27**) in good yield. Its molecular weight, as determined by ebulliometry, indicates a dimeric structure for **27**. The ^1H NMR spectrum in toluene-d_8 shows the same pattern as that for the alkyl derivative **22**: one singlet for the *t*-butyl group at 1.21 ppm, two singlets at 0.82 and 0.21 ppm due to the dimethylsilicon bridge, and three triplets centered at 6.27, 6.67 and 7.33 ppm assigned to hydrogens of the cyclopentadienyl ring. The hydride proton is not observed at temperatures between 25°C and -80°C. Extreme broadening due to the bridging of the hydrogen between two quadrupolar ^{45}Sc nuclei may explain this. However, when one equivalent of trimethylphosphine is added, a broad peak centered at 4.68 ppm appears in the ^1H NMR spectrum which is assigned to the hydride proton.



27

Structure Determination of $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$

In order to define the distortion produced by a bridge in the biscyclopentadienyl scandocene system, the X-ray structure of **21** was determined. Crystals were grown by slowly cooling a saturated solution of **21** in toluene from 100°C to room temperature. The compound crystallizes in space group # 14 ($P2_1/c$) with a = 17.151(4) Å; b = 9.466(3) Å; c = 18.123(4) Å; β = 90.14°. A perspective view of compound **14** and the atom labelling scheme are given in Figure 1 and 2 respectively. Selected bond distances and angles are summarized in Table 2.

The scandium center adopts a relatively distorted η^5-coordination of the cyclopentadienyl ring as is reflected in different Sc-C_{ring} distances: C1-Sc = 2.447(2) Å, C2-Sc = 2.498(3) Å, C3-Sc = 2.609(3) Å. This distortion is observed in the difference between the ring centroid-Sc-ring centroid angle (129.9(1)°) and the angle between the normals to the rings (117.2(2)°). The ring centroid-Sc-ring centroid angle (129.9(1)°) is contracted 14.7° relative to that in the structure of $Cp^*_2ScCH_3$.[1b] Although $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$ lies in a general four-fold position in $P2_1/c$, two nearly perfect mirror planes pass through Si1 (joining the two C_5Me_4 rings) and Sc. One of these planes contains Si2, Si3, C10 and C20; the other plane is perpendicular to it. The C27 shows essentially sp^2 hybridization, since the angles about this carbon (Sc-C27-Si2, Sc-C27-Si3 and Si2-C27-Si3) are all approximately 120°. The peaks in the electron density map indicated that the electron density of the hydrogen on C27 was split equally above and below the plane. This geometry arises from two causes: the three electropositive neighbors of C27 encourage maximum p-character in the bonds to them, and the bulky trimethylsilyl groups, which are forced for steric reasons to be in the plane bisecting the C_5Me_4 rings, require that the geometry about C27 be nearly planar and thus that the carbon atom adopt sp^2 hybridization. An almost pure p orbital remains to bond the hydrogen atom. Two of the trimethylsilyl groups are in the Sc-Si2-Si3 plane. One, C25, is 3.684(4) Å from the scandium atom; the other, C21, is 3.490(4) Å away. The hydrogens atoms on C25 are arranged so the closest Sc···H-C25 approach is 3.460(5) Å. In contrast on C21 one of the three hydrogen atoms approaches Sc with a Sc···H distance 2.832(7)

Å. This asymmetry about the pseudo-mirror plane in the molecule is not enough, however, to lock C27 into a single position; it appears to be equally above and below the plane. In comparison with the structure of $Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2$ this implies some kind of long range Sc····H····$C(SiMe_3)_2$ interaction rather than the Nd····CH_3····$SiMe_2CHSiMe_3$ interaction observed by Marks.[5] In $Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2$ the distortion of the hydrogens on the analogous carbon does not minimize any particular Nd····H distance; rather it is 2.862 Å away from Nd, which suggests a two-electron- bridging alkyl type of bonding. In contrast C21 and C25 in the Sc structure are extremely far from the metal center, 3.490 Å and 3.684 Å respectively.

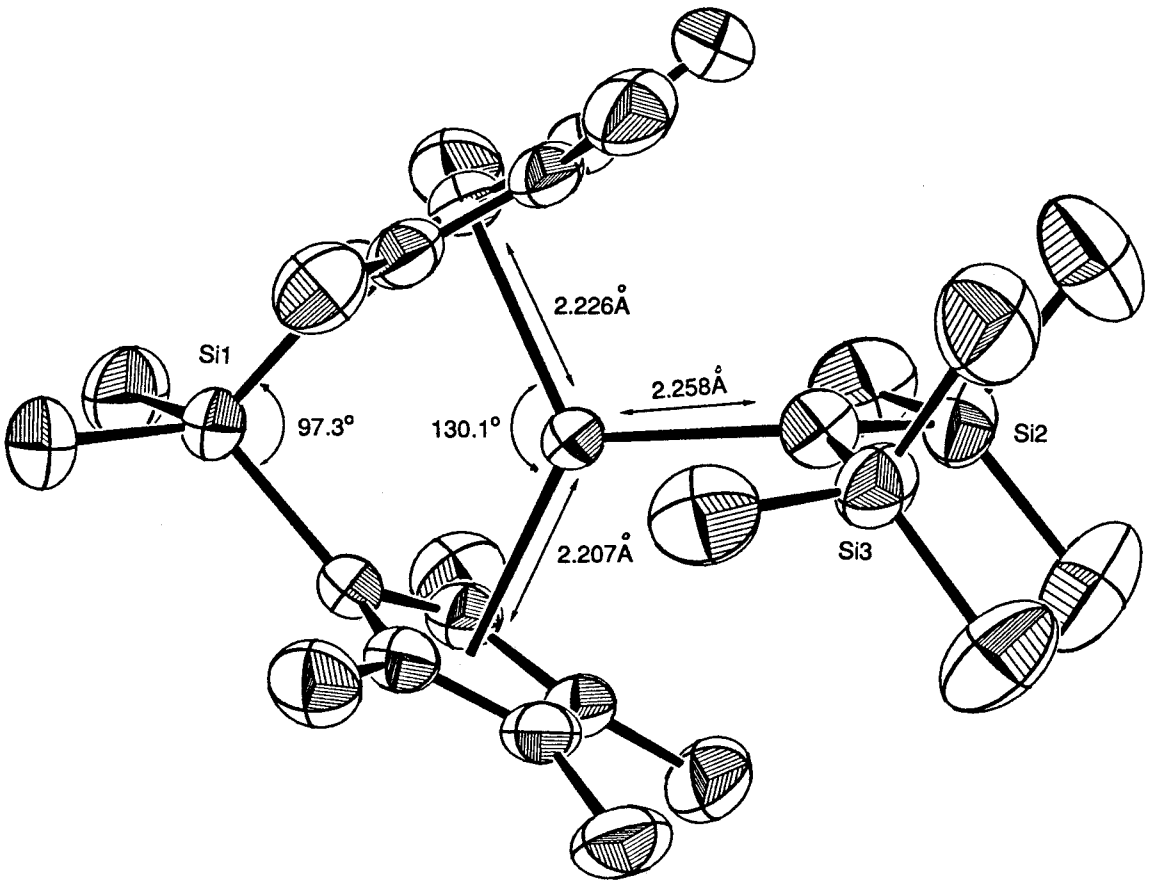


Figure 1: Molecular Structure of $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$.

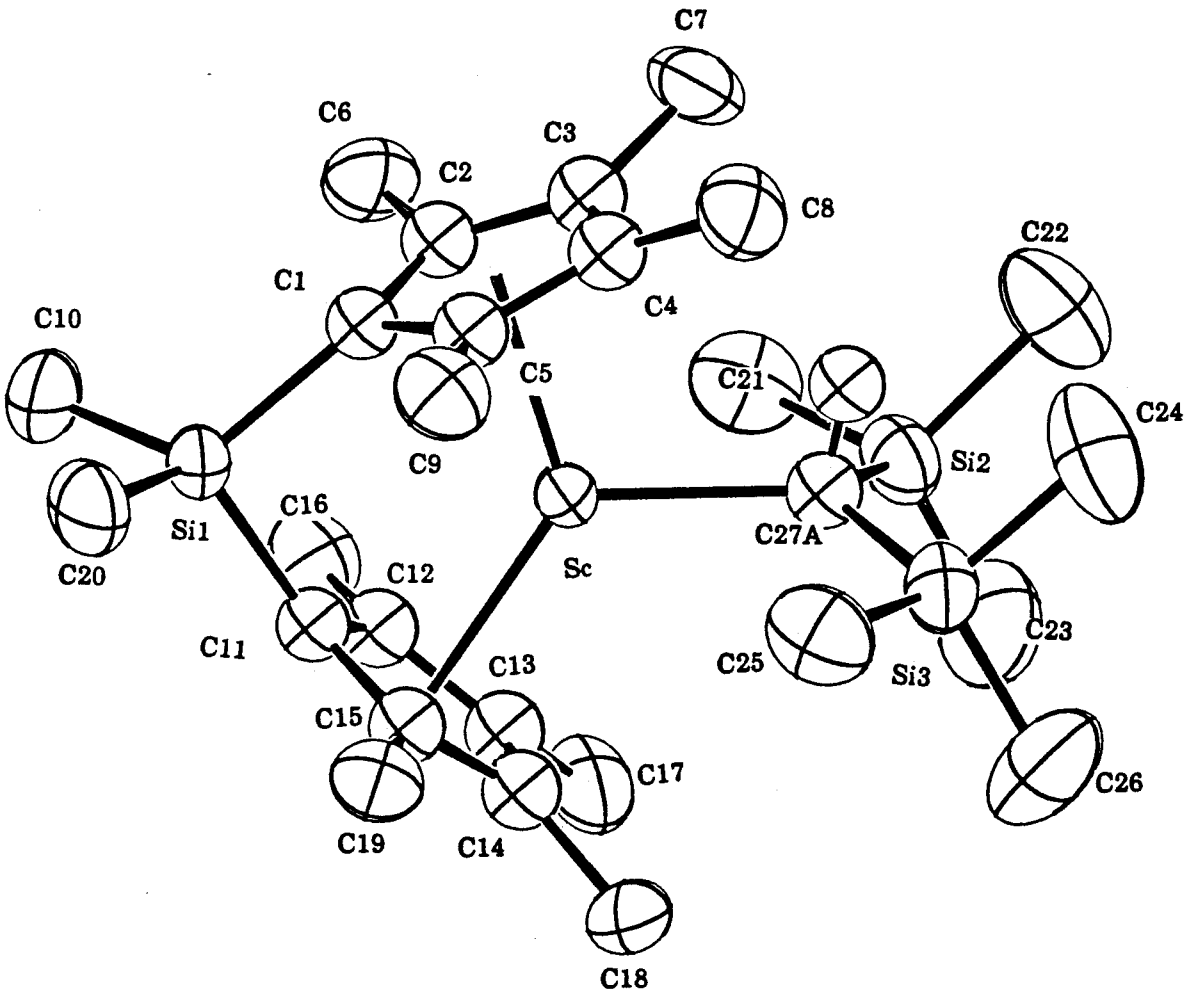


Figure 2: The atomic labeling for $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$.

Table 1: Crystal Data for $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$

Formula : $ScSi_3C_{27}H_{49}$	Formula weight : 502.91
Space group : $P2_1/c$(#14)	Temperature : 22°C
a = 17.151(6) Å	
b = 9.466(3) Å	β = 90.14(1) °
c = 18.123(7) Å	
V = 2942(3) $Å^3$	$\lambda MoK\alpha$ = 0.71073 Å
μ = 3.87 cm^{-1}	ρ = 1.135 g cm^{-3}
Crystal size 0.68x0.39x0.41 mm	μr_{max} = 0.17

Table 2: Bond Lengths (Å) and Angles (°) for $Me_2Si(C_5Me_5)_2ScCH(SiMe_3)_2$

Atoms	Distance	Atoms	Distance
Sc-C27A	2.270(2)	C3-C7	1.505(4)
Sc-C27B	2.272(7)	C4-C5	1.414(4)
Sc-Cp*1	2.226	C4-C8	1.505(4)
Sc-Cp*2	2.221	C5-C9	1.510(4)
Si1-C1	1.877(3)	C11-C12	1.439(4)
Si1-C10	1.869(3)	C11-C15	1.445(4)
Si1-C11	1.870(4)	C12-C13	1.410(4)
Si1-C20	1.870(4)	C12-C16	1.501(4)
Si2-C21	1.882(4)	C13-C14	1.404(4)
Si2-C22	1.867(4)	C13-C17	1.505(4)
Si2-C23	1.875(5)	C14-C15	1.414(4)
Si2-C27A	1.855(7)	C14-C18	1.492(4)
Si2-C27B	1.823(7)	C15-C19	1.504(4)
Si3-C24	1.885(5)	C-C_{ring} ave	1.420(16)
Si3-C25	1.881(4)	C_{ring} -CH_3 ave	1.505(7)
Si3-C26	1.873(4)	Sc-C1	2.447(2)
Si3-C27A	1.816(7)	Sc-C2	2.498(2)
Si3-C27b	1.862(7)	Sc-C3	2.609(3)
C27A-C27B	0.452(10)	Sc-C4	2.607(3)
C1-C2	1.429(4)	Sc-C5	2.489(3)
C1-C5	1.433(4)	Sc-C11	2.460(3)
C2-C3	1.412(4)	Sc-C12	2.507(3)
C2-C6	1.515(4)	Sc-C13	2.601(3)
C3-C4	1.397(4)	Sc-C14	2.558(3)
Sc-C15	2.486		

Atom	Atom	Angle	
Cp*1	Sc	Cp*2	129.9(1)
Cp*1	Sc	C27A	120.2(2)
Cp*2	Sc	C27B	109.8(2)
Cp*1	Sc	C27B	108.((2)
Cp*2	Sc	C27B	121.2(2)
C1	Si1	C11	97.2(1)
Cp*1	C1	Si1	161.5(2)
Cp*2	C11	Si1	160.0(3)
Sc	C27A	Si2	114.7(3)
Sc	C27B	Si2	116.0(3)
Sc	C27A	Si3	121.8(4)
Sc	C27B	Si3	119.5(3)
Si2	C27A	Si3	120.5(4)
Si2	C27B	Si3	119.7(2)
angle between normals to Cp*1 and Cp*2			117.0(2)

Table 3: Final Parameters X 10^4 for $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$

Atom	X	Y	Z	U_{eq}
Sc	7271(.3)	4783(.5)	3846(.3)	375(1)
Si1	5928(.4)	2736(.8)	4519(.5)	474(2)
Si2	8914(.5)	69.31(.9)	3960(.5)	591(2)
Si3	8200(.5)	6562(.9)	2346(.5)	593(2)
C1	5957(1)	4696(3)	4368(1)	409(6)
C2	5864(1)	5385(3)	3671(2)	449(6)
C3	6208(2)	6738(3)	3712(2)	489(7)
C4	6523(2)	6916(3)	4417(2)	475(7)
C5	6379(1)	5669(3)	4824(1)	449(6)
C6	5367(2)	4916(3)	3024(2)	669(8)
C7	6133(2)	7889(3)	3144(2)	727(9)
C8	6854(2)	8273(3)	4717(2)	718(9)
C9	6564(2)	5516(3)	5635(2)	650(8)
C10	5780(2)	2209(3)	5503(2)	748(9)
C11	6915(1)	2329(2)	4140(2)	432(6)
C12	7639(2)	2570(3)	4522(2)	461(6)
C13	8245(2)	2698(3)	4003(2)	505(7)
C14	7923(2)	2558(3)	3294(2)	509(7)
C15	7111(2)	2340(3)	3365(2)	476(7)
C16	7790(2)	2455(3)	5336(2)	671(8)
C17	9103(2)	2761(3)	4176(2)	723(9)
C18	8383(2)	2436(3)	2599(2)	748(9)
C19	6591(2)	1963(3)	2725(2)	670(8)
C20	5122(2)	1777(3)	4036(2)	784(10)
C21	8729(2)	6309(4)	4930(2)	809(10)
C22	9934(2)	6424(6)	3720(2)	1068(14)
C23	8932(3)	8909(4)	4017(3)	1179(15)
C24	9106(2)	5913(5)	1866(3)	1080(13)
C25	7354(2)	5682(4)	1870(2)	868(11)
C26	8145(3)	8491(4)	2121(2)	1066(13)
C27A	8250(4)	6018(8)	3306(4)	B = 4.0(2)
C27B	8106(4)	6401(7)	3366(4)	B = 3.6(1)

Structure Determination of $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$

Crystals of $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$ were grown by slowly cooling a saturated solution of **26** in toluene from 100°C to room temperature. The compound crystallizes in space group $P2_1/c$(#14), with *a* = 9.052(2) Å, b = 28.717(2) Å, c = 10.345(1) Å, β = 115.56(1)°. A perspective view of $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$ and the atom labelling scheme are given in Figure 3 and 4 respectively. Selected bond distances and angles are summarized in Tables 5 and 6.

The scandium-hydrogen distance, 1.87(3) Å, is somewhat longer than the sum of the covalent radius for hydrogen (0.30 Å) and the single-bond metallic radius for scandium (1.44 Å), but it is in the range of other distances between heavy atoms and hydrogen. The Sc-P bond length, 2.752(1) Å, is 0.21 Å longer than the sum of the radii, which suggests that the bond is weaker than a single bond. The ring centroid-Sc-ring centroid angle was found to be 4° bigger than that of the $Me_2Si(C_5Me_4)_2Sc$-$CH(SiMe_3)_2$. This indicates that the presence of a $CH(SiMe_3)_2$ group causes a much bigger distortion in the geometry probably due to the size of the alkyl group. Other distances and angles are normal and are in close agreement with those found for $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$.

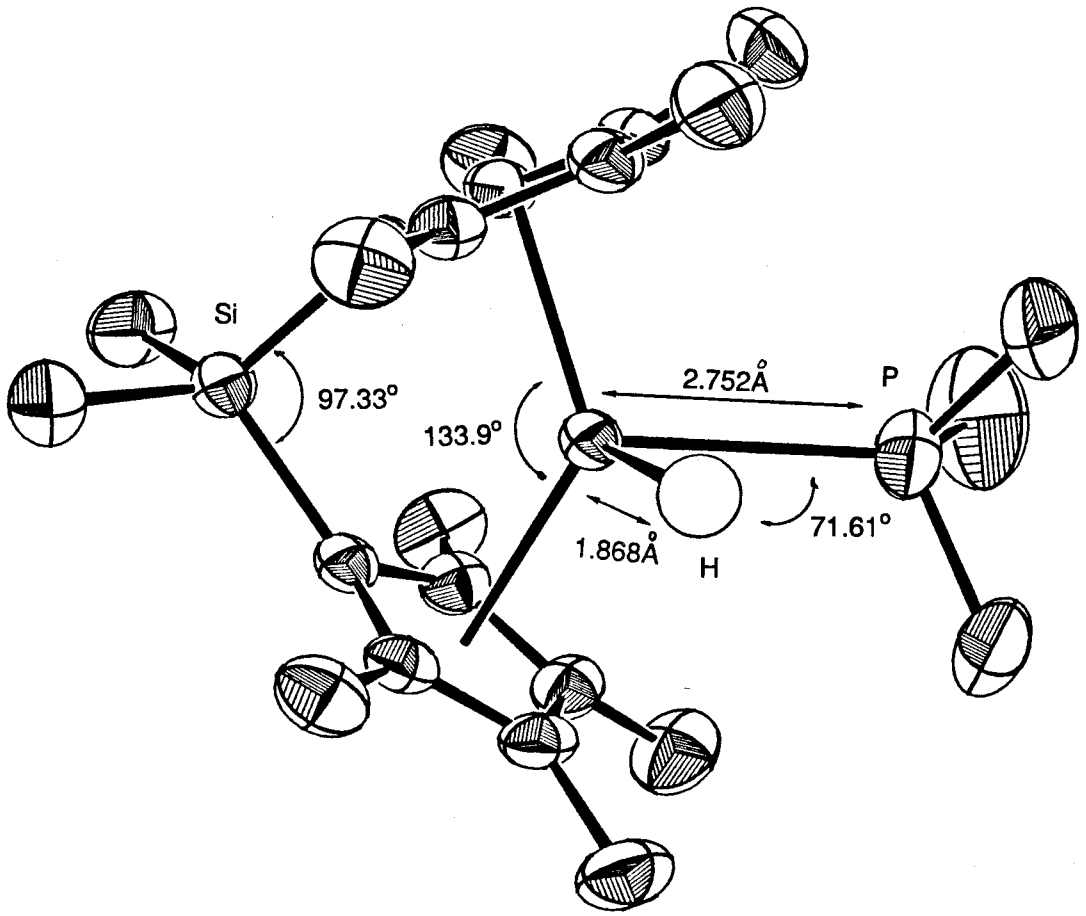


Figure 3: Molecular Structure of $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$.

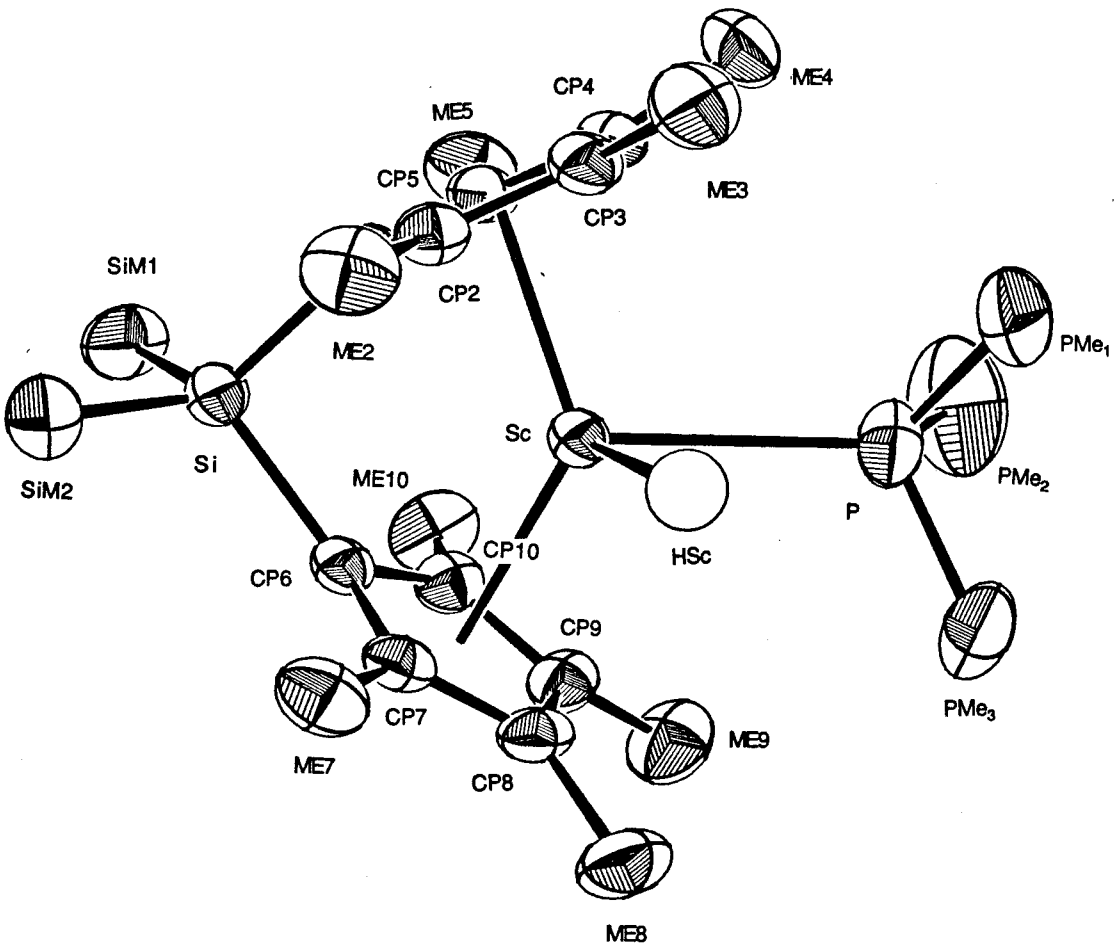


Figure 4: The atomic labeling for $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$.

Table 4: Crystal Data for $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$

Formula : $ScPSiC_{23}H_{40}$	Formula weight : 420.59
Space group : $P2_1/c$(#14)	Temperature : 23°C
a = 9.052(2) Å	
b = 28.717(2) Å	β = 115.56(1) °
c = 10.345(1) Å	
V = 2426.8(7) $Å^3$	$\lambda MoK\alpha$ = 0.71073 Å
μ = 4.56 cm^{-1}	ρ = 1.152 g cm^{-3}
Crystal size 0.90x0.14x0.15 mm	μr_{max} = 0.21

Table 5: Bond Lengths (Å) for $Me_2Si(C_5Me_5)_2Sc(H)(PMe_3)$

Atoms	Distance	Atoms	Distance
Sc-HSc	1.87(3)	CP1-CP2	1.431(4)
Sc-CP1	2.438(3)	CP1-CP5	1.438(4)
Sc-CP2	2.471(3)	CP2-CP3	1.407(4)
Sc-CP3	2.580(3)	CP3-CP4	1.406(4)
Sc-CP4	2.602(3)	CP4-CP5	1.417(4)
Sc-CP5	2.500(3)	CP2-Me2	1.502(4)
Sc-CP6	2.456(3)	CP3-Me3	1.508(4)
Sc-CP7	2.523(3)	CP4-Me4	1.506(4)
Sc-CP8	2.611(3)	CP5-Me5	1.500(4)
Sc-CP9	2.588(3)	CP6-CP7	1.440(4)
Sc-CP10	2.473(3)	CP6-CP10	1.447(4)
Sc-P	2.753(1)	CP7-CP8	1.414(4)
P-PMe1	1.828(4)	CP8-CP9	1.409(4)
P-PMe2	1.825(5)	CP9-CP10	1.404(4)
P-PMe3	1.826(4)	CP7-Me7	1.500(4)
Si-SiM1	1.850(4)	CP80Me8	1.496(4)
Si-SiM2	1.872(4)	CP9-Me9	1.508(4)
Si-CP1	1.879(3)	CP10-Me10	1.501(4)
Si-CP6	1.879(30)		

Table 6: Bond Angles(°) for $Me_2Si(C_5Me_5)_2Sc(H)(PMe_3)$

Atom	Atom	Atom	Angle
R1	Sc	R2	133.9(0)
SiM1	Si	SiM2	101.4(20)
CP1	Si	SiM1	114.7(1)
CP6	Si	SiM1	114.9(1)
CP1	Si	SiM2	114.2(1)
CP6	Si	SiM2	114.7(1)
CP1	Si	CP6	97.7(1)
Sc	P	PMe1	113.9(1)
Sc	P	PMe2	123.3(2)
Sc	P	PMe3	111.8(1)
PMe2	P	PMe1	102.5(2)
PMe3	P	PMe1	99.3(2)
PMe3	P	PMe2	102.8(2)
CP2	CP1	Si	125.4(2)
CP5	CP1	Si	123.8(2)
CP5	CP1	CP2	105.8(2)
CP3	CP2	CP1	109.1(2)
Me2	CP2	CP1	128.0(3)
Me2	CP2	CP3	122.8(3)
CP4	CP3	CP2	108.3(3)
Me3	CP3	CP2	124.5(3)
Me3	CP3	CP4	126.8(3)
CP5	CP4	CP3	108.2(3)
Me4	CP4	CP3	127.1(3)
Me4	CP4	CP5	123.9(3)
CP4	CP5	CP1	108.6(2)
Me5	CP5	CP1	129.1(3)
Me5	CP5	CP4	121.8(3)
CP7	CP6	Si	123.9(2)
CP10	CP6	Si	125.7(2)
CP10	CP6	CP7	105.0(2)
CP8	CP7	CP6	109.1(2)
Me7	CP7	CP6	128.0(3)
Me7	CP7	CP8	122.1(3)
CP9	CP8	CP7	108.3(3)
Me8	CP8	CP7	123.6(3)
Me8	CP8	CP9	127.1(3)
CP10	CP9	CP8	108.2(3)
Me9	CP9	CP8	126.2(3)
Me9	CP9	CP10	125.2(3)
CP9	CP10	CP6	109.4(2)
Me10	CP10	CP6	127.2(3)
Me10	CP10	CP9	123.3(3)

Table 7: Final Parameters X 10^4 for $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$

Atom	X	Y	Z	U_{eq}
Sc	1202(.6)	1342(.2)	2400(.5)	306(1)
P	3964(1)	1787	4337(1)	521(2)
Si	-1613(.9)	558(.3)	1058(.9)	377(2)
PMe1	5497(4)	1900(1)	3665(4)	811(11)
PMe2	5203(5)	1569(2)	6142(4)	1116(17)
PMe3	3533(5)	2386(1)	4662(5)	887(12)
SiM1	-3328(4)	552(1)	-759(4)	638(10)
SiM2	-1969(4)	1(1)	1820(4)	616(9)
CP1	475(3)	607(1)	1095(3)	334(6)
CP2	910(3)	916(1)	228(3)	354(6)
CP3	2607(3)	1000(1)	910(3)	387(7)
CP4	3269(3)	749(1)	2204(3)	388(7)
CP5	1974(3)	510(1)	2339(3)	363(7)
Me2	-175(4)	1104(1)	-1230(3)	545(8)
Me3	3544(4)	1268(1)	253(4)	597(8)
Me4	5055(4)	668(1)	3165(4)	611(10)
Me5	2287(4)	165(1)	3519(4)	568(9)
CP6	-1504(3)	1091(1)	2147(3)	320(6)
CP7	-531(3)	1123(1)	3673(3)	356(6)
CP8	-163(3)	1596(1)	4056(3)	382(7)
CP9	-886(3)	1868(1)	2802(3)	377(6)
CP10	-1692(3)	1567(1)	1638(3)	342(6)
Me7	-174(4)	747(1)	4773(3)	551(8)
Me8	570(4)	1767(1)	5571(3)	615(9)
Me9	-968(4)	2392(1)	2732(4)	576(9)
Me10	-2654(4)	1734(1)	130(3)	507(8)

CONCLUSIONS

The synthetic chemistry described offers straightforward routes to a broad family of ether- and halide-free bis (cyclopentadienyl)scandium complexes. Mixed ring derivatives containing one pentamethylcyclopentadienyl ring are easily obtained from $[Cp^*ScCl_2]_x$. Alkylation in the presence of trimethylphosphine, followed by hydrogenation yields mixed ring hydride derivatives. Dimethylsilicon-bridged bis(cyclopentadienyl)compounds were prepared as previously described for lanthanides. The use of bulky lithium alkyls such as $LiCH_2SiMe_3$ or $LiCH(SiMe_3)_2$ affords alkyl derivatives where the undesirable coordination of ether or halide is avoided. Hydrogenolysis readily yields the corresponding hydrides. The synthesis of $Me_2Si(C_5Me_4H)(R^*C_5H_4)$ offered a convenient approach to the synthesis of optically active scandium complexes by introduction of chiral groups (R*) in one cyclopentadienyl ring.

Table 8 : ^{1}H NMR Data.[a]

Compound	Assignment	δ(ppm) and J(Hz)
$Cp^*Sc(acac)_2$ (90MHz,C_6D_6)	η^5-$C_5(CH_3)_5$	2.1(s)
	$CH_3COCHCOCH_3$	1.8(s)
	$CH_3COCHCOCH_3$	5.2(s)
Cp^*ScCl_2 (90MHz,THF-d_8)	η^5-$C_5(CH_3)_5$	2.1(s)
$Cp^*CpScCl$ (400MHz,C_7D_8,80°C)	η^5-$C_5(CH_3)_5$	2.0(s)
	η^5-C_5H_5	6.3(s)
Cp^*Cp^oCsCl (90MHz,C_6D_6)	η^5-$C_5(CH_3)_5$	1.9(s)
	η^5-1,3,4-$C_5(CH_3)_3H_2$	1.9(s); 1.8(s)
	η^5-1,3,4-$C_5(CH_3)_3H_2$	6.2(s)
$Cp^*CpSc(CH_3)PMe_3$ (90MHz,C_6D_6)	η^5-$C_5(CH_3)_5$	1.9(s)
	η^5-C_5H_5	6.0(s)
	Sc-CH_3	-0.6(s)
	$P(CH_3)_3$	0.7(d, J=6Hz)
$Cp^*Cp^oSc(CH_3)PMe_3$ (90MHz,C_6D_6)	η^5-$C_5(CH_3)_5$	2.1(s)
	η^5-1,3,4-$C_5(CH_3)_3H_2$	1.9(s); 2.1(s)
	η^5-1,3,4-$C_5(CH_3)_3H_2$	5.8(s)
	Sc-CH_3	-0.7(s)
	$P(CH_3)_3$	0.83(d, J=4Hz)
Cp^*CpSc-(η^1,η^5-C_5H_4)ScH (90MHz,C_6D_6)	η^5-$C_5(CH_3)_5$	2.0(s); 2.1(s)
	η^5-C_5H_5	5.5(s)
	η^1,η^5-C_5H_4	6.0(m); 6.1(m); 6.4(m); 6.6(m)
$Cp^*Cp^oSc(H)PMe_3$ (90MHz,C_6D_6)	η^5-$C_5(CH_3)_5$	2.1(s)
	η^5-1,3,4-$C_5(CH_3)_3H_2$	1.7(s); 2.3(s)
	η^5-1,3,4-$C_5(CH_3)_3H_2$	5.8(s)
	$P(CH_3)_3$	0.8(d, J=4.5Hz)
$Me_2Si(C_5Me_4)_2Li_2$ (90MHz,THF-d_8)	CH_3Si	0.4(s)
	η^5-$C_5(CH_3)_4$	1.8(s); 2.0(s)

$Me_2Si(t\text{-butylCp})_2Li_2$ (90MHz,THF-d_8)	CH_3Si	0.3(s)
	η^5-t-C_4H_9-C_5H_3	1.2(s)
	η^5-t-C_4H_9-C_5H_3	5.7-5.8(m)
$Me_2Si(C_5Me_4)_2ScCl$-LiCl-$(Et_2O)_2$ (90MHz,THF-d_8)	CH_3Si	0.9(s)
	η^5-$C_5(CH_3)_4$	1.8(s); 1.9(s)
	$(CH_3CH_2)_2O$	1.1(t, J=6.6Hz)
	$(CH_3CH_2)_2O$	3.6(t, 6.6Hz)
$Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$ (400MHz,C_6D_6)	CH_3Si	0.9(s)
	η^5-$C_5(CH_3)_4$	1.83(s); 1.84(s); 1.85(s); 1.96(s)
	$CH(Si(CH_3)_3)_2$	0.1(s)
	$CH(Si(CH_3)_3)_2$	1.1(s)
$Me_2Si(C_5Me_4)_2Sc(H)PMe_3)$ (400MHz,C_7D_8,-10°C)	CH_3Si	0.92(s); 1.03(s)
	η^5-$C_5(CH_3)_4$	1.85(s); 1.94(s); 2.01(s); 2.46(s)
	$P(CH_3)_3$	0.78(d, J=3.5Hz)
$Me_2Si(t\text{-butylCp})_2ScCl$ (400MHz,CD_2Cl_2)	CH_3Si	0.5(s); 0.8(s)
	η^5-t-C_4H_9-C_5H_3	1.2
	η^5-t-C_4H_9-C_5H_3	6.3(m); 6.5(m); 6.7(m)
$Me_2Si(t\text{-butylCp})_2ScCH_2SiMe_3$ (90MHz,C_6D_6)	CH_3Si	0.3(s)
	$CH_2Si(CH_3)_3$	0.5(s); 0.8(m)
	$CH_2Si(CH_3)_3$	1.0(s)
	η^5-t-C_4H_9-C_5H_3	1.1(s)
	η^5-t-C_4H_9-C_5H_3	5.3(m); 5.8(m); 7.0(m)
$Me_2Si(t\text{-butylCp})_2ScH$ (90MHz,C_6D_6)	CH_3Si	0.2(s); 0.8(s)
	η^5-t-C_4H_9-C_5H_3	1.2(s)
	η^5-t-C_4H_9-C_5H_3	6.3(m); 6.7(m); 7.3(m)
$C_5Me_4H_2$ (90MHz,$CDCl_3$)	$C_5(CH_3)_4H_2$	1.8(s); 1.9(s)
	$C_5(CH_3)_4H_2$	2.7(s)
t-butylCpLi (90MHz,THF-d_8)	t-C_4H_9-C_5H_4	1.2(s)
	t-C_4H_9-C_5H_4	5.4(m)

$C_5Me_4SiMe_2Cl$		
(90MHz,C_6D_6)	$C_5(CH_3)_4Si(CH_3)_2Cl$	1.7(s); 1.9(s)
	$C_5(CH_3)_4Si(CH_3)_2Cl$	0.12(s)
$Me_2Si(C_5Me_4)$(t-butylCp)Li_2		
(90MHz,THF-d_8)	CH_3Si	0.6(s)
	$C_5(CH_3)_4$	1.9(s); 2.0(s)
	t-C_4H_9-C_5H_4	1.2(s)
	t-C_4H_9-C_5H_4	5.8-5.9(m)
$Me_2Si(C_5Me_4)$((-)-2-methylbutylCp)Li_2		
(500MHz,THF-d_8)	CH_3Si	0.4(s)
	$C_5(CH_3)_4$	2.05(s); 1.88(s)
	CH_3CH_2-$CH(CH_3)$-CH_2-	2.46(m); 2.23(m)
	C_5H_3	5.72(m); 5.71(m); 5.59(m)
$Me_2Si(C_5Me_4)$((+)-menthylCp)Li_2		
(500MHz,THF-d_8)	CH_3Si	0.39(s)
	$C_5(CH_3)_4$	2.1(s); 1.9(s)
	C_5H_3	5.85(m); 5.77(m); 5.73(m)
$Me_2Si(C_5Me_4)$(t-butylCp)ScCl(THF)		
(400MHz,C_6D_6)	CH_3Si	0.74(s); 0.87(s)
	η^5-$C_5(CH_3)_4$	1.59(s); 2.03(s); 2.22(s); 2.11(s)
	η^5-t-C_4H_9-C_5H_3	1.57(s)
	η^5-t-C_4H_9-C_5H_3	5.61(m); 5.94(m); 6.02(m)
	O-CH_2-CH_2	1.13(m)
	O-CH_2-CH_2	3.35(m)
$Me_2Si(C_5Me_4)$(t-butylCp)ScCH$(SiMe_3)_2$		
(400MHz,C_6D_6)	CH_3Si	0.85(s); 0.57(s)
	η^5-$C_5(CH_3)_4$	1.52(s); 1.80(s); 1.91(s); 2.11(s)
	η^5-t-C_4H_9-C_5H_3	1.08(s)
	η^5-t-C_4H_9-C_5H_3	5.92(m); 6.17(m); 7.00(m)
	$CH(Si(CH_3)_3)_2$	0.05(s)
	$CH(Si(CH_3)_3)_2$	-0.25(s); 0.33(s)
$Me_2Si(C_5Me_4)$((-)-2-methylbutylCp)ScCH$(SiMe_3)_2$		
(500MHz,C_6D_6)		
	η^5-$C_5(CH_3)_4$	1.72(s); 1.73(s); 1.74(s); 1.83(s); 1.85(s); 1.86(s)
	CH_3CH_2-$CH(CH_3)$-CH_2-	2.16(d); 2.43(d); 2.79(d); 3.01(d)
	η^5-C_5H_3	5.31(m); 5.36(m); 5.38(m);6.89(m)
	$CH(Si(CH_3)_3)_2$	0.08(s); 0.09(s); 0.18(s); 0.19(s)
$Me_2Si(C_5Me_4)$((+)-menthylCp)ScCH$(SiMe_3)_2$		
(500MHz,C_6D_6)		
	η^5-$C_5(CH_3)_4$	1.63(s); 1.69(s);

		1.771.78(s);
		1.92(s); 1.93(s); 2.02(s)
	η^5-C_5H_3	5.58(m); 5.68(m);
		5.92(m);
		6.15(m); 7.19(m); 7.23(m)
	$CH(Si(CH_3)_3)_2$	0.02(s); 0.03(s); 0.27(s);
		0.29(s)
$Me_2Si(C_5Me_4)$((+)-menthylCp)ScH (500MHz,C_6D_6)		
	η^5-$C_5(CH_3)_4$	1.68(s); 1.69(s); 2.08(s);
		2.11(s);
		2.17(s); 2.22(s); 2.23(s);
		2.24(s)(s)
	η^5-C_5H_3	5.69(m); 5.78(m);
		6.37(m);
		6.54(m); 7.00(m); 7.08(m)
	ScH	4.25(broad)

[a]NMR spectra were taken at ambient temperature, unless otherwise stated.

EXPERIMENTAL

All manipulations were carried out by using either high vacuum line or glove-box techniques.[6] Hydrogen, deuterium, and argon were purified by passing over MnO on vermiculite[7] and activated 4Å molecular sieves. Benzene, toluene, cyclohexane, methylcyclohexane, petroleum ether (bp 30-60 °C), perdeuterobenzene, and perdeuterotoluene were first vacuum transferred from $LiAlH_4$ or 4Å molecular sieves and then from titanocene prior to use[8]. Diethyl ether, tetrahydrofuran and perdeuterotetrahydrofuran were stored over benzophenone ketyl. Methanol, aluminum trichloride, scandium oxide, dimethyldichlorosilane and trimethylphosphine were used as received. $Sc(acac)_3$,[9] $LiCH_2SiMe_3$,[10] $(Me_3Si)_2CHLi \cdot 0.5\ Et_2O$,[11] $Cp^*MgCl \cdot THF$,[12] $ScCl_3 \cdot 3THF$,[13] Cp^0H,[14] *t*-butylC_5H_5,[15] (-)-2-methylbutylC_5H_5[16] and (+)-menthylC_5H_5[17] were prepared according to literature procedures. CpLi, Cp^0Li, (-)-2-methylbutylC_5H_4Li and (+)-menthylC_5H_4Li were prepared by reacting C_5H_6, Cp^0H, (-)-2-methylbutylC_5H_5 and (+)-menthylC_5H_5 with *n*-butyllithium in petroleum ether.

^1H NMR spectra were recorded on Varian EM 390 (90 MHz), JEOL GX 400 (399.78 MHz), and Brucker WM500 (500.13 MHz) spectrometers. Elemental analyses were performed by the analytical facility of the California Institute of Technology. Molecular weights were determined by using the vapor phase osmometry techniques developed by Signer and described by Clark[18]

$Cp^*Sc(acac)_2$ (1): $Sc(acac)_3$ (7.5 g, 21.9 mmol) and $Cp^*MgCl \cdot THF$ (6.0 g, 22.5 mmol) were stirred in toluene (50 mL) at room temperature for three hours. Toluene was removed *in vacuo*. The subsequent operations were carried out in air. Methanol (30 mL) was added to the solid residue. The mixture was stirred for 10 minutes, filtered, washed with three portions of methanol (30 mL each), and dried. Yield 7.2 g (86.7%). Recrystallization from hot toluene gave 1 as yellow crystals.

Anal. Calcd. for $C_{20}H_{29}ScO_4$: C, 63.48; H, 7.72. Found: C, 63.27; H, 7.52.

$[Cp^*ScCl_2]_x$ (2): $Cp^*Sc(acac)_2$ (2.0 g, 5.3 mmol) and aluminum trichloride (1.4 g, 10.5 mmol) were stirred in toluene (20 mL) at room temperature for three hours. The toluene was heated to boiling, and the precipitate was filtered off and dried. 1.1 g (82.7%) of white solid **2** were obtained.

Anal. Calcd. for $C_{10}H_{15}ScCl_2$: C, 47.83; H, 6.02. Found: C, 47.32; H, 5.73.

$Cp^*CpScCl$ (4): Cp^*ScCl_2 (7.0 g, 27.9 mmol) and CpLi (2.2 g, 30.6 mmol) were heated in toluene (80 mL) to 80°C for four hours. The toluene was removed *in vacuo*, and the solid residue was soxhlet extracted with benzene over twelve hours. The benzene was removed and petroleum ether (*ca.* 20 mL) was added. The solid was filtered and washed with petroleum ether. 5.9 g (75.4%) of yellow solid **4** were obtained. Recrystallization from hot toluene gave an analytically pure sample.

Anal. Calcd. for $C_{15}H_{20}ScCl$: C, 64.18; H, 7.18. Found: C, 64.19; H, 7.11.

Cp^*Cp^0ScCl (5): Cp^*ScCl_2 (2.09 g, 8.3 mmol) and Cp^0Li (1.0 g, 8.8 mmol) suspended in toluene (30 mL) were heated to 80 °C for four hours. The solution was filtered, the toluene was removed *in vacuo*, and petroleum ether *(ca.* 10 mL) was added. The yellow solid **5** was filtered and dried. Yield 1.75 g (65%). **5** was purified by sublimation at 140 °C and 10^{-4} torr.

Anal. Calcd. for $C_{18}H_{26}ScCl$: C, 66.97; H, 8.12. Found: C, 66.60; H, 7.99.

$Cp^*CpSc(CH_3)(PMe_3)$ (6): $Cp^*CpScCl$ (0.315 g, 1.12 mmol), methyl lithium (0.03 g, 1.36 mmol), and PMe_3 (0.12 mL, 1.24 mmol) were dissolved in diethyl ether (20 mL). After stirring at room temperature for three hours, the diethyl ether was removed *in vacuo* and replaced with petroleum ether (*ca.* 20 mL). The lithium chloride was removed from the solution by filtration, and the solution was cooled overnight (-78°C) to afford **6** (0.22 g, 58.4%) as white crystals.

Anal. Calcd. for $C_{19}H_{32}ScP$: C, 67.84; H, 9.42. Found: C, 67.62; H, 9.42.

$Cp^*Cp^0Sc(CH_3)(PMe_3)$ (7): The procedure for **6** was followed except Cp^*Cp^0ScCl (1.00 g, 31 mmol), methyl lithium (0.08 g, 3.6 mmol), and PMe_3 (0.35 mL, 3.6 mmol) were dissolved in diethyl ether(20 mL). The product is less soluble in petroleum ether than $Cp^*CpSc(CH_3)(PMe_3)$ and required several extractions to remove it from the lithium chloride. Cooling the solution to -78 °C for two hours afforded **7** (0.65 g, 55.5%) as white crystals.

Anal. Calcd. for $C_{22}H_{38}ScP$: C, 69.82; H, 10.12. Found: C, 69.79; H, 10.11.

$Cp^*CpSc\text{-}(\eta^1\text{-}\eta^5\text{-}C_5H_4)Cp^*Sc\text{-}H$ (8): $Cp^*CpSc(CH_3)(PMe_3)$ (0.5 g, 1.48 mmol) dissolved in petroleum ether (*ca.* 5 mL) was loaded into a thick-walled glass reaction vessel. The flask was cooled to -196 °C, and one atmosphere of dihydrogen was admitted. After stirring for thirty minutes a white solid began to precipitate. Stirring was continued for two hours, and the suspension was transferred to a frit assembly. The white solid **9** was filtered and dried. Yield 0.23 g (63%). Recrystallization from hot methylcyclohexane afforded **9** as white crystals.

Anal. Calcd. for $C_{30}H_{40}Sc_2$: C, 73.45; H, 8.21. Found: C, 73.32; H, 8.06.

$Cp^*Cp^0Sc(H)(PMe_3)$ (9): The same procedure was used as described for $Cp^*CpSc\text{-}(\eta^1\text{-}\eta^5\text{-}C_5H_4)Cp^*Sc\text{-}H$. **8** is very soluble in petroleum ether; to obtain crystals a concentrated petroleum ether solution was cooled to -78 °C for twenty four hours. $Cp^*Cp^0Sc(CH_3)(PMe_3)$ (0.2 g, 53 mmol) yielded 0.12 g (62%) of **8** as yellow crystals.

Anal. Calcd. for $C_{21}H_{36}ScP$: C, 69.21; H, 9.96. Found: C, 69.31; H, 10.20.

$C_5Me_4H_2$: $LiAlH_4$ (14.16 g, 723 mmol) and anhydrous diethyl ether (500 mL) were placed in a 2 L three-necked flask equipped with a reflux condenser, a magnetic stirrer and a dropping funnel. 2,3,4,5-Tetramethyl-2-cyclopentenone (100 g, 373 mmol) dissolved in anhydrous diethyl ether (120 mL) was added, dropwise and with stirring, to the reaction flask at a rate which maintained gentle refluxing. After the addition was complete, the reaction solution was refluxed for an additional 30 minutes and cooled to room temperature. The complex was

hydrolyzed and the excess $LiAlH_4$ was destroyed by the cautious addition, dropwise and with stirring, of water (35 mL). The resulting reaction mixture was poured into 1200 mL of cold aqueous 10% sulfuric acid. The ether layer was separated, and the residual aqueous phase extracted with three 300 mL portions of ether. The combined ether solutions were concentrated *in vacuo* to *ca.* 200 mL, and concentrated sulfuric acid (1 mL) was added (argon atmosphere). The mixture was stirred for three hours at room temperature, and the mixture was washed successively with one 100-mL portion of water and one 100-mL portion of saturated, aqueous $NaHCO_3$ and then dried over $MgSO_4$. The product was vacuum distilled (bp: 60-70°C/37-40 torr). Yield 38 g (43%).

C_5Me_4HLi: $C_5Me_4H_2$ (20.0 g, 164 mmol) was dissolved in tetrahydrofuran (100 mL) and cooled to -78°C. *n*-Butyllithium (1.6M in hexanes,105 mL, 168 mmol) was added *via* syringe. The reaction mixture was slowly warmed to room temperature and stirred for two hours. The white precipitate was filtered and washed with petroleum ether and dried. Yield 19 g (90.5%).

$Me_2Si(C_5Me_4)_2Li_2$ (10): C_5Me_4HLi (15.0 g, 117 mmol) was suspended in tetrahydrofuran (500 mL). Me_2SiCl_2 (7.0 mL, 58 mmol) was added *via* syringe against an argon counterflow, and the mixture was refluxed for 60 hours. The tetrahydrofuran was removed *in vacuo* and replaced with petroleum ether (200 mL). The lithium chloride was removed from the solution by filtration. The petroleum ether was removed *in vacuo* leaving an oily residue. The oil was redissolved in petroleum ether (200 mL), cooled to -78°C, and *n*-butyllithium (1.6M in hexanes, 75 mL, 120 mmol) was added. The solution was warmed to room temperature and stirred overnight. The product was filtered, washed with petroleum ether and dried. Yield 15.4 g (89.7%).

***t*-butylC_5H_4Li:** *t*-ButylC_5H_5 (20.0 g, 164 mmol) dissolved in diethyl ether (100 mL) was cooled to -78°C and *n*-butyllithium (1.6M in hexanes, 105 mL, 168 mmol) was added *via* syringe against an argon counterflow. The mixture was warmed to 0°C and stirred for one hour. The mixture was warmed to room temperature and stirred for two additional hours. The white crystalline solid was filtered, washed with diethyl ether, and dried. Yield 16.8 g (80%).

$Me_2Si(t\text{-}butylC_5H_3)_2Li_2$ (11): *t*-ButylC_5H_4Li (10.0 g, 78 mmol) was dissolved in tetrahydrofuran (100 mL) and cooled to -78°C. Me_2SiCl_2 (4.7 mL, 38.7 mmol) was added *via* syringe against an argon counterflow, and the solution was stirred at room temperature for one hour. The tetrahydrofuran was removed *in vacuo* and replaced with petroleum ether (*ca.* 80 mL). The lithium chloride was removed from the solution by filtration. A reflux condenser was attached to the reaction flask, and *n*-butyllithium (1.6M in hexanes, 50 mL, 80 mmol) was added against argon counterflow over 30 minutes due the exothermicity of the reaction. The mixture was refluxed for two hours. The white solid, **13**,was filtered, washed with petroleum ether, and dried. Yield 11.6 g (95%).

$(C_5Me_4)SiMe_2Cl$ (12): C_5Me_4HLi (10.0 g, 78.1 mmol) was suspended in tetrahydrofuran (150 mL) and cooled to -78°C. Me_2SiCl_2 (9.7 mL, 80 mmol) was added *via* syringe against an argon counterflow. The mixture was warmed to room temperature and stirred for two hours. The tetrahydrofuran was removed *in vacuo* and replaced with petroleum ether (ca. 100mL). The lithium chloride was removed from the solution by filtration. The petroleum ether was removed *in vacuo*, leaving the product as a colorless liquid that solidified upon cooling to -40°C. Yield 16 g (95.5%).

$Me_2Si(C_5Me_4)(t\text{-}butyl\text{-}C_5H_3)Li_2$ (13): *t*-ButylC_5H_4Li (3.0 g, 23.4 mmol) dissolved in tetrahydrofuran (40 mL) was added to $C_5Me_4HSiMe_2Cl$ (5.0 g, 23.3 mmol) dissolved in tetrahydrofuran (20 mL). The solution was stirred for twelve hours, and the tetrahydrofuran was removed *in vacuo* and replaced with petroleum ether (c.a. 50mL). The lithium chloride was removed from the solution by filtration. The petroleum ether was removed *in vacuo* leaving an oily liquid. Diethyl ether (*ca.* 80 mL) was added, the solution was cooled to -78°C, and *n*-butyllithium (1.6 M solution in hexanes, 30 mL, 48 mmol) was added. The solution was warmed to room temperature and stirred for three hours. Diethyl ether was removed *in vacuo* and replaced with petroleum ether (*ca.* 100 mL). The white solid, **13**, was filtered, washed with fresh petroleum ether, and dried. Yield 7.0 g (92%).

$Me_2Si(C_5Me_4)$((-)-2-methylbutyl$C_5H_3)Li_2$ (14): The same procedure was used as described for **13**, except that 13.0 g (94.3%) of **14** were isolated from ((-)-2-Methyl butylC_5H_4)Li (6.0 g, 42.2 mmol) dissolved in 80 mL of tetrahydrofuran and $C_5Me_4HSiMe_2Cl$ (9.0 g, 41.9 mmol) dissolved in 40 mL of tetrahydrofuran.

$Me_2Si(C_5Me_4)$((+)-menthyl$C_5H_3)Li_2$ (15): The same procedure was used as described for **13**, except that 5.0 g (98%) of **15** were isolated from ((+)-MenthylC_5H_4)Li (2.93 g, 13.9 mmol) and $C_5Me_4HSiMe_2Cl$ (3.0 g, 14 mmol).

$Me_2Si(C_5Me_4)_2ScCl \cdot LiCl \cdot (Et_2O)_2$ (16): $Me_2Si(C_5Me_4)_2Li_2$ (4.0 g, 12.8 mmol) and $ScCl_3 \cdot 3THF$ (4.7 g, 12.8 mmol) suspended in toluene (80 mL) were heated at 80°C for three days. The lithium chloride was removed from the solution by filtration. The solution was concentrated to *ca.* 10 mL, and petroleum ether (50 mL) was added *in vacuo*. The precipitate was filtered, washed three times with fresh solvent, and dried. Yield 3.5 g (48 %). **16** was isolated as long white needles by recrystallization from diethyl ether cooled to -78°C.

Anal. Calcd. for $C_{28}H_{50}ScLiCl_2O_2$: C, 59.04; H, 8.85. Found: C, 59.20; H, 8.52.

***meso*-Me_2Si(*t*-butyl$C_5H_3)_2ScCl$ (17):** Me_2Si(*t*-butyl$C_5H_3)_2Li_2$ (31.3 g, 100.3 mmol) and $ScCl_3 \cdot 3THF$ (36.9 g, 100.4 mmol) were heated to 80°C in toluene (500 mL) for two days. The lithium chloride was removed from the solution by filtration. Toluene was removed *in vacuo* and replaced with petroleum ether (*ca* 100mL). The solid **17** was filtered, washed with fresh petroleum ether, and dried. Yield 18.7 g (49.2 %). Recrystallization from boiling toluene yielded **17** as white crystals.

Anal. Calcd. for $C_{20}H_{30}SiScCl$: C, 63.33; H, 7.98. Found C, 62.85; H, 7.59.

$Me_2Si(C_5Me_4)$(*t*-butyl-$C_5H_3)ScCl \cdot LiCl \cdot THF_2$ (18): $ScCl_3 \cdot 3THF$ (2.6 g, 7.07 mmol) and $Me_2Si(C_5Me_4)$(*t*-butyl-$C_5H_3)Li_2$ (2.24 g 7.17 mmol) were heated in toluene (50 mL) for 12 hours. The lithium chloride was removed from the solution by filtration. The toluene was removed *in*

vacuo and replaced with petroleum ether (50 mL), and the insoluble white product was filtered and dried. Recrystallization from boiling cyclohexane yielded white crystals of **18** (1.3 g, 40.8%).

Anal. Calcd. for $C_{28}H_{46}SiScCl_2O_2Li$: C, 59.46; H, 8.20. Found: C, 58.98; H,7.46.

$Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$ (21): $Me_2Si(C_5Me_4)_2ScCl$-LiCl-$(Et_2O)_2$ (1.16 g, 2 mmol) and $(Me_3Si)_2CHLi \cdot 0.5\ Et_2O$ (0.49 g, 2.4 mmol) were dissolved in toluene (20 mL) and stirred at room temperature for twelve hours. The mixture was heated to 100°C, filtered, and slowly cooled to room temperature. The bright yellow crystalline product, **21**, was filtered and dried. Yield 0.86 g (84%).

Anal. Calcd. for $C_{27}H_{49}Si_3Sc$: C, 64.49; H, 9.82. Found: C, 64.56; H, 9.61.

***meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2ScCH_2SiMe_3$ (22):** *meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2ScCl$ (18.7 g, 49.4 mmol) and $LiCH_2SiMe_3$ (1.0M in pentane, 50 mL, 50 mmol) were stirred in toluene (150 mL) at room temperature for twelve hours. Toluene was removed *in vacuo* and replaced with petroleum ether (*ca.* 80 mL). The lithium chloride was removed from the solution by filtration, and the solution was cooled overnight to -78°C to afford **22** as yellow crystals. Yield 12.3 g (57.8%).

Anal. Calcd. for $C_{24}H_{41}Si_2Sc$: C, 66.93; H, 9.60. Found: C, 66.81; H, 9.49.

$Me_2Si(C_5Me_4)(t\text{-butyl-}C_5H_3)ScCH(SiMe_3)_2$ (23): $Me_2Si(C_5Me_4)(t\text{-butyl-}C_5H_3)ScCl \cdot THF$ (1.0 g, 2.2 mmol) and $(Me_3Si)_2CHLi \cdot 0.5\ Et_2O$ (0.45 g, 2.2 mmol) were dissolved in toluene (30 mL). The solution was stirred at room temperature for 5 hours. The toluene was removed *in vacuo* and replaced with petroleum ether (10 mL). The lithium chloride was removed from the solution by filtration, and the petroleum ether solution was cooled to -78°C. Cold filtration afforded 0.69 g (62.7%) of **23** as yellow crystals.

Anal. Calcd. for $C_{27}H_{49}Si_3Sc$: C, 64.49; H, 9.82. Found: C, 64.25; H, 9.42.

$Me_2Si(C_5Me_4)$((-)-2-methylbutylC_5H_3)ScCH($SiMe_3$)$_2$ (24): $Me_2Si(C_5Me_4)$((-)-2-methylbutylC_5H_3)Li_2 (1.0 g, 3.2 mmol) and $ScCl_3 \cdot 3THF$ (1.2 g, 3.2 mmol) were refluxed for twelve hours in toluene (30 mL). The solution was filtered to remove the lithium chloride. The toluene was removed *in vacuo* leaving a viscous oil (**19**). The oil was redissolved in toluene (30 mL), and $(Me_3Si)_2CHLi \cdot 0.5\ Et_2O$ (0.65 g, 3.2 mmol) was added. The bright yellow solution was stirred at room temperature for 5 hours. The toluene was removed *in vacuo* and replaced with petroleum ether (ca. 20mL). The lithium chloride was removed from the solution by filtration. The petroleum ether was removed *in vacuo* and replaced with diethyl ether. Cooling to -78°C afforded 0.62 g (37% overall yield from **14**) of **24** as yellow crystals.

Anal. Calcd. for $C_{28}H_{51}Si_3Sc$: C, 65.06; H, 9.94. Found: C, 64.89; H, 9.49.

$Me_2Si(C_5Me_4)$((+)-menthylC_5H_3)ScCH($SiMe_3$)$_2$ (25): **15** (3.0 g, 8.2 mmol) and $ScCl_3 \cdot 3THF$ (3.0 g, 8.2 mmol) were dissolved in toluene (50 mL). The mixture was heated at 80°C for 5 hours, filtered to remove the lithium chloride, and dried. $Me_2Si(C_5Me_4)$((+)-MenthylC_5H_3)ScCl·THF (**20**) was isolated as a white powder from petroleum ether. $Me_2Si(C_5Me_4)$((+)-MenthylC_5H_3)ScCl·THF (1.0 gr, 20mmol) and $(Me_3Si)_2CHLi \cdot 0.5\ Et_2O$ (0.4 g, 20 mmol) were stirred for 4 hours in toluene (30 mL). Yellow crystals of **25** were isolated as described in the case of **24**. Yield 0.30 g (30 % overall yield from **15**).

Anal. Calcd. for $C_{33}H_{59}Si_3Sc$: C, 67.75; H, 10.16. Found: C, 67.79; H, 9.66.

$Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$ (26): The same procedure was used as described for **9**. $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$ (0.35 g, 0.7 mmol) and PMe_3 (0.06 g, 0.8 mmol) were dissolved in petroleum ether (*ca.* 5mL) and after stirring for 12 hours under 4 atmospheres of dihydrogen, 0.23 g (78%) of **26** were isolated. Recrystallization from hot toluene yields **26** as yellow crystals.

Anal. Calcd. for $C_{23}H_{40}SiScP$: C, 65.68; H, 9.59. Found: C, 65.32; H, 9.32.

meso-**$Me_2Si(t\text{-butyl}C_5H_3)_2ScH$ (27):** The same procedure was used as described for **9**. *meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2ScCH_2SiMe_3$ (0.5 g, 1.16 mmol) was dissolved in petroleum ether (*ca.* 10ml), and after stirring for 12 hours under 4 atmospheres of dihydrogen, 0.24 g (60%) of **27** were isolated. Recrystallization from hot methylcyclohexane yielded **27** as white crystals.

Anal. Calcd. for $C_{20}H_{31}ScSi$: C, 69.73; H, 9.07. Found: C, 69.80; H, 8.98.

$Me_2Si(C_5Me_4)((+)\text{-menthyl}C_5H_3)ScH$ (28): **25** (0.2 g, 0.34 mmol) was dissolved in petroleum ether (5 mL) and the solution was loaded in a thick-walled glass bomb. One atmosphere of dihydrogen was admitted at -196°C, the system was warmed slowly to room temperature and stirred for 12 hours. The suspension formed was transferred to a frit and the solid product filtered as a yellow powder. Yield 0.085g (58%).

Anal. Calcd. for $C_{33}H_{59}SiSc$: C, 73.19; H, 9.69. Found: C, 71.52; H, 9.17.

X-ray Structure Determination of $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$: Crystals of $Me_2Si(C_5Me_4)_2ScCH(SiMe_3)_2$ were grown by slowly cooling a saturated solution of **21** in toluene from 100°C to room temperature and sealed in glass capillaries under dinitrogen to prevent decomposition. Photographs of an irregular crystal about 0.68 x 0.39 x 0.41 mm showed monoclinic symmetry. It was centered on a Nonius CAD-4 diffractometer equipped with graphite-monochromated MoKα radiation and cell dimensions plus an orientation matrix were obtained from the setting angles of 25 reflections with $40° < 2\theta < 47°$. Altogether 12,623 reflections were scanned in a θ-2θ mode in the quadrants $\pm h, \pm k, l$ with $3° \leq 2\theta \leq 50°$, including three check reflections measured every 10,000 seconds of X-ray exposure. The check reflections showed no fluctuations greater than those expected from counting statistics. Backgrounds were measured for each reflection at each end of the scan; an average background as a function of 2θ was calculated and used to correct the measured scan counts. Absences in the data of 0k0, k = 2n+1, and h0l, l = 2n+1 uniquely identify the space group as $P2_1/c$, #14. After deleting space group absences and merging equivalent reflections, 5174 reflections remained of which 4662 had $F_o^2 >$

0 and 4049 had $F_o^2 > 3\sigma(F_o^2)$. The data were corrected for Lorentz and polarization factors but not for absorption; μr_{max} is 0.17 and the two forms of data averaged together with a goodness of fit of 1.07. Variances of the individual reflections were assigned based on counting statistics plus an additional term, 0.014 I^2. Variances for the merged reflections were obtained by standard propagation of error plus another term, 0.014 $\overline{I}^2$. Scattering factors were taken from reference 19.

All 5174 measured reflections were used in the solution and refinement of the structure. The coordinates of the scandium atom were obtained from a Patterson map and the remaining non-hydrogen atoms were found with successive structure factor-Fourier calculations. After a few cycles of full-matrix least squares, minimizing $\sum w(F_o^2 - F_c^2)$, hydrogens atoms were included at idealized positions based on difference Fourier maps calculated in the planes where they were expected. A C-H distance of 0.95Å was assumed. Each hydrogen atom was given an isotropic thermal parameter of 10 % greater than that of the carbon to which it was bonded. The hydrogen parameters were not refined, but they were adjusted 3 times during the refinement. No hydrogen was assigned to C27, the carbon atom directly bonded to scandium, because that atom displayed planar coordination by scandium, Si2 and Si3. The least squares converged (all atoms anisotropic except C1-C5 and C11-C15) with R = 0.068 for all the reflections with $F_o^2 > 0$; the goodness of fit was 4.21. The thermal ellipsoid of C27 was elongated perpendicular to the Sc-Si2-Si3 plane, suggesting that C27 might be disordered, with half occupancy of a site above the plane and half below. A search of a three-dimensional difference map for a hydrogen atom bonded to C27 revealed two small peaks, one above and one below the plane, approximately where they were expected. Refinement continued with new hydrogen positions, all non-hydrogen atoms except C27 anisotropic, C27 split into two half atoms and including a secondary extinction parameter. At convergence, R = 0.054 and the goodness of fit was 3.31; for the data with $F_o^2 > 3\sigma(F_o^2)$, R = 0.045. The secondary extinction parameter refined to $0.72(7)X10^{-6}$.

X-ray Structure Determination of $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$: Crystals were grown by slowly cooling a saturated solution of **26** in toluene from 100°C to room temperature, and sealed

in glass capillaries under dinitrogen to prevent decomposition. Unit cell dimensions were obtained from the setting angles of 24 reflections (four members of each six forms) with $2\theta = 37°$. The three check reflections showed only small changes in intensity; no corrections were made for decay. The data were corrected for absorption, and the scandium, silicon and phosphorus were obtained from a Paterson map. A subsequent structure factor-Fourier calculation showed the 23 carbon atoms. Refinement was by full matrix least squares, with the methyl hydrogen atoms placed at calculated positions and then included in the refinement. The maximum excursion in the final difference map was +0.41 $e\text{Å}^{-3}$.

Calculations were done with programs of the CRYM Crystallographic Computing System and Ortep. Scattering factors and corrections for anomalous scattering were taken from the literature[17]. The final R-index was 0.065 and the final goodness of fit 1.45.

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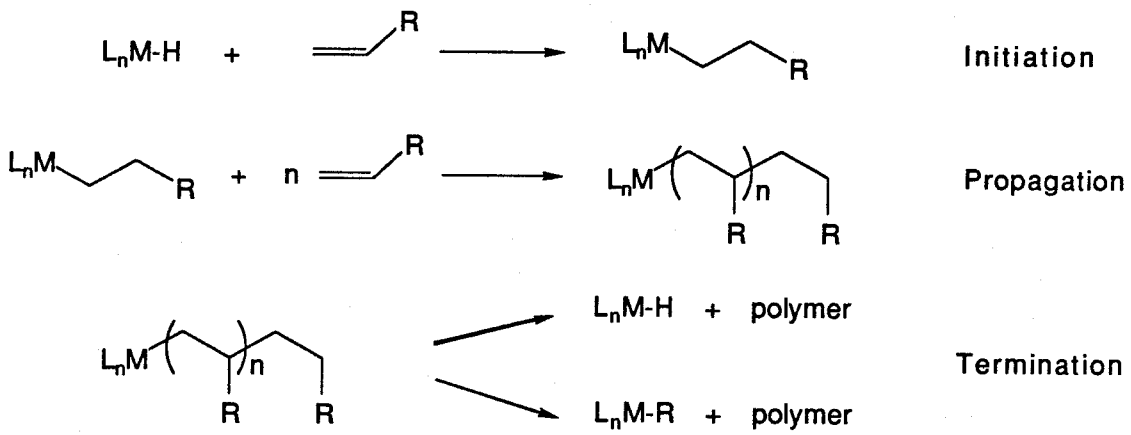
CHAPTER 2

CARBON-CARBON BOND FORMATION CATALYZED BY SCANDOCENE HYDRIDES DERIVATIVES. THE CATALYTIC DIMERIZATION OF α-OLEFINS AND CYCLIZATION OF α,ω-DIOLEFINS.

INTRODUCTION

The polymerization of olefins catalyzed by transition metal complexes constitutes a widely utilized procedure for the construction of carbon-carbon bonds. The polymerization or oligomerization of α-olefins is catalyzed by either soluble or insoluble catalysts, the former being better understood. Most of the work on the soluble catalysts had its origin in the work developed by Ziegler and Natta. The polymerization or oligomerization of α-olefins, promoted by Ziegler-Natta type catalysts (e.g. Cp_2TiCl_2-R_nAlCl_{3-n}), involves the following steps:[1]



The molecular weight distribution depends on the relative rates of the propagation and termination steps. A "Schultz/Flory" type molecular weight distribution is most common. However, two extreme situations can arise. If the rate of propagation is much greater than the rate of termination high molecular weight polymers are formed. If the rate of termination is much faster than the rate of propagation, only dimers are expected.

A new generation of Ziegler-Natta type catalysts,[2] those that do not require a co-catalyst, is based on bispentamethylcyclopentadienyl-early transition metal or -lanthanide alkyl or hydride derivatives. The first example reported was Cp^*_2Lu-CH_3.[3] This catalyst polymerizes

ethylene at a high rate to give high density polyethylene, even in the presence of Lewis bases such as diethylether. The insertion of ethylene into the metal-hydride or metal-alkyl bond provides a new metal-alkyl fragment which is a catalyst itself for the continued polymerization of ethylene. Mechanistic studies have provided evidence for a transition state wherein metal-carbon bond breaking and making occur concertedly.[4] From kinetic studies of the insertion of ethylene into the Sc-C bonds in the Cp^*_2Sc-R system, it was concluded that the rate of insertion is faster when the alkyl group is a long chain (Cp^*_2Sc-CH_3 compared with Cp^*_2Sc-$CH_2CH_2CH_3$).[4]

However, despite the ease with which ethylene is polymerized by catalysts of the type Cp^*_2M-R (M = lanthanide ; R = H, alkyl), higher olefins such as propene, 1-butene, or 1-pentene are oligomerized at best suggesting that the rate of termination is close to the rate of propagation and oligomers are normally obtained. Furthermore, decomposition pathways such as σ-bond metathesis severely limit catalyst lifetimes so that only a few turnovers have been observed.[5] This same type of behavior is widely found with Ziegler-Natta catalysts. The majority of the studies in this area have been intended to elucidate the mechanism of carbon-carbon bond formation. Practical applications for the synthesis of polymers and utilization of these compounds as catalysts for other simple transformations have not yet been reported.

Organoscandium complexes, based on the bispentamethylcyclopentadienyl scandium system,[6] react with α-olefins *via* a sigma-bond metathesis pathway, and hence no catalytic activity is expected. This chapter describes the olefin chemistry of the scandium-hydride compounds reported in Chapter 1. Surprisingly, we found that although α-olefins are not polymerized, there is a clean catalytic reaction which promotes almost exclusively the formation of head to tail dimers. Under the same conditions, α,ω-diolefins are catalytically converted to methylenecycloalkanes. Remarkably, the presence of nitrogen and sulfur in the α,ω-diolefin is tolerated by the catalyst. Further investigation showed that multiple insertions occur for

5-methylene-1,8-nonadiene and 5,8-dimethylene-1,11-dodecadiene in an intramolecular fashion to produce catalytically spiro hydrocarbons.

RESULTS AND DISCUSSION

Catalytic Dimerization of α-olefins

In order to evaluate the reactivity of $Cp^*Cp^oSc(H)(PMe_3)$, $Cp^*CpSc(\eta^1-\eta^5-C_5H_4)Cp^*Sc(H)$, $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$ and (*meso*-$(Me_2Si(t\text{-butyl}C_5H_3)_2ScH)_2$ with α-olefins, each was treated with excess propene (ca. 20 equivalents/mol Sc(H)) under the same conditions (solvent and concentration). The reactions were followed by ^1H NMR to monitor the disappearance of α-olefin. The time and the temperature required to complete the conversion of 20 equivalents of propene are shown in Table 1.

Table 1: Catalytic Dimerization of Propene

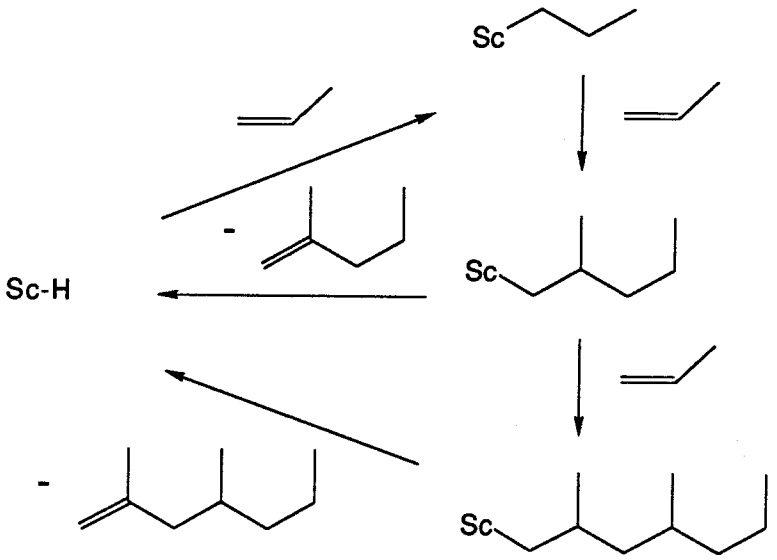
Complex	Conditions
$Cp^*Cp^oSc(H)(PMe_3)$	1 hr, 80°C
$Cp^*CpSc(\eta^1-\eta^5)CpCp^*Sc(H)$	18 hrs, 80°C
$[Me_2Si(t\text{-butyl}C_5H_3)_2Sc(H)]_2$	1 hr, 80°C
$Me_2Si(C_5Me_4)_2Sc(H))PMe_3)$	< 5 min, 25°C

In each case the product formed from propene was identified by NMR (^1H,^{13}C) and gas chromatography and corresponds to 2-methyl-1-pentene. Additionally, in the reaction with $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$ a small proportion (ca. 9%) of 2,4-dimethyl-1-heptene was formed.

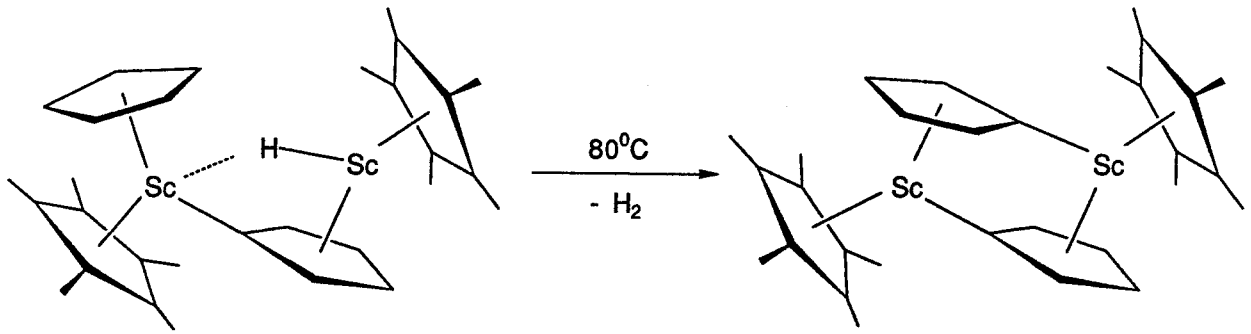
The observation that all of the scandium hydrides shown in Table 1 promote the selective head-to-tail insertion of propene to give only one dimer contrasts with product distributions obtained with other catalysts, for which the dimerization of propene affords a mixture of all four isomers.[7] The formation of only one dimer demonstrates the selectivity of the catalyst; the two

the two cyclopentadienyl ligands force olefin insertion to afford the least crowded of the alkyl intermediates. The catalytic cycle which explains the formation of 2-methyl-1-pentene and 2,4-dimethyl-1-heptene is shown in Scheme 1.

Scheme 1

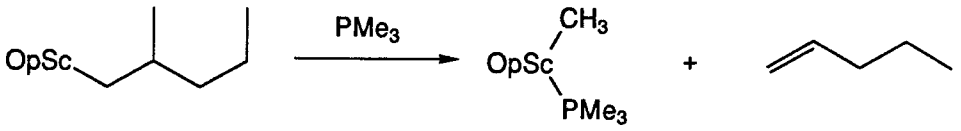


Unfortunately, Cp*Cp°Sc(H)(PMe_3) and Cp*CpSc(η^1-η^5-C_5H_4)Cp*Sc(H) decompose during the reaction, the former to unidentified products and the latter to **1**. The low thermal stability of Cp*Cp°Sc(H)(PMe_3) and Cp*CpSc(η^1-η^5-C_5H_4)Cp*Sc(H) discourages their use in promoting catalytic transformations. However, (*meso*-Me_2Si(*t*-butylC_5H_3)$_2$ScH)$_2$ (abbreviated (DpScH)$_2$) and $Me_2Si(C_5Me_4)_2$Sc(H)(PMe_3) (abbreviated OpSc(H)(PMe_3)) show higher thermal stability than the mixed ring scandium hydrides.



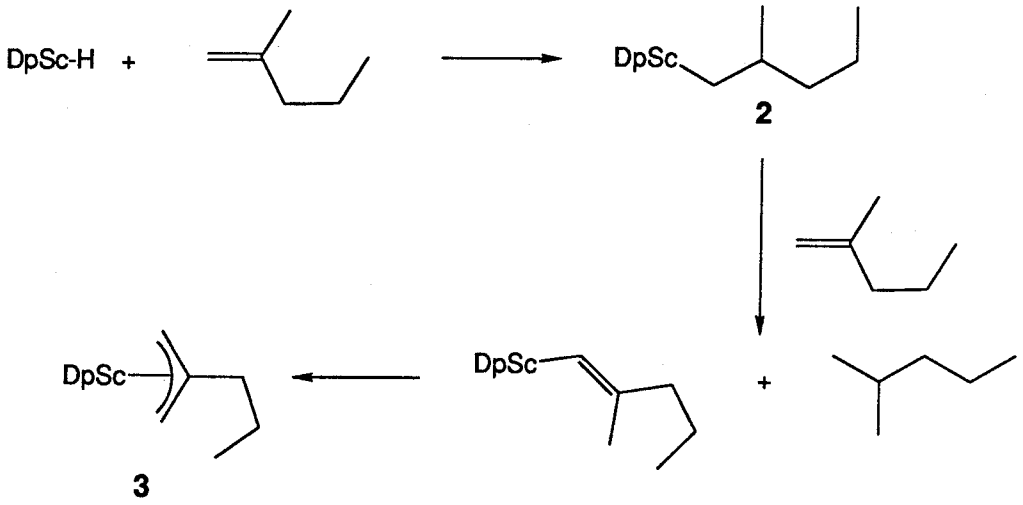
1

After all the propene is converted to 2-methyl-1-pentene in the $OpSc(H)(PMe_3)$ system, $OpSc\text{-}CH_2CH(CH_3)\text{-}CH_2CH_2CH_3$ is the only scandium product as characterized by ^1H NMR. Ultimately, $OpSc\text{-}CH_2CH(CH_3)\text{-}CH_2CH_2CH_3$ is converted to $OpSc(CH_3)(PMe_3)$ in approximately 24 hours at room temperature. Significantly, this reaction corresponds to β-methyl elimination, which has been recognized as a possible termination step in the polymerization of olefins.[8]



$(DpScH)_2$ exhibits a quite different behavior toward 2-methyl-1-pentene. When the dimerization of propene is carried out at 80°C, the final scandium compound is the π-allyl complex **3** as characterized by ^1H NMR. **3** can be independently prepared from the reaction of $(DpScH)_2$ and 2-methyl-1-pentene. A possible mechanism for the formation of **3** is given in Scheme 2.

Scheme 2



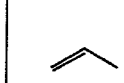
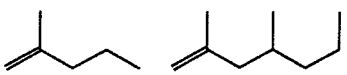
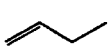
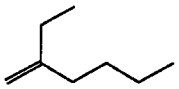
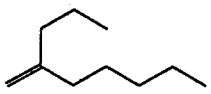
3 is probably formed *via* a 1,3-hydrogen shift in the sigma-bond metathesis product of **2** with 2-methyl-1-pentene. The same pathway, i.e. sigma-bond metathesis followed by a 1,3-hydrogen shift, will appear in several examples throughout this chapter. One characteristic of

$(DpScH)_2$ is that there is no spectroscopic (^1H NMR) evidence of the formation of **2** during the reaction, which is in contrast with the [OpSc] system where derivatives like **2** are always observed. This observation suggests that the stability of DpSc-alkyl complexes is rather low in comparison to that of OpSc-alkyl complexes and that processes such as olefin insertion and β-hydrogen elimination occur more readily in the former. The thermodynamic driving force for β-hydrogen elimination can be attributed to the stability of $(DpScH)_2$ formed.

When the dimerization of 20 equivalents of propene was conducted at 25°C, the total disappearance of starting material took approximately 72 hours, and the only scandium compound detected by ^1H NMR during the reaction is $(DpScH)_2$. Due to the remarkable stability of $(DpScH)_2$ in the presence of olefins, the dimerization of liquid α-olefins can be carried out in neat olefin without any noticeable decomposition of the catalyst during the reaction.

Propene is not the only α-olefin that can be dimerized; 1-butene and 1-pentene produce 2-ethyl-1-hexene and 2-propyl-1-heptene respectively. The conditions of the reactions and the purity of the products are shown in Table 2. The catalytic dimerization of 1-pentene and 1-butene by $(DpScH)_2$ must be carried out at 25°C; otherwise substantial isomerization of the double bond into internal positions is observed. The dimerization fails when attempted with bulky olefins such as allyltrimethylsilane or 4,4-dimethyl-1-pentene; in these cases only stoichiometric reactions are observed.

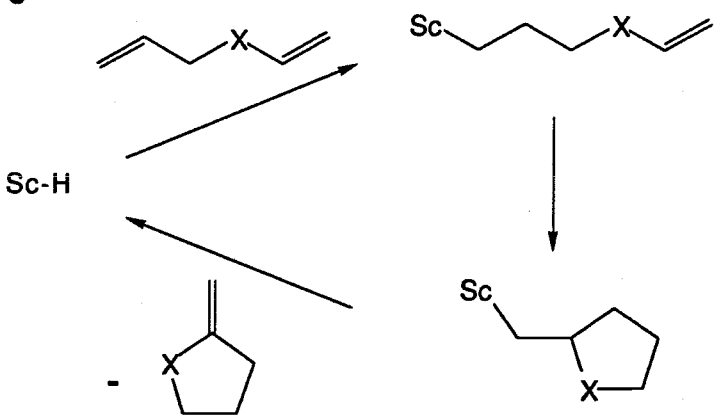
Table 2: Catalytic Dimerization of α,ω–Diolefins

		[DpSc-H]$_2$	OpSc(H)(PMe$_3$)
		40 equiv. / 1 hr, 80°C 96.4% ; 0%	45 equiv. / 1 hr, 25°C 90.6% ; 8.7%
		30 equiv. / 132 hrs, 25°C 99.9%	43 equiv. / 1 hr, 25°C 98%
		37 equiv. / 132 hrs, 25°C 99.2%	45 equiv. / 1 hr, 25°C 99.6%

Catalytic Cyclization of α,ω-diolefins

A transformation which is closely related to α-olefin dimerization takes place when $(DpScH)_2$ or $OpSc(H)(PMe_3)$ are treated with α,ω-diolefins. Both hydrides promote the catalytic cyclization of α,ω-diolefins to methylenecycloalkanes with ring sizes between 5 and 9 carbon atoms. The catalytic reaction proceeds analogously to the dimerization of α-olefins, but involves the intramolecular rather than intermolecular insertion of two olefins to produce cycloalkylmethylscandium derivatives, which undergo β-hydrogen elimination to produce a methylenecycloalkane. Scheme 3 shows the catalytic cycle for the formation of methylenecycloalkanes from α,ω-diolefins. The conditions required in the cyclizations and the purity of the methylenecycloalkanes formed are presented in Table 3.

Scheme 3



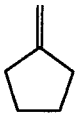
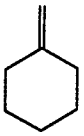
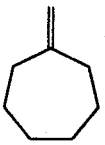
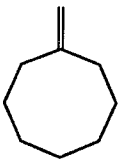
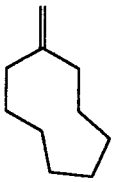
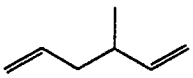
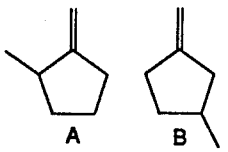
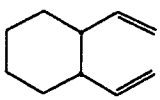
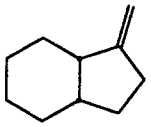
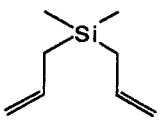
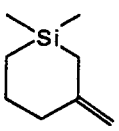
$X = (CH_2)_n$, n = 1,2,3,4,5

A noticeable difference is observed between $OpSc(H)(PMe_3)$ and $(DpScH)_2$ in the formation of C_7, C_8, and C_9 rings. The cyclization of 1,7-octadiene, 1,8-nonadiene and 1,9-decadiene to methylenecycloheptane, methylenecyclooctane and methylenecyclononane respectively, can only be achieved with $(DpScH)_2$ as catalyst; if $OpSc(H)(PMe_3)$ is used, a viscous material is formed, perhaps from intermolecular coupling.

The cyclization of 1,5-hexadiene to methylenecyclopentane with $(DpScH)_2$ as the catalyst must be performed at room temperature; otherwise a substantial amount of 1-methyl-

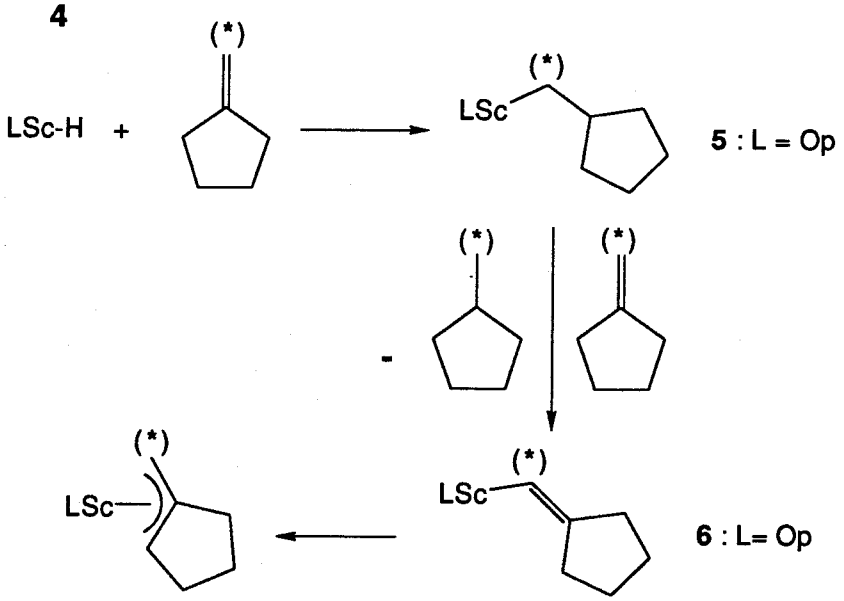
cyclopentene is formed (40% at 80 °C). The formation of 1-methyl-cyclopentene corresponds to double bond isomerization of the methylenecyclopentane formed initially.

Table 3: Catalytic Cyclization of α,ω–Diolefins

		[DpSc-H]$_2$	OpSc(H)(PMe$_3$)
		78 equiv./132 hrs, 25°C 99.2%	82 equiv./1 hr, 25°C 99.6%
		97 equiv./1 hr, 80°C 97.1%	76 equiv./1 hr, 25°C 96.8%
		20 equiv./ 72 hrs, 25°C 99.3%	
		16 equiv./ 72 hrs, 25°C 99.9%	
		11 equiv./ 72 hrs, 25°C 85.3%	
	 A B	18 equiv./ 10 min, 80°C A : 33%; B : 66%	23 equiv./ 10 min, 80°C A : 45%; B : 54%
		19 equiv./ 10 min, 80°C 99.9%	18 equiv./ 10 min, 80°C 99.5%
			18 equiv./ 10 min, 80°C 99.5%

When $(DpScH)_2$ is treated with excess 1,5-hexadiene at 80°C a π-allyl complex (4) is obtained. The formation of **4** can be explained analogously to the formation of **3**, as is shown in Scheme 4. The same type of structure is observed when $OpSc(H)(PMe_3)$ is treated with excess methylenecyclopentane. When the reaction of $OpSc(H)(PMe_3)$ with methylenecyclopentane, labelled with ^{13}C in the exocyclic carbon, was monitored by ^{13}C NMR, the first intermediate observed is **5** (54 ppm, t, J = 113Hz), which is rapidly converted to **6** (175 ppm, t, J = 102Hz), and finally to **7** (56 ppm, t, J = 142Hz). All other methylenecycloalkanes, from methylenecyclohexane to methylenecyclononane, react with $OpSc(H)(PMe_3)$ to give the cycloalkylmethylscandium derivatives which are unreactive under the same conditions to excess methylenecycloalkane.

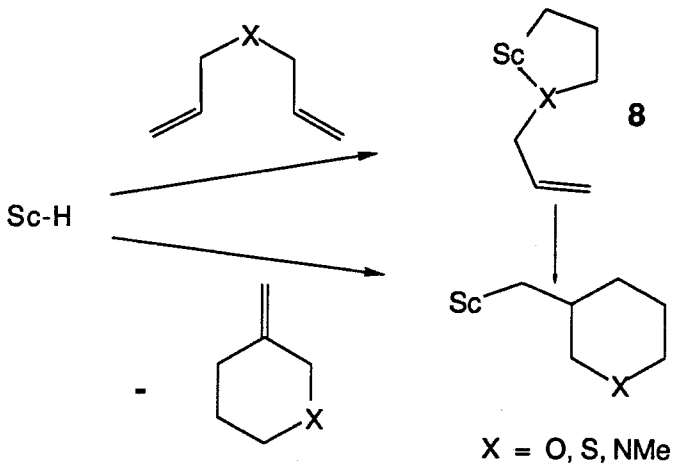
Scheme 4



Another variation of the catalytic cyclization is the preparation of heterocycles by introduction of heteroatoms into the chain. Surprisingly for an extremely Lewis acidic metal center, where binding of Lewis bases to the metal center is expected, nitrogen and sulfur were tolerated without noticeably decreasing the activity of the catalyst. Treating $OpSc(H)(PMe_3)$ with 10 to 15 molar excess of diallyl sulfide and bisallylmethylamine at 80°C gave 3-methyleneperhydro-thiane and 3-methylene-N-methylpiperidine as is shown in Scheme 5. The

steric bulk of the alkyl groups on the nitrogen of bisallylmethylamine likely prohibits binding of the nitrogen to scandium thus allowing catalytic cyclization to 3-methylene-N-methylpiperidine.

Scheme 5



When nitrogen or sulfur are replaced with oxygen, the intermediate **8** is very stable, and intramolecular insertion of the free double bond across the scandium-carbon bond occurred only slowly even at 120°C. Table 4 shows the conditions for these transformations and the purity of the heterocyclic compounds. Attempts to dimerize monoolefinic sulfides or ethers were unsuccessful, and only one insertion to produce compounds of general structure **9** was observed even at 140°C.

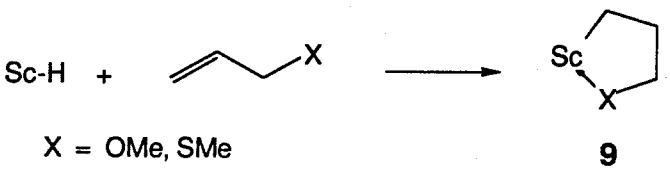
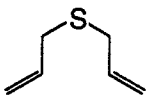
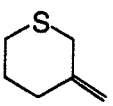
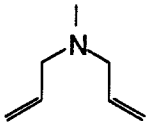
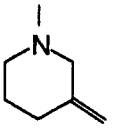
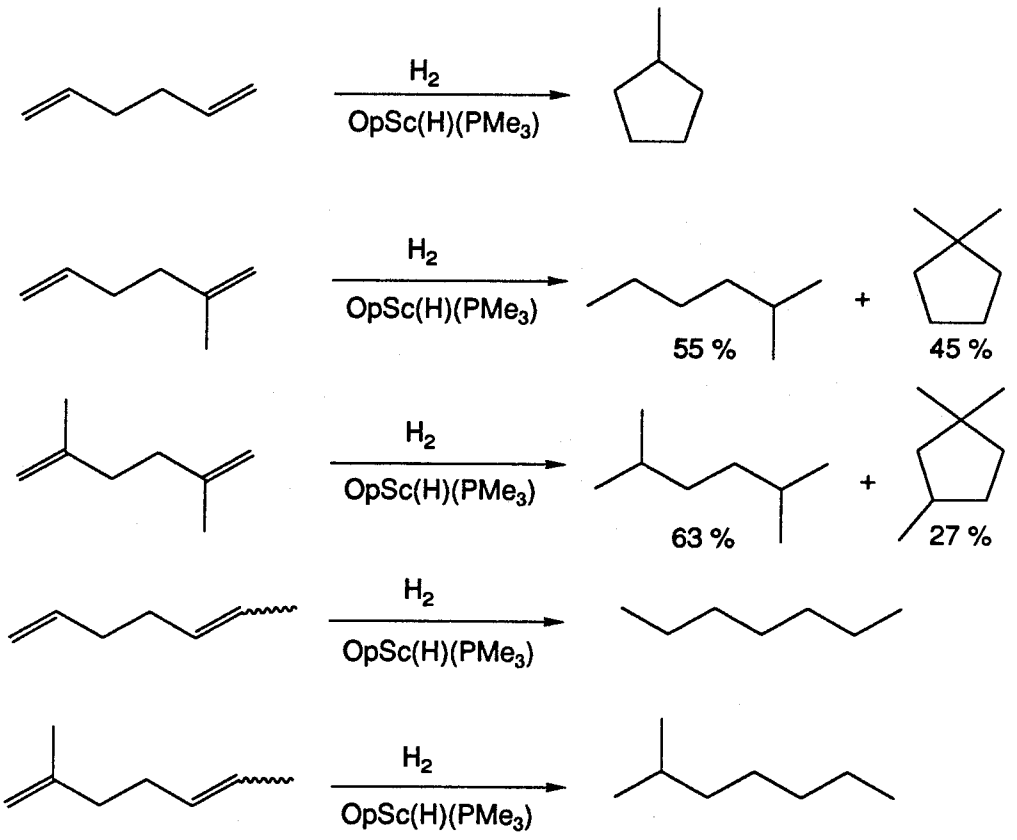


Table 4: Catalytic Cyclization of α,ω–Diolefins Containing Heteroatoms

		$OpSc(H)(PMe_3)$
		10 equiv. / 10 min, 80°C 99.5%
		27 equiv. / 10 min, 80°C 93%

After examining the cyclization of terminal diolefins we were interested in exploring the reactivity of internal olefins or β,β-disubstituted olefins for similar insertions. In order to do this, $OpSc(H)(PMe_3)$ was treated with several diolefins in the presence of hydrogen. The set of diolefins, together with the products formed under these conditions is shown in Scheme 6. The same reactions were also performed in the absence of hydrogen, and after 3 hours of stirring at 25 °C the reaction mixture was hydrogenated. The volatile materials from the hydrogenation were analyzed by NMR (^1H, ^{13}C) and/or gas chromatography. No significant difference was found in the composition of the products obtained by both methods.

Scheme 6



[Olefin]/[$OpSc(H)(PMe_3)$] = 10

Assuming that internal and β-β-disubstituted olefins may insert into a Sc-alkyl bonds and that addition of Sc-H to a carbon-carbon double bond always occurs in a anti-Markovnikov fashion, the intermediates **10** - **17**, shown in Scheme 7, are expected. In structures **10**, **12**, **14**, **15**, or **16**, a simple pathway to generate a free olefin would be *via* β-hydrogen elimination. However, β-hydrogen elimination only happens for **10**, and there is no evidence of formation of intermediates **12**, **14**, **15**, and **16**, from NMR or gc. Intermediates **11**, **13**, and **17** do not have β-hydrogens so there is no pathway to regenerate the Sc-H; hence, no catalytic activity is expected and none is observed. Moreover, β-methyl elimination, although possible, does not appear to take place for **11**, **13** or **17**.

From the results of Scheme 6 and the possible structures shown in Scheme 7 it is possible to conclude:

1. Sc-H adds to terminal, internal and β,β-disubstituted olefins. As expected from steric considerations, Sc-H adds to α-olefins faster than β,β-disubstituted terminal olefins or internal olefins.

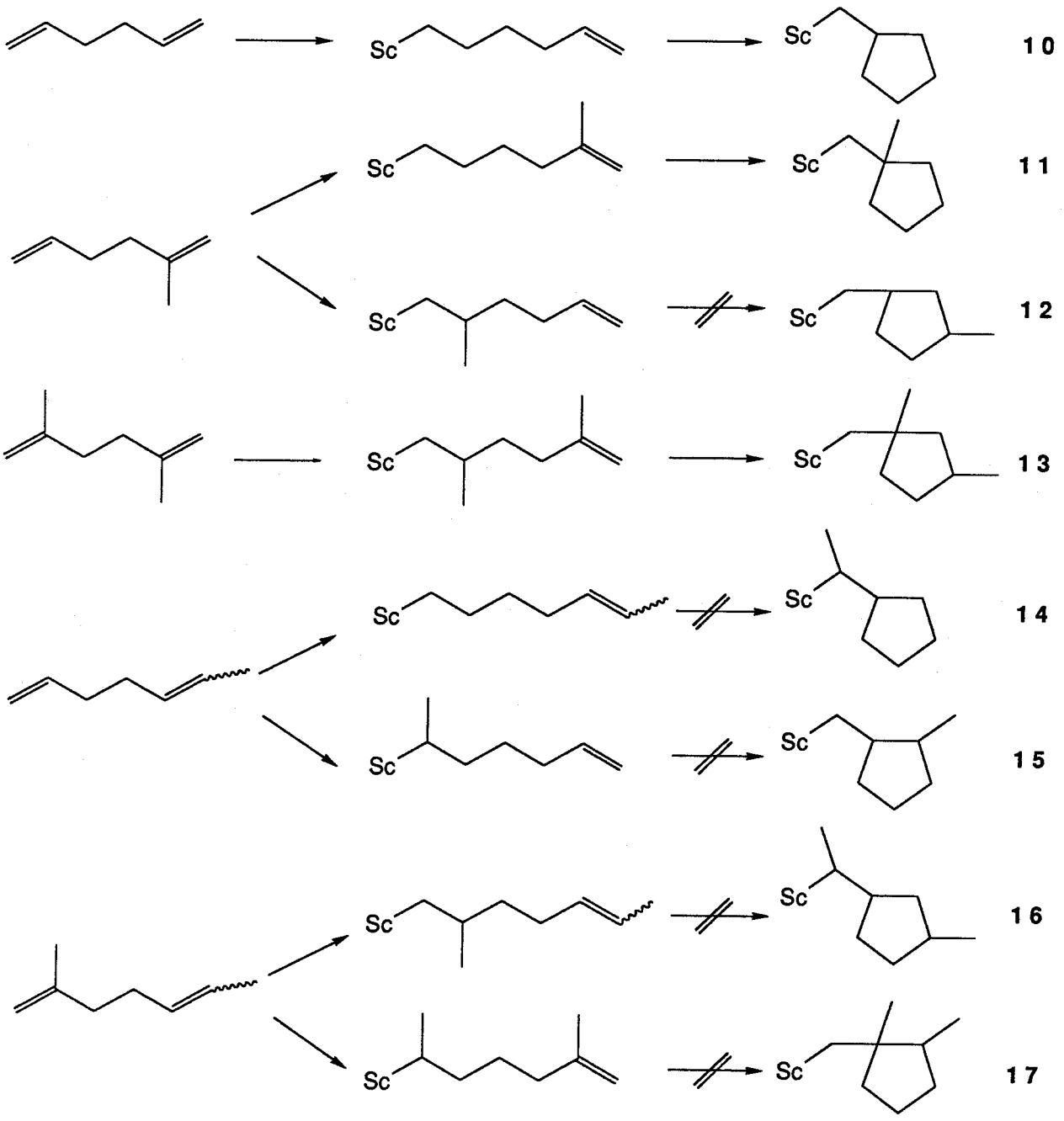
2. α-olefins insert into Sc-alkyl bonds faster than β,β-disubstituted terminal olefins do. Internal olefins do not insert into Sc-alkyl bonds.

To design a plausible catalytic transformation, a β-hydrogen is required in the last step to regenerate the scandium hydride and complete the catalytic cycle. Without this, the reaction can only be stoichiometric. A β-hydrogen can be obtained only from insertion of α-terminal or internal olefins into Sc-alkyl bonds. Since internal olefins do not insert into Sc-alkyl bonds, the only useful substrates are those with at least one terminal olefin.

As an extension, $OpSc(H)(PMe_3)$ and $(DpScH)_2$ were treated with α,ω-diolefins which contain exomethylene units along the chain. Clean conversion to spiro hydrocarbons is found. Treating $(DpScH)_2$ or $OpSc(H)(PMe_3)$ with excess 5-methylene-1,8-nonadiene and 5,8-dimethylene-1,11-dodecadiene results in the catalytic formation of 2-

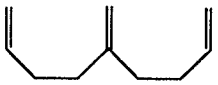
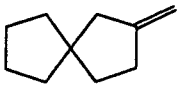
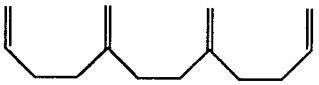
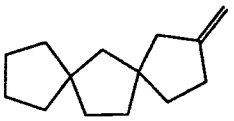
methylenespiro[4.4]nonane and 2-methylenedispiro[4.1.4.2]tridecane, respectively, as shown in Scheme 8. The catalytic conditions and the purity of the compounds are shown in Table 5.

Scheme 7

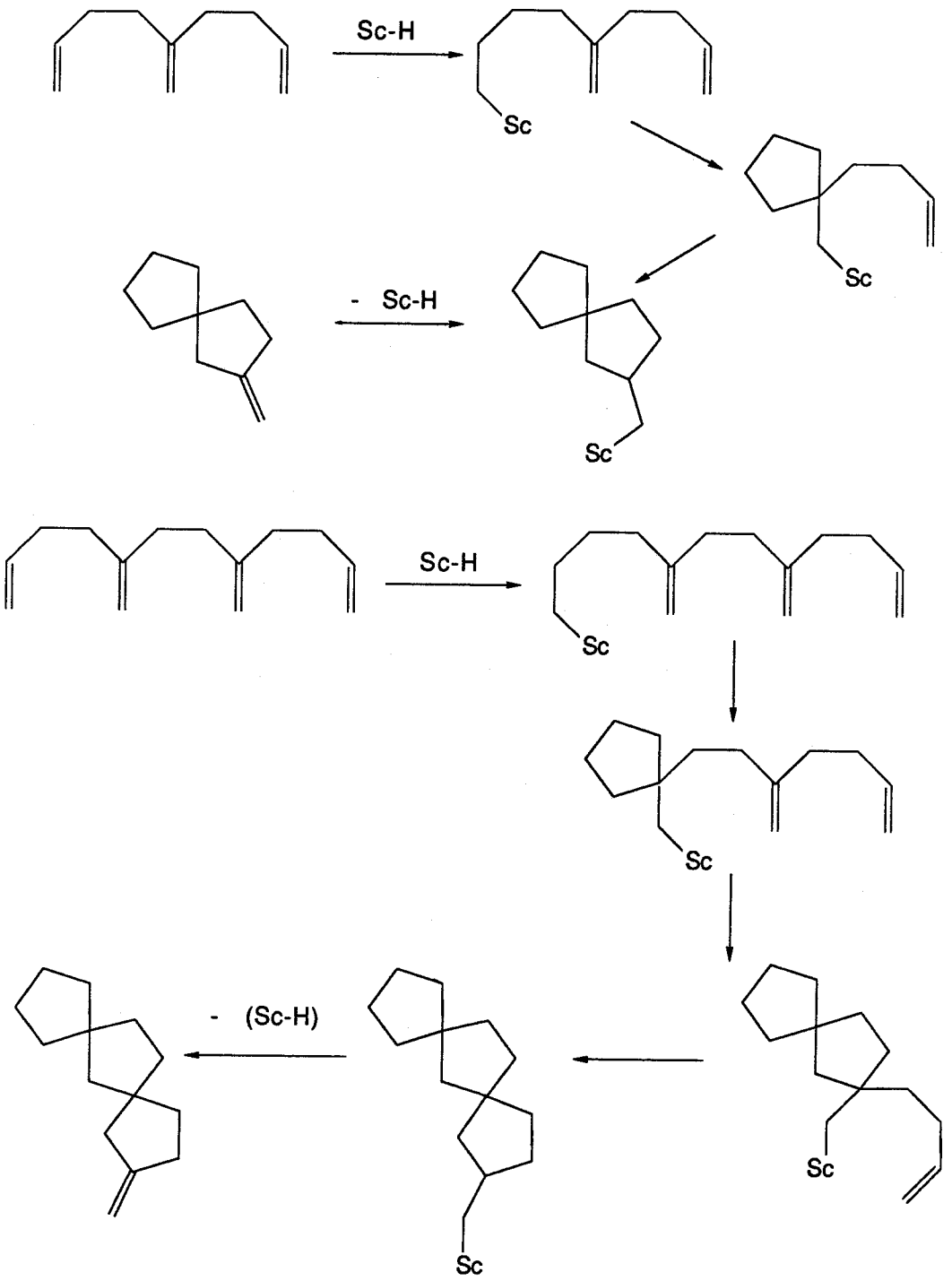


This last transformation, quite apart from being important from a synthetic point of view, shows that multiple insertion of olefins into scandium alkyl bonds are possible, but only in an intramolecular fashion.

Table 5: Catalytic Formation of Spiro Hydrocarbons

		$[DpSc\text{-}H]_2$	$OpSc(H)(PMe_3)$
		7 equiv. 10 min, 80°C 90.1%	8 equiv. 10 min, 80°C 92.9%
		12 equiv. 24 hrs, 25°C 85.7%	12 equiv. 30 min, 25°C 98.8%

Scheme 8



CONCLUSIONS

The introduction of a dimethylsilicon bridge between the rings in the bis(pentamethylcyclopentadienyl)scandium system significantly increases the reactivity for sterically sensitive processes such as olefin insertion into a scandium-carbon bond. Thus, $Me_2Si(C_5Me_5)_2Sc(H)(PMe_3)$ and (*meso*-Me_2Si(t-butyl$C_5H_3)_2ScH)_2$ catalyze the head to tail dimerization of α-olefins, the catalytic cyclization of α,ω-diolefins to methylenecycloalkanes, and the cascade cyclization of polymethylene α,ω-diolefins to spiro hydrocarbons. Key steps in these catalytic transformations are olefin insertion and β-hydrogen elimination. From the experimental data described previously, the following conclusions are drawn:

1. α-Olefins, β,β-disubstituted terminal olefins, and internal olefins add across the scandium hydride bond.

2. α-Olefins insert into scandium-alkyl bonds. After this insertion occurs, a β-hydrogen is available on a tertiary carbon, and β-hydrogen elimination occurs readily.

3. β,β-Disubstituted olefins insert into scandium alkyl bonds in an intramolecular fashion. Further insertion of a second equivalent of α-olefin or β,β-disubstituted olefin occurs in an intramolecular fashion and this process continues until a β-hydrogen is available, whereupon β-hydrogen elimination releases olefin.

4. Internal olefins do not insert into scandium-alkyl bonds.

5. Vinylic C-H bond activation is slow relative to olefin insertion and is observed only after catalytic oligomerization is completed.

Table 6 : ^{1}H, ^{13}C NMR Data (C_6D_6, 400MHz)

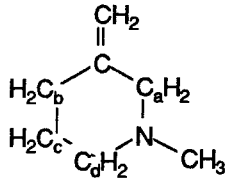
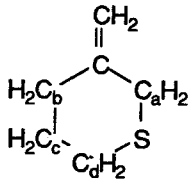
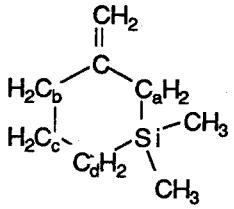
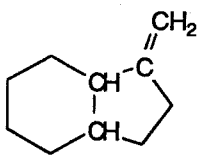
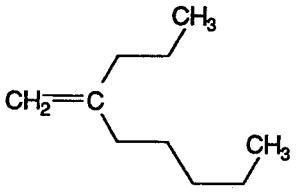
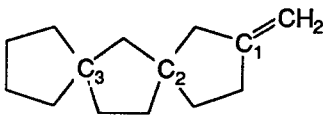
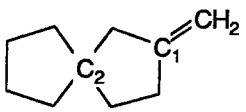
	^{1}H NMR : δ (ppm)	^{13}C NMR : δ (ppm)
	CH_3 : 2.08(s) $=CH_2$: 4.74(s), 4.71(s) C_1H_2 ,C_3H_2 : 2.19(m), 1.97(m) C_2H_2 : 1.52(m)	CH_3 : 46 $C_{a\text{-}d}H_2$: 62, 56, 32, 26 $=CH_2$: 108 C : 145
	C_aH_2 : 2.9(s) C_bH_2, C_dH_2 : 2.3(m), 1.9(m) C_cH_2 : 1.6(m) $=CH_2$: 4.6(s)	$C_{a\text{-}d}H_2$: 35.3, 35.1, 31, 29 $=CH_2$: 108.5 C : 145
	CH_3 : -0.02(s) C_aH_2 : 1.51(s) C_bH_2 : 0.5(m) C_cH_2 : 1.68(m) C_dH_2 : 2(m)	CH_3 : -3 $C_{a\text{-}d}H_2$: 39, 27.5, 26, 14 $=CH_2$: 107 C : 149
	CH_2 : 4.98(s), 4.90(s)	CH_2 : 30.4, 28.9, 27.8, 26.7, 24.7, 22.5 CH : 44.4, 39.8 $=CH_2$: 105 C : 154
	CH_2 : 4.73(s)	CH_3 : 14.2, 14 CH_2 : 38, 36, 32, 28, 23, 21 $=CH_2$: 109 C : 150
	$=CH_2$: 4.98, 4.95	CH_2 : 52, 48, 40.9, 40.7, 40.5 39, 38, 32, 24.7, 24.6 $=CH_2$: 106 C_1 : 152 C_2, C_3 : 50.8, 50.3
	$=CH_2$: 4.9	CH_2 : 46.6, 38.8, 38.2, 31.9, 25 $=CH_2$: 105 C_1 : 152 C_2 : 50.7

Table 7 : ^{1}H and ^{13}C NMR Data (C_6D_6)

Compound	Assignment	δ(ppm) and Coupling(Hz)
Cp*Sc(η^1-η^5-C_5H_4)$_2$ScCp*		
	$C_5(CH_3)_4$	2.0(s)
	η^1-$\eta^5C_5H_4$	7.0(m); 5.2(m)
	$C_5(CH_3)_4$	11.8(q, 126)
	$C_5(CH_3)_4$	121(s)
	η^1-η^5-C_5H_4	123(d, 161); 122(d, 162)
OpSc(CH_3)($P(CH_3)_3$)		
	$(CH_3)_2Si$	0.94(s)
	$C_5(CH_3)_4$	2.02(s); 1.98(s)
	Sc-CH_3	-0.77(s)
	Sc-$P(CH_3)_3$	0.66(d, 3.4)
	$(CH_3)_2Si$	4.4(q, 120)
	$C_5(CH_3)_4$	15(q, 126); 13(q, 125)
	$C_5(CH_3)_4$	126(s); 121.5(s); 101.7(s)
	Sc-CH_3	not located
	Sc-$P(CH_3)_3$	14.2(J_{PC}=8.6, J_{CH}=128)
DpSc-(η^3-$CH_2CCHCH_2CH_2CH_2$)		
	$(CH_3)_2Si$	0.72(s); 0.21(s)
	$C_5H_3(C(CH_3)_3)$	1.15(s)
	$C_5H_3(C(CH_3)_3)$	6.63(m); 6.03(m); 5.35(m)
	$CH_2CCHCH_2CH_2CH_2$	5.28(m)
	$CH_2CCHCH_2CH_2CH_2$	2.64(s)
	$CH_2CCHCH_2CH_2CH_2$	not located
	$CH_2CCHCH_2CH_2CH_2$	1.84(m)
	$CH_2CCHCH_2CH_2CH_2$	not located

$(\mathbf{C}H_3)_2Si$	-2.2(q, 120); -6.6(q, 122)
$C_5H_3(C(\mathbf{C}H_3)_3)$	32(q, 127)
$C_5H_3(\mathbf{C}(CH_3)_3)$	32.8(s)
$\mathbf{C}_5H_3(C(CH_3)_3)$	149(s); 114(s); 117(d,167), 114(d,174); 110(d,164)
$\mathbf{C}H_2\overset{\frown}{C}CHCH_2CH_2CH_2$	52
$CH_2\overset{\frown}{\mathbf{C}}CHCH_2CH_2CH_2$	168(s)
$CH_2\overset{\frown}{C}\mathbf{C}HCH_2CH_2CH_2$	91(d, 151)
$CH_2\overset{\frown}{C}CH\mathbf{C}H_2\mathbf{C}H_2\overset{\frown}{C}H_2$	41.6(t, 128); 33(t, 130); 22.6(t, 131)

DpSc-(η^3-$CH_2C(CH_2CH_2CH_3)CH_2$)

$(CH_3)_2Si$	0.73(s); 0.20(s)
$C_5H_3(C(CH_3)_3$	1.11(s)
$C_5\mathbf{H}_3(C(CH_3)_3$	6.7(m); 6.1(m); 5.6(m)
$CH_2C(CH_2CH_2\mathbf{C}H_3)CH_2$	1.0(t, 7.3)
$\mathbf{C}H_2C(CH_2CH_2CH_3)\mathbf{C}H_2$	2.4(s)
$(CH_3)_2Si$	-1.9(q, 120); -6.5(q, 120)
$C_5H_3(C(\mathbf{C}H_3)_3)$	31.7(q, 128)
$C_5H_3(\mathbf{C}(CH_3)_3)$	31.9(s)
$\mathbf{C}_5H_3(C(CH_3)_3)$	148(s); 114(s); 118(d, 170); 114(d,159); 110(d, 172)
$\mathbf{C}H_2C(CH_2CH_2CH_3)\mathbf{C}H_2$	66
$CH_2\mathbf{C}(CH_2CH_2CH_3)CH_2$	172(s)
$CH_2C(\mathbf{C}H_2CH_2CH_3)CH_2$	47(t, 130)
$CH_2C(CH_2\mathbf{C}H_2CH_3)CH_2$	25(t, 127)
$CH_2C(CH_2CH_2\mathbf{C}H_3)CH_2$	14.4(q, 125)

OpSc-(η^3-$CH_2\overline{CCHCH_2CH_2CH_2}$)

$(CH_3)_2Si$	0.88(s)
$C_5(CH_3)_4$	2.02(s); 1.75(s)
$CH_2\overline{CCHCH_2CH_2CH_2}$	2.37(s)
$CH_2\overline{CCHCH_2CH_2CH_2}$	2.72(m)
$CH_2\overline{CCHCH_2CH_2CH_2}$	4.9(m)
$CH_2\overline{CCHCH_2CH_2CH_2}$	not located
$(CH_3)_2Si$	4.8(q, 118)
$C_5(CH_3)_4$	15(q, 121); 13(q, 120)
$C_5(CH_3)_4$	104(s); 121(s); one not located
$CH_2\overline{CCHCH_2CH_2CH_2}$	56(t, 141)
$CH_2\overline{CCHCH_2CH_2CH_2}$	170(s)
$CH_2\overline{CCHCH_2CH_2CH_2}$	91(d, 147)
$CH_2\overline{CCHCH_2CH_2CH_2}$	40(t, 127); 32.7(t,126)
$CH_2\overline{CCHCH_2CH_2CH_2}$	25(t, 127)

EXPERIMENTAL

$Cp^*Cp^0Sc(H)(PMe_3)$, $Cp^*CpSc\text{-}(\eta^1\text{-}\eta^5)Cp^*Sc(H)$, (*meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2ScH)_2$, and $Me_2Si(C_5Me_4)_2Sc(H)(PMe_3)$ were prepared as described in Chapter 1. Propene, 1-butene (Matheson) were degassed by several freeze-pump-thaw cycles. 1-Pentene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, allyl ether, allyl sulfide, allyl ethyl ether, allyl methyl sulfide, 2-methyl-1,5-hexadiene, allyl trimethylsilane, 4,4-dimethyl-1-pentene, 3-methyl-1,5-hexadiene (all Aldrich), cis-divinylcyclohexane (Alfa), 1,5-heptadiene, diallyldimethyl silane, diallylmethyl amine (all Pfaltz & Bauer), and 2-methyl-1,5-heptadiene (K & K) were dried over molecular sieves 4 Å, and then vacuum transferred prior to use. 5-Methylene-1,8-nonadiene was prepared according to a published procedure.[9] 5,8-Dimethylene-1,11-dodecadiene was prepared *via* Wittig reaction of dodeca-1,11-dien-5,8-dione[10] with two equivalents of $CH_2=P(C_6H_5)_3$ in benzene.

The standards for NMR and/or gc, methylenecyclopentane, methylenecyclohexane, 2-methyl-1-pentene, methylcyclopentane, 1-methyl-1-cyclopentene, 2-methyl-hexane, 2-methyl-heptane, heptane, and 2,5-dimethylhexane (all Aldrich) were used as received. Methylenecycloheptane, methylenecyclooctane, methylenecyclononane, and 2-ethyl-1-hexene were prepared *via* Wittig reaction of cycloheptanone, cyclooctanone, cyclononanone, and 3-heptanone (all Aldrich) respectively with $CH_2=P(C_6H_5)_3$ in benzene. The specifically labeled $^{13}C\text{-}C_1$Methylenecyclopentane[11] and $CH_2=P(C_6H_5)_3$[12] were prepared as reported in the literature.

NMR spectra were recorded on Varian EM-390 (^1H, 90MHz) and JEOL GX 400 (^1H:399.78MHz, ^{13}C:100.38MHz) instruments. The gc analyses were carried out in either a Hewlett-Packard 5790-A using a 4 m column packed with 5% B,B-Oxydipropionitrile on Chromosorb W or in a Perkin-Elmer 8410 using a RSL-150 (Alltech) column.

General Procedure for Olefin Dimerization: The scandium hydride (*ca.* 0.06-0.07 mmol) was loaded into an NMR tube and benzene-d_6 (*ca.* 0.5 g) was added to the tube. A rubber septum was fitted onto the tube and it was sealed with "Parafilm". The substrate was added *via* syringe. Experiments involving propene and 1-butene were performed in sealed NMR tubes. The reaction was monitored by ^1H NMR. Chromatographic analyses were performed either by injecting the solution directly into the gc or, after the volatiles were vacuum transferred (10^{-4} torr, 25°C to 100°C) using a high vacuum line, by injecting volatile components into the gc.

General Procedure for Hydrogenation: $OpSc(H)(PMe_3)$ (*ca.* 30 mg, 0.07 mmol) and benzene-d_6 (*ca.* 0.5 g) were loaded into a thick-walled reaction vessel. The benzene was frozen at -80°C, and the diolefin (*ca.* 5 to 7-fold molar excess) was added *via* syringe under an argon counterflow. The reaction vessel was evacuated, and one atmosphere of dihydrogen was admitted at -196°C. The mixture was warmed to room temperature and stirred for 30 minutes. The excess hydrogen was released, and the volatile materials were vacuum transferred and analyzed by NMR (^1H or ^{13}C) and/or gc.

$Cp^*Sc(\eta^1\text{-}\eta^5\text{-}C_5H_4)_2ScCp^*$: $Cp^*CpSc(\eta^1\text{-}\eta^5\text{-}C_5H_4)Cp^*ScH$ (0.5 g, 1.02 mmol) were dissolved in 5 mL of methylcyclohexane. The solution was heated at 80°C for four days. The solution was cooled to room temperature and transferred to a frit-assembly. Methylcyclohexane was removed *in vacuo* and replaced with petroleum ether (*ca.* 5 mL). The yellow solid was filtered and dried. Yield 0.21 g (42.1%).

Anal. Calcd. for $C_{15}H_{19}Sc$: C, 73.55; H, 8.22. Found: C, 73.71; H, 7.88.

$Me_2Si(C_5Me_4)_2Sc(CH_3)(PMe_3)$: $OpSc(H)(PMe_3)$ (0.3 g, 0.71 mmol) and 2-methyl-1-pentene (90 μL, 0.73 mmol) were dissolved in petroleum ether (*ca.* 5 mL). The solution was stirred at room temperature for 24 hours. The yellow precipitate, $Me_2Si(C_5Me_4)_2Sc(CH_3)(PMe_3)$, was filtered and dried. Yield 0.22 g (71%).

Anal. Calcd. for $C_{24}H_{42}ScSiP$: C, 66.33 H, 9.74. Found: C, 66.07 H, 9.48.

$Me_2Si(C_5Me_4)_2Sc$-(η^3-$CH_2\overline{CCHCH_2CH_2CH_2}$) : OpSc(H)($PMe_3$) (0.35 g, 0.83 mmol) and methylenecyclopentane (0.45 mL, 4.3 mmol) were dissolved in petroleum ether (*ca.* 7 mL). The solution was stirred at room temperature for 24 hours. Petroleum ether and excess methylenecyclopentane were removed *in vacuo* and replaced with fresh petroleum ether (*ca.* 10 mL). The solution was cooled to -78°C for three hours to afford $Me_2Si(C_5Me_4)_2Sc$-(η^3-$CH_2\overline{CCHCH_2CH_2CH_2}$). Yield 0.28 g (79.2%).

Anal. Calcd. for $C_{26}H_{39}SiSc$: C, 73.54, H, 9.26. Found: C, 73.40, H, 9.66.

***meso*-Me_2Si(*t*-butyl$C_5H_3)_2Sc$-(η^3-$CH_2\overline{CCHCH_2CH_2CH_2}$)** : DpScH (0.30 g, 0.87 mmol) and methylenecyclopentane (0.30 mL, 2.85 mmol) were dissolved in petroleum ether (*ca.* 10 mL). The solution was heated to 80°C for 5 hours. Petroleum ether and excess methylenecyclopentane were removed *in vacuo* and replaced with fresh petroleum ether (*ca.* 10 mL). The solution was cooled to -78°C for three hours to afford *meso*-Me_2Si(*t*-butyl$C_5H_3)_2Sc$-(η^3-$CH_2\overline{CCHCH_2CH_2CH_2}$). Yield 0.2 g (54 %).

Anal. Calcd. for $C_{26}H_{39}SiSc$: C, 73.54, H, 9.26. Found: C, 73.56, H, 9.53.

***meso*-Me_2Si(*t*-butyl$C_5H_3)_2Sc$-(η^3-$CH_2C(CH_2CH_2CH_3)CH_2$)** : DpScH (0.35 g, 1.02 mmol) and 2-methyl-1-pentene (0.6 mL, 4.86 mmol) were dissolved in petroleum ether (ca. 10 mL). The solution was heated to 80°C for two hours. Petroleum ether and excess 2-methyl-1-pentene were removed in vacuo and replaced with fresh petroleum ether (*ca.* 10 mL). The solution was cooled to -78°C overnight to afford *meso*-Me_2Si(*t*-butyl$C_5H_3)_2Sc$-(η^3-$CH_2C(CH_2CH_2CH_3)CH_2$). Yield 0.15 g, (34.6%).

Anal Calcd. for $C_{26}H_{41}SiSc$: C, 73.19, H, 9.68. Found: C, 72.87, H 9.25.

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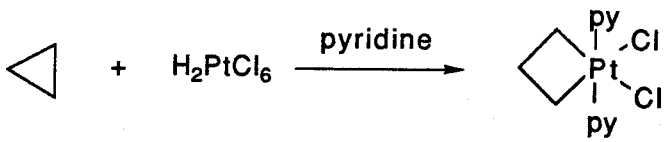
CHAPTER 3

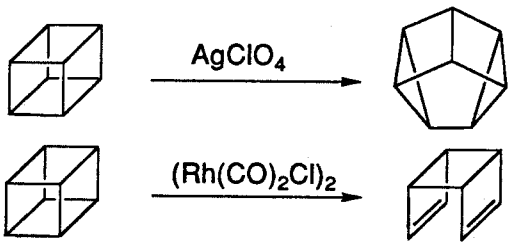
CARBON-CARBON BOND ACTIVATION VIA β-ALKYL ELIMINATION. REVERSIBLE BRANCHING OF 1,4-PENTADIENES CATALYZED BY SCANDOCENE HYDRIDE DERIVATIVES.

INTRODUCTION

Although impressive advances have recently been made in activating carbon-hydrogen bonds of hydrocarbons,[1] the activation of carbon-carbon bonds by soluble transition-metal complexes remains one the most prominent challenges in organometallic chemistry. The first example of carbon-carbon bond activation dates back to 1955 when it was reported that H_2PtCl_6 reacts with cyclopropane to give a platinacyclobutane.[2]



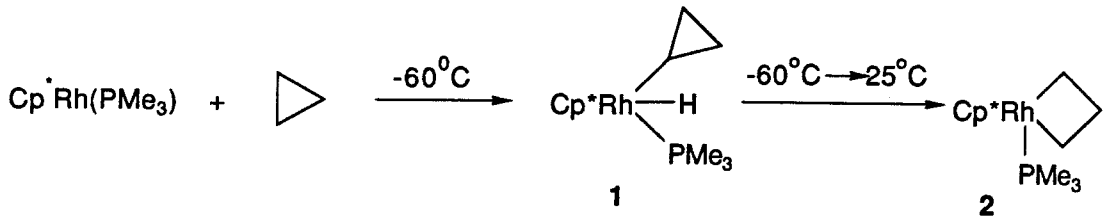
The silver- and rhodium-catalyzed rearrangements of strained hydrocarbons are further examples of the same type of reaction.[1a] The silver system probably involves an electrophilic attack of Ag^+ at the C-C bond, while that for rhodium involves an oxidative addition process.



Another approach to C-C bond activation is the generation of "naked" metal atoms both in the gas phase and in matrices which react with alkanes. In the case of Fe^+ ions, generated in the gas phase, C-C bond cleavage is the preferred mode of activation.[3] This preference for C-C bond activation correlates with the relative $Fe\text{-}CH_3^+$ and $Fe\text{-}H^+$ bond strengths of 69 ± 5 kcal·mol^{-1} and 58 ± 5 kcal·mol^{-1}, respectively.[4]

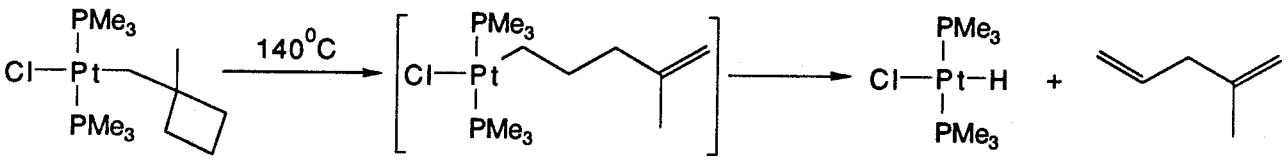
Despite the preference for C-C bond cleavage by "naked" metal atoms cations, C-C bond activation by transition metal complexes is slow due to the poor steric accessibility of the metal center. As a result of this steric disadvantage, saturated hydrocarbons interact with transition

metal centers through their C-H bonds. This suggests that one route to C-C activation could be *via* prior C-H bond activation. For example, only C-H activation occurs when the unsaturated fragment [Cp*Rh(PMe_3)] is treated with cyclopropane, to yield **1** at -60 °C. **1** rearranges at higher temperatures, via C-C bond activation, to give **2**.[5]



1 **2**

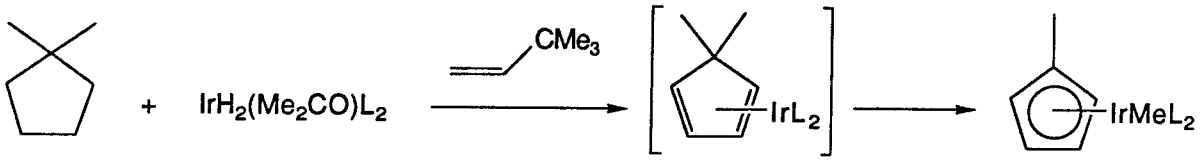
A platinum system that does not involve a initial C-H activation has been reported.[6] Thermolysis of **3** yielded 2-methyl-1,4-pentadiene as the only organic product. This reaction proceeds through the formation of **4** *via* β-alkyl elimination, which then undergoes β-hydrogen elimination to give 2-methyl-1,4-pentadiene and $Pt(PMe_3)_2(H)(Cl)$.



3 **4**

The absence of β-hydrogens in **3** guarantees that the only pathway for decomposition is *via* β-alkyl elimination. β-hydrogen elimination is generally much faster providing a well-known route for the decomposition of metal-alkyl fragments.[7]

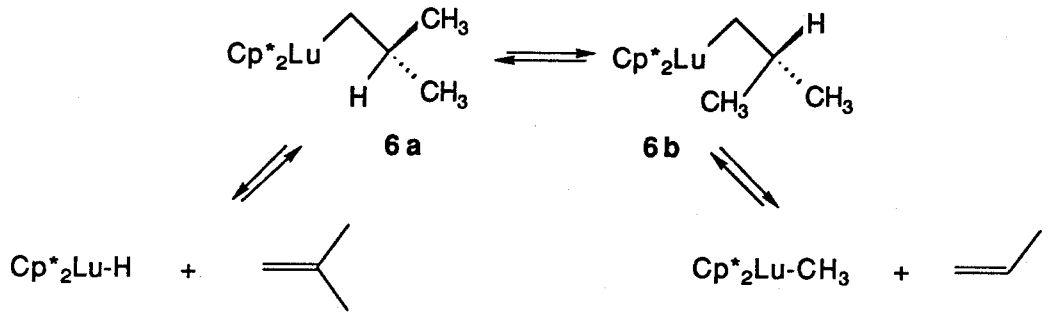
In most of the examples described in the literature, the driving force for β-alkyl elimination is the relief of strain in the hydrocarbon fragment. However, a few examples where strain is not involved have been reported. One example is the reaction of $Ir_2H_2(Me_2CO)_2L_2$ (L=PR_3) with dimethylcyclopentane in the presence of *t*-butylethylene to yield **5** as the isolable product.[8]



5

In this example, a methyl group from the cyclopentane ring is transferred to Ir. The exact mechanism of the reaction is still unclear, however.

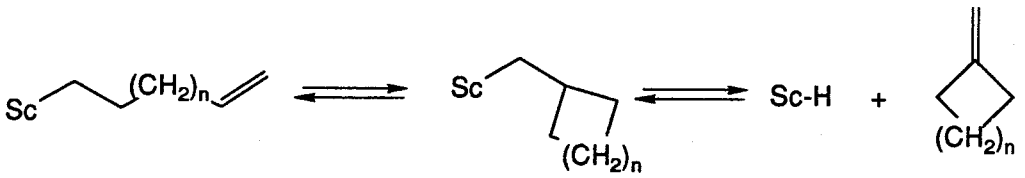
In the thermal decomposition of $Cp^*_2LuCH_2CHMe_2$ in which there is no associated ring strain, both β-hydrogen and β-alkyl elimination occur competitively. The propene resulting from the β-methyl elimination is removed from the equilibrium mixture by subsequent reactions. For this reaction, a four centered transition state (**6a** or **6b**) was proposed to explain both migrations. The transition state derived from conformation **6b** is more favorable than that derived from **6a** due to the orientation of the methyl groups with respect to the Cp* rings. This renders β-alkyl elimination an important decomposition pathway for $Cp^*_2LuCH_2CHMe_2$.[9]



The observation that, in the $[Cp^*_2Lu]$ system, olefin insertion into metal-hydride or metal-alkyl bonds and β-hydrogen and/or β-alkyl elimination occur competitively opens the possibility for a new variety of catalytic transformations involving C-C bond making and breaking. This chapter describes a scandocene hydride complex which catalyzes the reversible branching and cyclization of 1,4-pentadienes. The key feature responsible for this unusual reactivity is reversible olefin insertion and β-alkyl elimination.

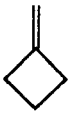
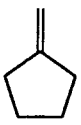
RESULTS AND DISCUSSION

In the previous chapter it was shown that (*meso*-$Me_2Si(t\text{-butyl}C_5H_3)_2Sc\text{-}H)_2$ ($(DpScH)_2$) promotes the catalytic cyclization of α, ω-diolefins to methylenecycloalkanes. The cyclization involves the insertion of one double bond across the Sc-H bond, followed by the intramolecular insertion of the free olefin into the previously formed Sc-alkyl bond to yield a cycloalkylmethyl scandium intermediate which rapidly undergoes β-hydrogen elimination to give methylenecycloalkane and $(DpScH)_2$.



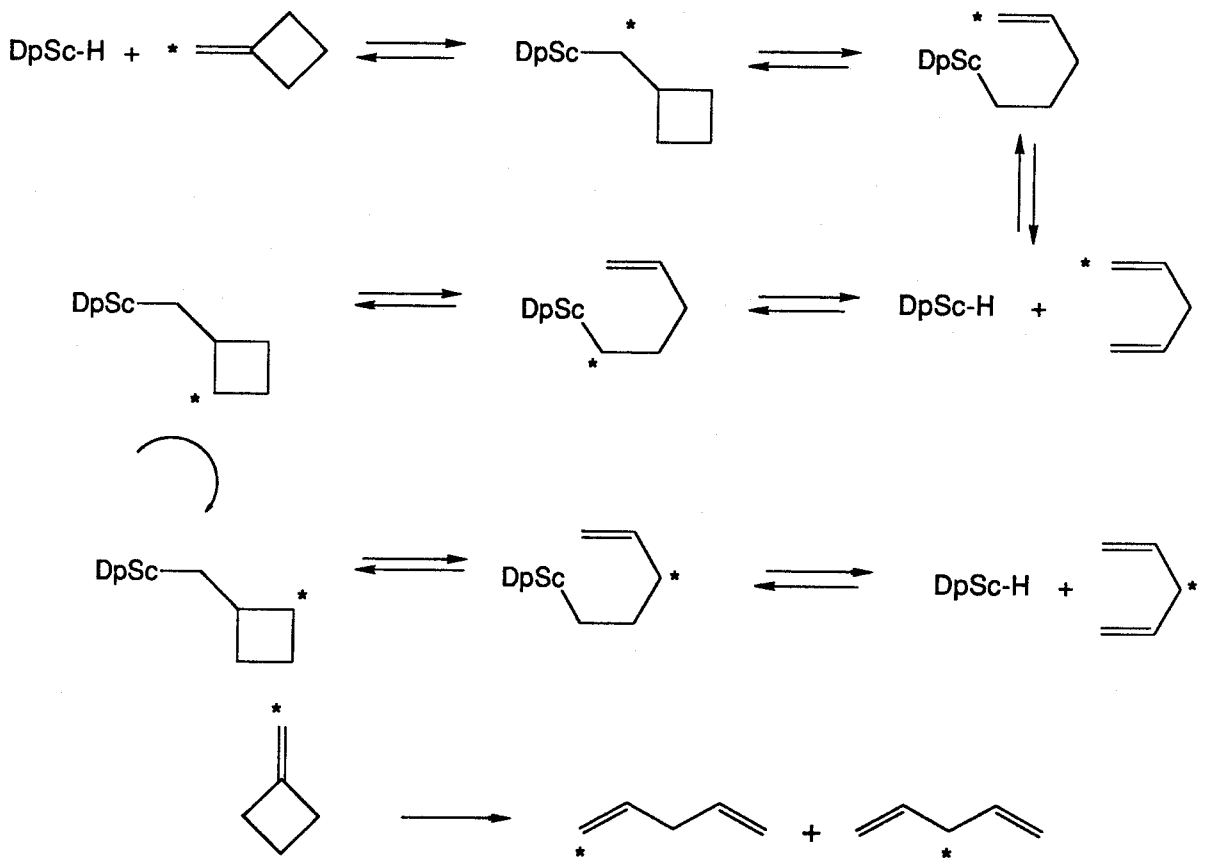
n = 0, 1, 2

We imagined that a cycloalkylmethyl scandium derivative, depending on ring strain, could undergo β-alkyl elimination competitively with β-hydrogen elimination and olefin insertion. Through a combination of β-alkyl elimination, olefin insertion and β-hydrogen elimination, an equilibrium between a methylenecycloalkane and a ring open diene could be established. The

	ΔH_f (kcal mol^{-1})	$\Delta H_{cyclization}$ (kcal mol^{-1})
	26.0	21.9
	47.9	
	25.3	3.8
	29.1	
	20.2	-17.3
	23.5	

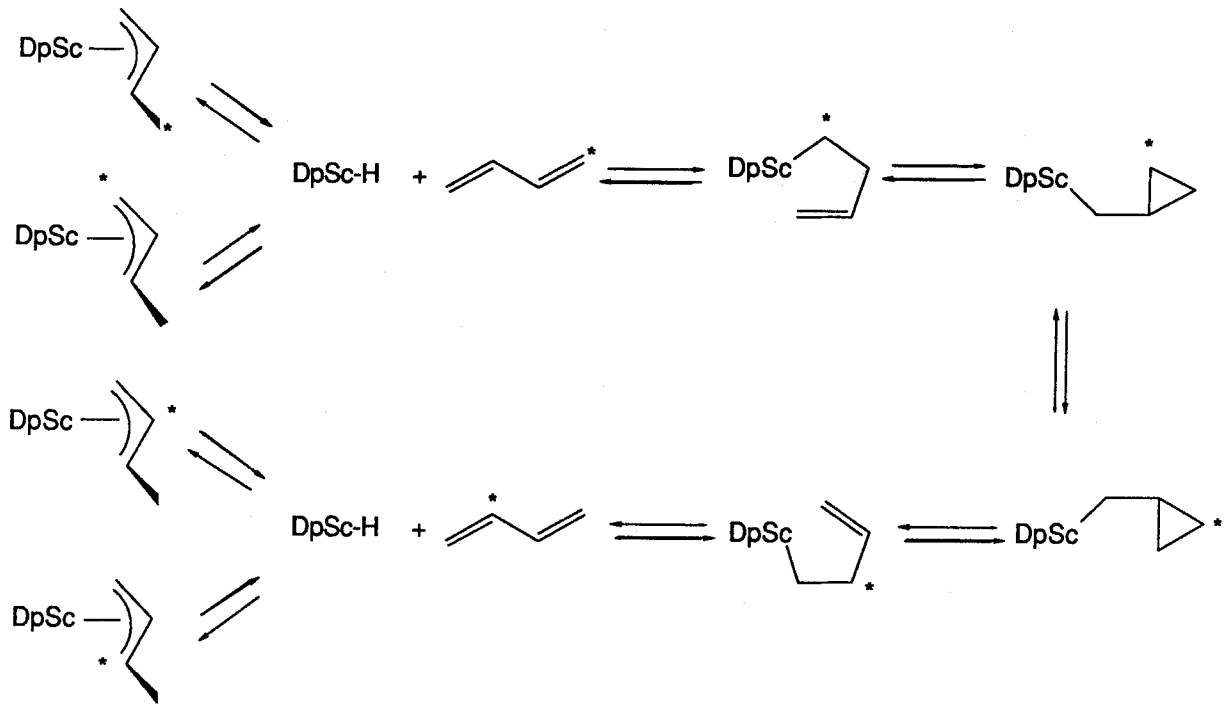
ease of this equilibration process can be judged by comparing the heats of formation for the exocyclic olefins and the corresponding dienes.[10] These values indicate that equilibration between the cyclobutylmethyl scandium complex and the 4-pentenyl-scandium complex should be close to thermoneutral. In order to test for this equilibration, labelling experiments were done with methylenecyclopentane and methylenecyclobutane labelled with ^{13}C in the exocyclic position and $^{13}CH_2$=CH-CH=CH_2. As shown in Scheme 1 for the case of methylenecyclobutane, if β-hydrogen elimination, β-alkyl elimination and olefin insertion are all ocurring in competition, the label should scramble among some of the positions in the diolefin and/or the methylenecycloalkane.

Scheme 1



Treating $(DpScH)_2$ with four equivalents of labelled butadiene at 80°C yields DpSc-(η^3-$^{13}CH_2$-CH-CH-CH_3) and DpSc-(η^3-CH_2-CH-CH-$^{13}CH_3$) (**7**) with no scrambling of the free butadiene. When the reaction temperature was increased to 140°C, only decomposition of **7** was observed, and when the volatiles were analyzed by ^{13}C NMR only $^{13}CH_2$=CH-CH=CH_2 was detected. However, when isolated DpSc-(η^3-$^{13}CH_2$-CH-CH-CH_3) and DpSc-(η^3-$^{13}CH_2$-CH-CH-$^{13}CH_3$) were heated to 140°C, ^{13}C scrambling into all four crotyl positions was observed. This result is explained in Scheme 2, and suggests that an equilibrium between the cyclopropylmethylscandium complex and the 3-butenylscandium complex can be established at high temperature without excess free butadiene in solution. Multiple insertion of butadiene into **7** is probably the mayor pathway when excess butadiene is used.

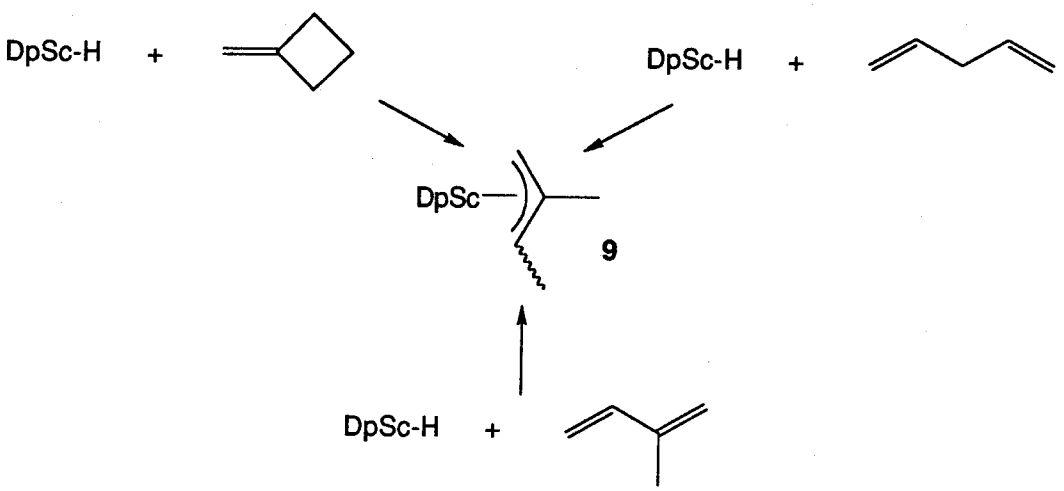
Scheme 2



Treatment of $(DpScH)_2$ with labelled methylenecyclopentane at 80°C yields DpSc-(η^3-$^{13}CH_2$-C-CH-$CH_2CH_2CH_2$) (**8**) as described in Chapter 2. Heating **8** with or without labelled methylenecyclopentane does not scramble the label on the allyl fragment of **8** or the excess methylenecyclopentane at temperatures up to 140°C. The only reaction observed, besides the thermal decomposition of **8** to unidentified products, is the conversion of methylenecyclopentane to 1-methylcyclopentene.

In contrast to the reactions described above, treating $(DpScH)_2$ with four equivalents of labelled methylenecyclobutane yields at 25°C $^{13}CH_2$=CH-CH_2-CH=CH_2 and CH_2=CH-$^{13}CH_2$-CH=CH_2. Under these conditions, DpScH is the only scandium species detected by ^1H or ^{13}C NMR. This result shows that under very mild conditions the equilibria shown in Scheme 1 are operating, but the reaction is driven thermodynamically toward the formation of 1,4-pentadiene.

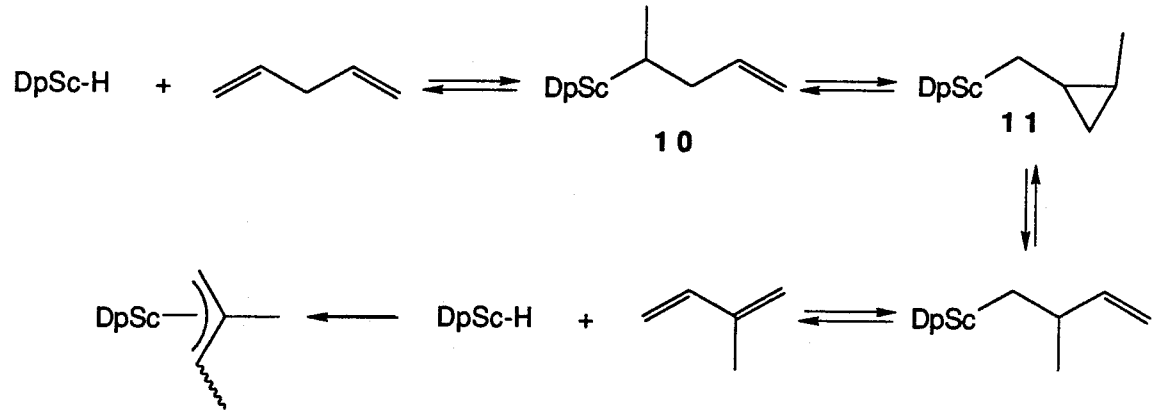
When DpScH is treated with methylenecyclobutane or 1,4-pentadiene at 80°C, a clean conversion to DpSc-η^3-CH_2-$CH(CH_3)CHCH_3$ (**9**) is observed. The same product is obtained if DpScH is treated with isoprene at 80°C. **9** was characterized by ^1H and ^{13}C NMR (see Table 1).



These results indicate that methylenecyclobutane is being converted to 1,4-pentadiene, and that there is a new species at higher temperatures responsible for the formation of **9**. The suggested intermediate (**11**) is shown in Scheme 3. The same type of intermediate was proposed in the

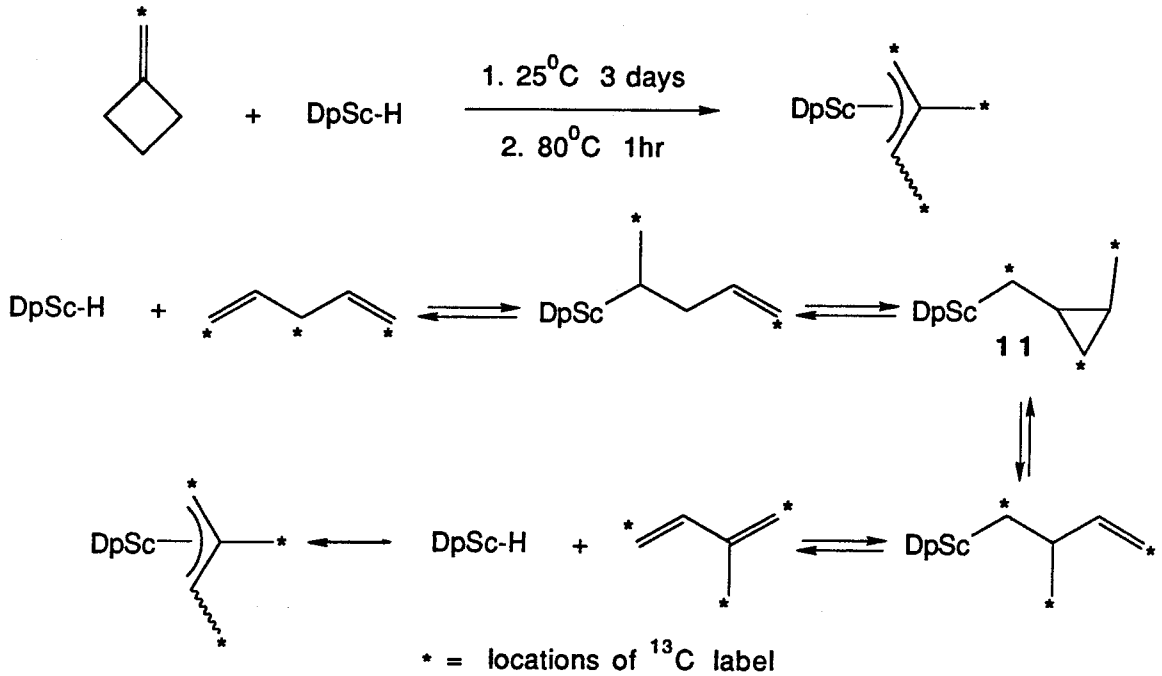
reaction of $NiCl_2(PBut_3)_2/AlCl(CH_2CHMe_2)_2$ with 1,4-pentadiene to explain the catalytic formation of isoprene.[11]

Scheme 3



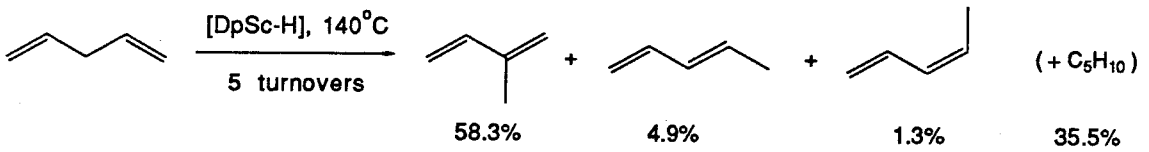
In order to test the validity of the proposed mechanism, DpScH was treated with labelled methylenecyclobutane. First methylenecyclobutane was ring-opened to $^{13}CH_2=CH-CH_2-CH=CH_2$ and $CH_2=CH-^{13}CH_2-CH=CH_2$, and then heated to 80°C to produce DpSc-(η^3-$^{13}CH_2$-C(CH_3)-CH(CH_3)), DpSc-(η^3-CH_2-C($^{13}CH_3$)-CH(CH_3)) and DpSc-(η^3-CH_2-C(CH_3)-CH($^{13}CH_3$)). As shown in Scheme 4, this label distribution agrees with the mechanism previously depicted in Scheme 3.

Scheme 4



* = locations of ^{13}C label

When excess 1,4-pentadiene or methylenecyclobutane are used, they are catalytically converted to isoprene at 140°C. Unfortunately, the thermal instability of **9** at 140°C results in the production of trimethylethylene as well as isoprene. The formation of trimethylethylene probably arises from the reaction of the allyl moiety with the ligand C-H bonds to give an unidentified "tuck-in" product. Besides isoprene and trimethylethylene, which have the original hydrocarbon skeleton, cis- and trans-piperylene are formed.

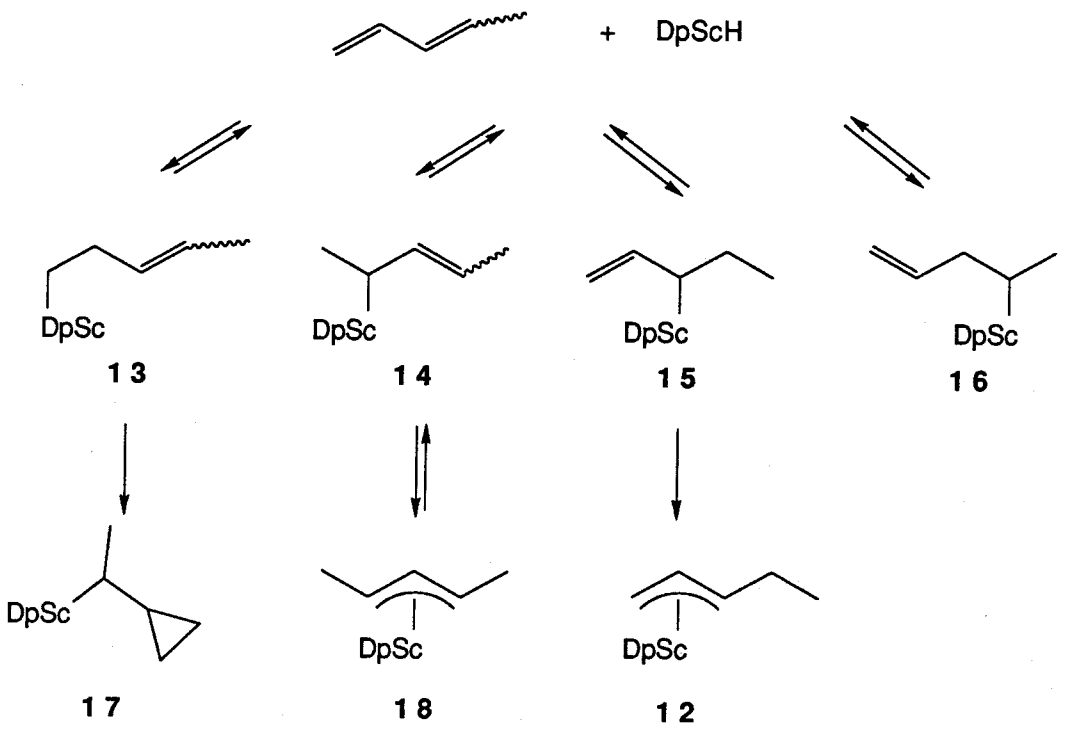


Cis- and trans-piperylene are formed from **10** via β-hydrogen elimination prior to the formation of **11**. The formation of isoprene is kinetically controlled as evidenced by the deviation of the product ratio from the expected composition of a thermodynamic mixture of 1,4-pentadiene, cis- and trans-piperylene and isoprene. The equilibrium concentrations are estimated as follows at 413 K: 1,4-pentadiene (0.05%), cis-piperylene (40.5%), trans-piperylene (26.7%), and isoprene (31.8%). The experimental ratios were: 0.03%, 2%, 7.6% and 90.4%.[12]

Because of the formation of cis- and trans-piperylene in the isomerization of 1,4-pentadiene to isoprene, we thought it could be possible to convert these compounds to isoprene through the formation of the same intermediate **11**. However the reaction of DpScH with cis- or trans-piperylene is only stoichiometric and yields a linear chain π-allyl complex DpSc-(η^3-CH_2-CH-CH-CH_2CH_3) (**12**). No isomerization to 1,4-pentadiene or conversion to isoprene was observed. This suggests that the addition of Sc-H to the conjugated olefin, which in principle could yield **13-16**, only produces **14** and **15**. Intermediate **16** is apparently not formed competitively and **9** or isoprene are not formed. The conversion of **13** to **17**, namely the insertion of a terminal olefin into a Sc-alkyl bond as was discussed in Chapter 2, is not likely to occur, but if it would occur the symmetric structure of **17** does not allow the formation of a new hydrocarbon

skeleton. In the early stages of the reaction the formation of **18** was detected, but **12** was the final product isolated.

Scheme 5

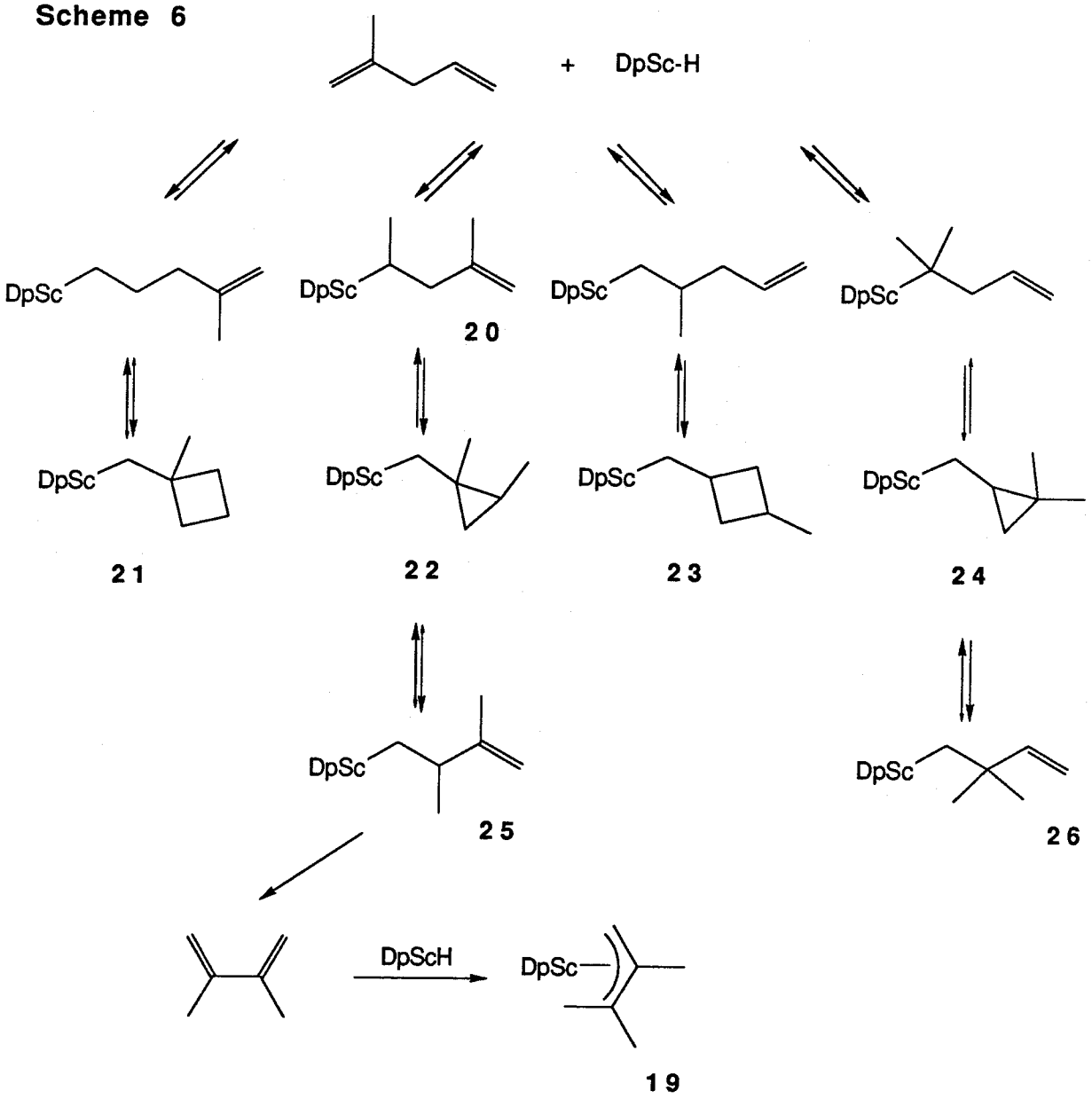


The type of rearrangement found for the conversion of 1,4-pentadiene to isoprene was found to be general for other dienes. 2-Methyl-1,4-pentadiene was converted to 2,3-dimethyl-1,3-butadiene and 3-methyl-1,4-pentadiene was converted to methylenecyclopentane. Treatment of DpScH with a stoichiometric amount of 2-methyl-1,4-pentadiene yields the π-allyl complex DpSc-(η^3-CH_2-C(CH_3)-C(CH_3)$_2$) (**19**). **19** is independently synthesized by treating DpScH with 2,3-dimethylbutadiene at 80°C. Heating DpScH with excess 2-methyl-1,4-pentadiene at 80°C affords 2,3-dimethylbutadiene as well as **19**. Scheme 6 shows a proposed mechanism for the formation of 2,3-dimethyl-1,3-butadiene from 2-methyl-1,4-pentadiene.

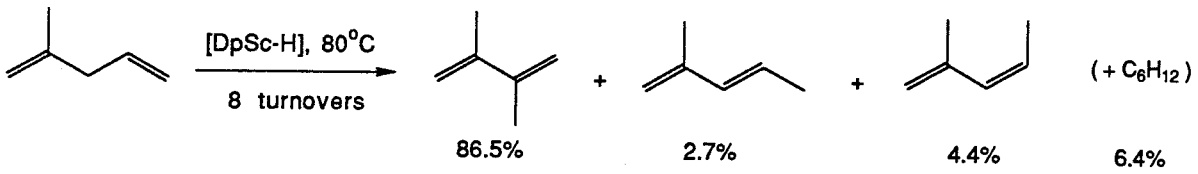
Four possible different intermediates could be formed in the reaction of 2-methyl-1,4-pentadiene with DpScH. Olefin insertion yields the cyclopropylmethyl or cyclobutylmethyl scandium derivatives **21-24**. Due to the symmetric structure of **21** and **23**, there is only one way

in which β-alkyl elimination may occur, that which regenerates the original open chain compound. β-alkyl elimination from **24** yields **26** which cannot be transformed further because of the absence of β-hydrogens. In conclusion, of all four intermediates only **22** has a productive β-alkyl elimination pathway to yield **19**. 2,3-Dimethyl-1,3-butadiene is obtained catalytically via β-hydrogen elimination from **25**.

Scheme 6

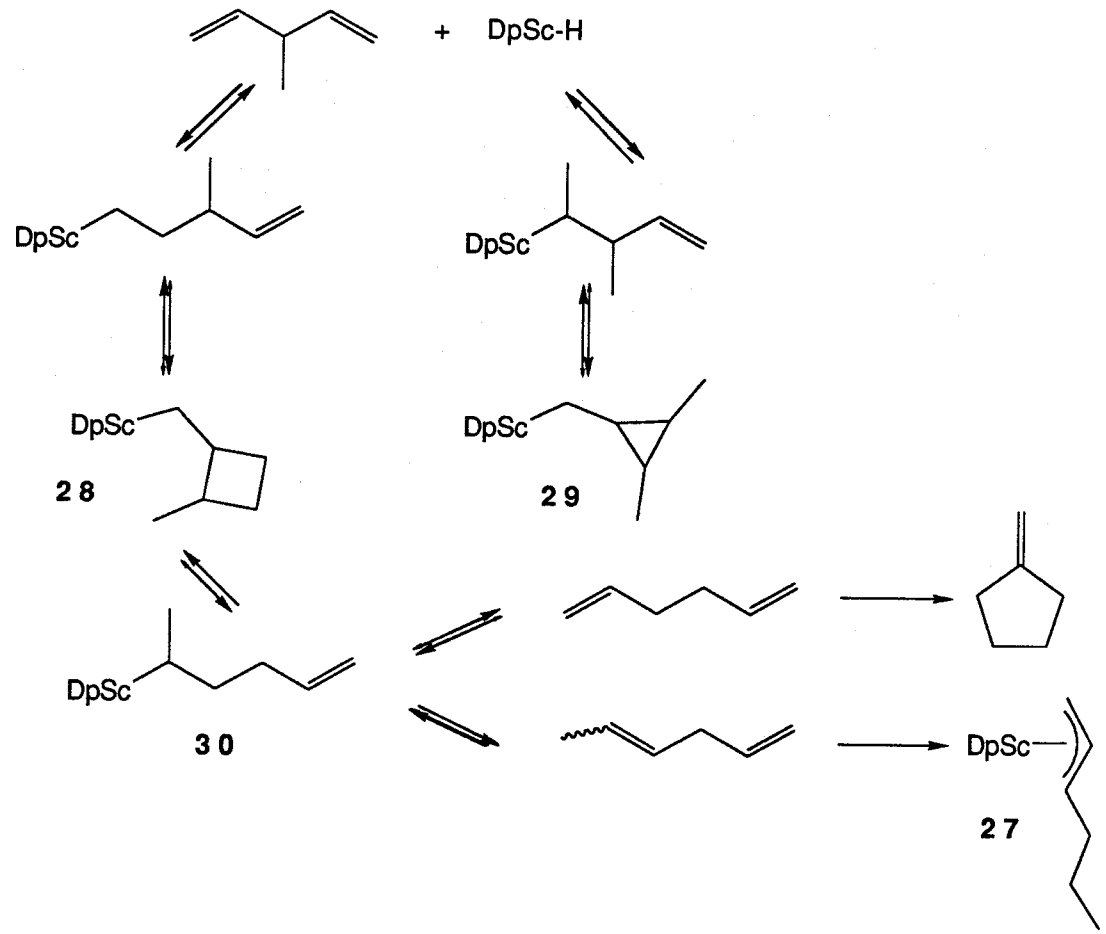


The formation of tetramethylethylene probably is due to side reactions involving metallation of the ligand rings. Cis- and trans-2-methyl-1,3-pentadiene are formed from β-hydrogen elimination from **20** prior to olefin insertion.



The reaction of DpScH with 3-methyl-1,4-pentadiene was also investigated. In this case, the stoichiometric reaction of DpScH with 3-methyl-1,4-pentadiene yields a π-allyl complex DpSc-(η^3-CH_2-CH-CH-$CH_2CH_2CH_3$) (**27**) which has a different carbon skeleton from the organic product obtained catalytically. **27** is independently prepared by treating 1,3-hexadiene with DpScH at 80°C. The formation of methylenecyclopentane from 3-methyl-1,4-pentadiene is explained in Scheme 7.

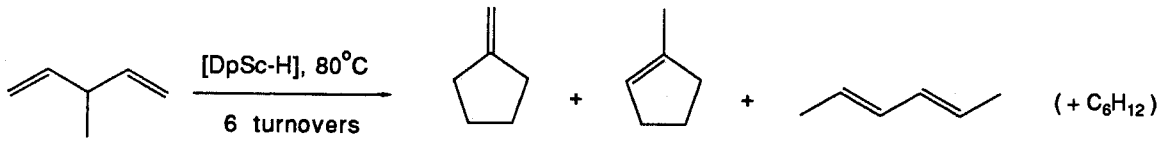
Scheme 7



Intermediate **29** is symmetric so there is no productive β-alkyl elimination pathway; however, **28** has a different pathway for β-alkyl elimination. β-hydrogen elimination from **30** yields 1,5-hexadiene and 1,4-hexadiene. The former is catalytically cyclized to methylenecyclopentane, while 1,4-hexadiene reacts stoichiometrically yielding **27**.

The formation of **27** by treating $(DpScH)_2$ with excess 1,4-hexadiene was monitored by ^1H and ^{13}C NMR. $(DpScH)_2$ catalyzes first the isomerization of 1,4-hexadiene to 2,4-hexadiene and then 2,4-hexadiene is slowly converted to 1,3-hexadiene which finally yields **27**. The formation of **27** from the reaction of 2,4-hexadiene with DpScH occurs much more slowly than the isomerization to 2,4-hexadiene.

The catalytic conversion of 3-methyl-1,4-pentadiene to methylenecyclopentane is accompanied by the simultaneous formation of 1-methyl-1-cyclopentene and 2,4-hexadiene. The formation of the later was discussed previously, and 1-methylcyclopentene has been shown previously to form when $(DpScH)_2$ is treated with methylenecyclopentane at 80 °C.



CONCLUSIONS

The interconversion between a cyclopropylmethyl-scandium complex and a 3-alkenyl-scandium complex and between a cyclobutylmethyl-scandium complex and a 4-alkenyl-scandium complex has been demonstrated by labelling experiments. These observations implicate the reverse of olefin insertion into Sc-alkyl bonds, namely β-alkyl elimination, as a relatively facile process in this system. As in many of the examples reported in the literature, the driving force for β-alkyl elimination was found to be the ring strain in the cyclopropylmethyl and cyclobutylmethyl scandium derivatives. However, unlike literature precedents, in the scandium system strained cycloalkylmethyl derivatives are formed from open chain compounds. Catalytic reactions were performed with excess 1,4-pentadiene, 2-methyl-1,4-pentadiene and 3-methyl-1,4-pentadiene, although after several turnovers some other pathway leads to a significant amount of saturated products in conjunction with slowing down the catalytic cycle.

Table 1 : ^{1}H and ^{13}C NMR Data

Compound	Assignment	δ(ppm) and Coupling(Hz)
DpSc-(η^3-$CH_2CHCH(CH_3)$)		
(C_6D_6, 80°C)	$(CH_3)_2Si$	0.23(s); 0.70(s)
	$C_5H_3(C(CH_3)_3)$	1.12(s)
	$C_5H_3(C(CH_3)_3)$	5.14(m); 5.94(m); 6.78 (m)
	η^3-$CH_2CHCH(CH_3)$	2.80(m)
	η^3-$CH_2CHCH(CH_3)$	7.08(m,11,5.6)
	η^3-$CH_2CHCH(CH_3)$	4.60(m,5.6,15)
	η^3-$CH_2CHCH(CH_3)$	1.30(d,5.6)
	$(CH_3)_2Si$	-6(q,120); -2(q,119)
	$C_5H_3(C(CH_3)_3)$	32(q,124)
	$C_5H_3(C(CH_3)_3)$	33(s)
	$C_5H_3(C(CH_3)_3)$	110(d,169); 115(d,164); 118(d,166); 114(s); 184(s)
	η^3-$CH_2CHCH(CH_3)$	57(t,144)
	η^3-$CH_2CHCH(CH_3)$	151(d,141)
	η^3-$CH_2CHCH(CH_3)$	86(d,148)
	η^3-$CH_2CHCH(CH_3)$	19(q,125)
DpSc-(η^3-$CH_2C(CH_3)CH(CH_3)$)		
(C_6D_6, 80°C)	$(CH_3)_2Si$	0.21(s); 0.73(s)
	$C_5H_3(C(CH_3)_3)$	1.13(s)
	$C_5H_3(C(CH_3)_3)$	5.43(m); 6.07(m); 6.63(m)
	η^3-$CH_2C(CH_3)CH(CH_3)$	2.86(m)
	η^3-$CH_2C(CH_3)CH(CH_3)$	1.96(s)
	η^3-$CH_2C(CH_3)CH(CH_3)$	5.13(q,6)

	η^3-$CH_2C(CH_3)CH(\mathbf{C}H_3)$	1.18(d,6)
	$(\mathbf{C}H_3)_2Si$	-7(q,123); -2(q,121)
	$C_5H_3(C(\mathbf{C}H_3)_3)$	32(q,124)
	$C_5H_3(\mathbf{C}(CH_3)_3)$	33(s)
	$\mathbf{C}_5H_3(C(CH_3)_3)$	117(d,168); 115(d,165); 110(d,163); 114(s); 149(s)
	η^3-$\mathbf{C}H_2C(CH_3)CH(CH_3)$	60(t,143)
	η^3-$CH_2\mathbf{C}(CH_3)CH(CH_3)$	164(s)
	η^3-$CH_2C(\mathbf{C}H_3)CH(CH_3)$	24(q,125)
	η^3-$CH_2C(CH_3)\mathbf{C}H(CH_3)$	81(d,139)
	η^3-$CH_2C(CH_3)CH(\mathbf{C}H_3)$	14(q,125)

DpSc-(η^3-$CH_2CHCHCH_2CH_2CH_3$)

(C_6D_6, 80 °C)	$(CH_3)_2Si$	0.26(s); 0.72(s)
	$C_5H_3(C(CH_3)_3)$	1.13(s)
	$C_5\mathbf{H}_3(C(CH_3)_3)$	5.22(m); 5.96(m); 6.83(m)
	η^3-$\mathbf{C}H_2CHCHCH_2CH_2CH_3$	2.88(m)
	η^3-$CH_2\mathbf{C}HCHCH_2CH_2CH_3$	7.11(m,11.2,15)
	η^3-$CH_2CH\mathbf{C}HCH_2CH_2CH_3$	4.81(m,6.6,15)
	η^3-$CH_2CHCH\mathbf{C}H_2CH_2CH_3$	not located
	η^3-$CH_2CHCHCH_2\mathbf{C}H_2CH_3$	not located
	η^3-$CH_2CHCHCH_2CH_2\mathbf{C}H_3$	0.88(t,7.3)
	$(\mathbf{C}H_3)_2Si$	-7(q,121); -3(q,120)
	$C_5H_3(C(\mathbf{C}H_3)_3)$	32(q,126)
	$C_5H_3(\mathbf{C}(CH_3)_3)$	33(s)
	$\mathbf{C}_5H_3(C(CH_3)_3)$	110(d,166); 116(d,165); 148(s); 113(s)

	η^3-**C**H_2CHCHCH_2CH_2CH_3	57(t,148)
	η^3-CH_2**C**HCHCH_2CH_2CH_3	150(d,144)
	η^3-CH_2C**H**CHCH_2CH_2CH_3	92(d,140)
	η^3-CH_2CHC**H**CH_2CH_2CH_3	36(t,126)
	η^3-CH_2CHCHCH_2**C**H_2CH_3	25(t,129)
	η^3-CH_2CHCHCH_2CH_2**C**H_3	14(q,125)

DpSc-(η^3-$CH_2C(CH_3)C(CH_3)_2$)

(C_6D_6, 80°C)	$(CH_3)_2$Si	0.36(s); 0.78(s)
	$C_5H_3(C(CH_3)_3)$	1.08(s)
	$C_5H_3(C(CH_3)_3)$	5.32(m); 5.99(m); 6.90 (m)
	η^3-CH_2C(CH_3)C$(CH_3)_2$	2.75(s)
	η^3-CH_2C(CH_3)C$(CH_3)_2$	1.84(s); 1.91(s); 1.95(s)
	$(CH_3)_2$Si	-6(q,122); -3(q,120)
	$C_5H_3(C(CH_3)_3)$	31(q,126)
	$C_5H_3(C(CH_3)_3)$	32(s)
	$C_5H_3(C(CH_3)_3)$	112(d,162); 119(d,165); 120(d,169); 116(s); 142(s)
	η^3-CH_2C(CH_3)C$(CH_3)_2$	58(t,147)
	η^3-CH_2C(CH_3)C$(CH_3)_2$	149(s)
	η^3-CH_2C(CH_3)C$(CH_3)_2$	106(s)
	η^3-CH_2C(CH_3)C$(CH_3)_2$	21(q,128); 24(q,123); 24 (q,125)

DpSc-(η^3-$CH_2CHCHCH_2CH_3$)

(C_6D_6, 80°C)	$(CH_3)_2$Si	0.26(s); 0.72(s)
	$C_5H_3(C(CH_3)_3)$	1.13(s)
	$C_5H_3(C(CH_3)_3)$	5.20(m); 5.95(m); 6.82(m)
	η^3-CH_2CHCHCH_2CH_3	2.84(m)

η^3-$CH_2CHCHCH_2CH_3$	7.07(m)
η^3-$CH_2CHCHCH_2CH_3$	4.77(m)
η^3-$CH_2CHCHCH_2CH_3$	not located
η^3-$CH_2CHCHCH_2CH_3$	0.82(t,)
$(CH_3)_2Si$	-6.94(q,121); -2.50(q,120)
$C_5H_3(C(CH_3)_3)$	31.6(q,121)
$C_5H_3(C(CH_3)_3)$	32.8(s)
$C_5H_3(C(CH_3)_3)$	148; 115; 110; two were not located
η^3-$CH_2CHCHCH_2CH_3$	56.6(d,147)
η^3-$CH_2CHCHCH_2CH_3$	150(d,143)
η^3-$CH_2CHCHCH_2CH_3$	94(d,138)
η^3-$CH_2CHCHCH_2CH_3$	27.1(t,125)
η^3-$CH_2CHCHCH_2CH_3$	16.2(t,126)

EXPERIMENTAL

The hydride derivative (*meso*-Me_2Si(t-butyl$C_5H_3)_2ScH)_2$ was prepared as described in Chapter 1. Butadiene (Matheson) and butadiene-1-^{13}C (MSD Isotopes) were used as received. 1,4-Pentadiene, methylenecyclobutane, methylenecyclopentane, 2-methyl-1,4-pentadiene, 3-methyl-1,4-pentadiene, 1,4-hexadiene (cis & trans), isoprene, 2,3-dimethylbutadiene, trimethylethylene, cis-piperylene, trans-piperylene, 1-methyl-1-cyclopentene, 2-methyl-1,3-pentadiene (cis & trans), 1,3-hexadiene (mostly trans), 1,4-hexadiene (cis & trans), 2,4-hexadiene (mixture of isomers) were purchased from Aldrich and stored over 4Å molecular sieves. Methylenecyclobutane-^{13}C and methylenecyclopentane-^{13}C were prepared as reported in the literature[13]. Perdeuterobenzene and petroleum ether were vacuum transferred from titanocene prior to use.

NMR spectra were recorded on Varian EM-390 (^1H, 90MHz) and JEOL GX 400 (^1H, 399.78MHz; ^{13}C, 100.38MHz) instruments. The gc analyses were carried out on a Hewlett-Packard 5790-A using a 4m column packed with 5% B,B-Oxydipropionitrile on Chromosorb W.

General Procedure for Olefin Rearrangement: (*meso*-Me_2Si(t-butyl$C_5H_3)_2ScH)_2$ (*ca.* 0.06-0.07 mmol) was loaded into an NMR tube, and benzene-d_6 (*ca.* 0.5 g) was added to the tube. The substrate was condensed into the NMR tube and then the tube was sealed. The reaction was monitored by ^1H and ^{13}C NMR. After the reaction was completed, as determined by NMR, the NMR tube was opened and the volatiles were vacuum transferred (10^{-4} torr, 25°C) in a high vacuum line and then injected to the gc.

***meso*-Me_2Si(t-butyl$C_5H_3)_2Sc$-(η^3-$CH_2CHCHCH_3$) (7):** $(DpScH)_2$ (0.30 g, 0.87 mmol) was dissolved in petroleum ether (ca. 15mL), the solution was cooled to -196°C and butadiene (1.3 mmol) was condensed. The solution was heated to 80°C for three hours. Petroleum ether

and excess butadiene were removed *in vacuo* and replaced with petroleum ether (ca. 5 mL). The solution was cooled overnight (-78 °C) to afford **7** as orange crystals. Yield 0.22 g, (62 %).

Anal. Calc. for $C_{24}H_{37}ScSi$: C, 72.32; H, 9.36. Found C, 71.98; H, 9.24.

***meso*-$Me_2Si(t\text{-}butylC_5H_3)_2Sc\text{-}(\eta^3\text{-}CH_2C(CH_3)CHCH_3)$ (9)**: The same procedure for **7** was followed except 1,4-pentadiene was substituted for butadiene. **9** was obtained as orange crystals. Yield 0.19 g, (53 %)

Anal. Calc. for $C_{25}H_{39}ScSi$: C, 72.77; H, 9.53. Found C, 72.30; H, 9.49.

***meso*-$Me_2Si(t\text{-}butylC_5H_3)_2Sc\text{-}(\eta^3\text{-}CH_2CHCHCH_2CH_3)$ (12)**: The same procedure for **7** was followed except 1,3-pentadiene was substituted for butadiene. **12** was obtained as orange crystals. Yield 0.20 g, (56 %)

Anal. Calc. for $C_{25}H_{39}ScSi$: C, 72.77; H, 9.53. Found C, 72.50; H, 9.27.

***meso*-$Me_2Si(t\text{-}butylC_5H_3)_2Sc\text{-}(\eta^3\text{-}CH_2C(CH_3)C(CH_3)_2)$ (19)**: The same procedure for **7** was followed except 2-methyl-1,4-pentadiene was substituted for butadiene. **19** was obtained as red crystals. Yield 0.22 g, (59 %)

Anal. Calc. for $C_{26}H_{41}ScSi$: C, 73.19; H, 9.87. Found C, 72.56; H, 9.27.

***meso*-$Me_2Si(t\text{-}butylC_5H_3)_2Sc\text{-}(\eta^3\text{-}CH_2CHCHCH_2CH_2CH_3)$ (27)**: The same procedure for **7** was followed except 3-methyl-1,3-pentadiene was substituted for butadiene. **17** was obtained as red crystals. Yield 0.19 g, (51 %)

Anal. Calc. for $C_{26}H_{41}ScSi$: C, 73.19; H, 9.87. Found C, 72.84; H, 9.33.

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