Carbon–hydrogen and carbon–carbon bond activation with highly electrophilic transition metal complexes
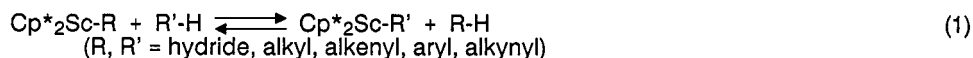
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Abstract - Highly electron deficient scandocene derivatives of the types $(\eta^5\text{-}C_5Me_5)_2ScR$, $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}ScR$ and $\{(\eta^5\text{-}C_5H_3CMe_3)_2SiMe_2\}ScR$ catalyze the polymerization of ethylene, the head-to-tail dimerization of α olefins, the cyclization of α,ω dienes to methylene cycloalkanes, and the branching of 1,4 pentadienes to isoprenes. The mechanisms of the individual steps have been studied. Key steps involve sequential and reversible olefin insertion/β H elimination/β alkyl elimination, the last of which is particularly facile in these systems. $[\{(\eta^5\text{-}C_5Me_4)Me_2Si(\eta^1\text{-}NCMe_3)(PMe_3)Sc(\mu\text{-}H)]_2$, catalyzes the polymerization of α olefins. Evidence is presented in support of a well defined, one component catalyst system with all scandium centers functioning alike.

INTRODUCTION

Organometallic compounds of scandium resemble those of aluminum, particularly in their tendency to form dimeric or oligomeric structures with bridging alkyl or hydride groups. Recently our research group has reported the synthesis and some features of the reactivity of alkyl and hydride derivatives of bis(pentamethylcyclopentadienyl)scandium, Cp^*_2ScR $(Cp^* = (\eta^5\text{-}C_5Me_5))$ (ref.1). The bulky $(\eta^5\text{-}C_5Me_5)$ ligands prevent dimerization and restrict the types of ligands which can coordinate to the formally 14 electron, d^0 scandium center. We have suggested the name "sigma bond metathesis" for a dominant reaction type for these highly electrophilic compounds:

$$Cp^*_2Sc\text{-}R + R'\text{-}H \rightleftharpoons Cp^*_2Sc\text{-}R' + R\text{-}H \qquad (1)$$
$$(R, R' = \text{hydride, alkyl, alkenyl, aryl, alkynyl})$$

More recently we have turned our attention to the reactivity of these compounds with olefins. Early indications were that they readily polymerize ethylene without coordinating bases or co-catalysts, common complications for Ziegler-Natta polymerizations using group 4 transition metal catalysts. We have therefore undertaken a study of this model system (ref. 2).

$$Cp^*_2Sc\text{-}R + n\ CH_2{=}CH_2 \longrightarrow Cp^*_2Sc(CH_2CH_2)_nR \qquad (2)$$
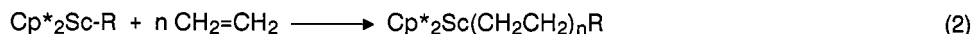
Due to unfavorable steric interactions with the $(\eta^5\text{-}C_5Me_5)$ ligands, α olefins do not undergo insertion into the scandium-carbon bonds of Cp^*_2ScR; rather, they react by sigma bond metathesis (eq. 1). Less crowded scandocene derivatives were prepared, and, indeed, these proved to be very efficient α olefin dimerization catalysts. Moreover, with 1,4-pentadienes, skeletal rearrangement to isoprenes are observed. A related system with linked cyclopentadienyl and amide ligands $\{(\eta^5\text{-}C_5Me_4)SiMe_2(\eta^1\text{-}NCMe_3)\}ScR$ catalyzes the polymerization of α olefins in a quasi-living manner.

ETHYLENE INSERTION AND βH ELIMINATION FOR PERMETHYLSCANDOCENE ALKYLS

The rates of ethylene insertion into the Sc-C bond for Cp^*_2ScR (R = H, CH_3, CH_2CH_3, $CH_2CH_2CH_3$) have been examined at -80°C by ^{13}C NMR spectroscopy.

$$Cp^*_2Sc\text{-}R + CH_2{=}CH_2 \xrightarrow{k_1} Cp^*_2ScCH_2CH_2R \xrightarrow{CH_2{=}CH_2} etc. \qquad (3)$$
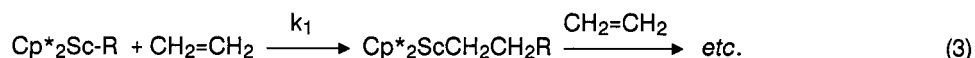
The following second order rate constants (k_1; $M^{-1}{\cdot}sec^{-1}$, -80°C) have been measured: R = H (>10^{-2}); R = CH_3 (8.1(2) x 10^{-4}); R = CH_2CH_3 (4.4(2) x 10^{-4}); R = $CH_2CH_2CH_3$ (6.1(2) x 10^{-3}). The fast rate for the hydride derivative is expected, and almost certainly is due to the greater overlap, hence better bonding in the transition state for H (nondirectional 1s orbital) vs. alkyl (more directional sp^3 orbital). On the other hand, the greater insertion rate for the scandium propyl relative to the scandium methyl is likely due to ground state differences. Equilibrium measurements indicate that the relative ordering of Sc-R bond dissociation energies (BDEs) mirrors that for the corresponding H-R BDEs (ref 3); hence, BDE(Sc-CH$_3$) - BDE(Sc-CH$_2$CH$_2$CH$_3$) $\ge$ ca. 6 kcal·mol^{-1}. The observation that the scandium ethyl complex is slowest to insert ethylene cannot be rationalized by these types of metal-carbon bond
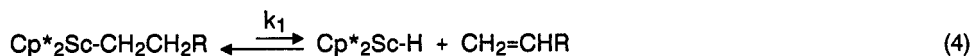
strength considerations or by transition state differences. Spectroscopic data and an X-ray diffraction study indicate a β agostic interaction for the stable form of Cp*$_2$ScCH$_2$CH$_3$. A similar β agostic interaction is, of course, possible for Cp*$_2$ScCH$_2$CH$_2$CH$_3$. Whereas such a structure (**A**) is electronically favored, it is sterically less favorable than the conventional structure (**B**), due to adverse interactions of the methyl group with a (η^5-C$_5$Me$_5$) ligand.

A   **B**
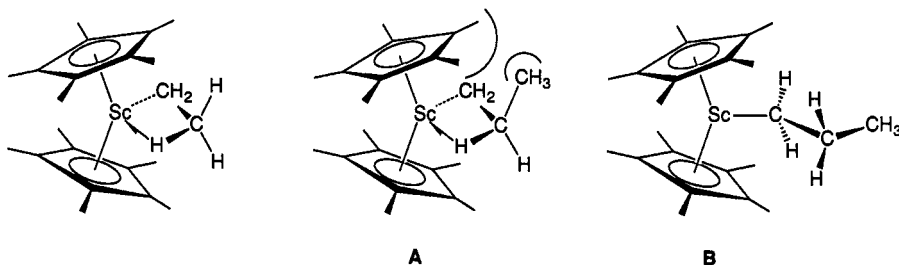
Presumably this β agostic interaction for Cp*$_2$ScCH$_2$CH$_3$ must be broken prior to ethylene insertion, thus increasing the barrier relative to the other alkyls. Cp*$_2$ScCH$_3$ undergoes a single insertion with 2-butyne with a moderate enthalpy of activation ($\Delta H^\ddagger$ = 9.7(3) kcal·mol^{-1}) and a large, negative entropy of activation ($\Delta S^\ddagger$ = -36(20) eu), indicating highly ordered transition states for these insertion reactions.

The distributions of molecular weights for ethylene oligomers (CH$_3$(CH$_2$)$_n$CH$_3$, n = 11-47) produced from known amounts of ethylene and Cp*$_2$ScCH$_2$CH$_2$CH$_3$ at -78°C satisfactorily fit a Poisson distribution, indicative of a "living" Ziegler-Natta polymerization system. From the measured, slower initiation rates of insertion for Cp*$_2$ScCH$_3$ and Cp*$_2$ScCH$_2$CH$_3$ and propagation rates equal to that for Cp*$_2$ScCH$_2$CH$_2$CH$_3$, the molecular weight distributions of ethylene oligomers are also predicted.

The rates for β hydrogen elimination for members of the series of permethylscandocene alkyl complexes Cp*$_2$ScCH$_2$CH$_2$R (R = H, CH$_3$, CH$_2$CH$_3$, C$_6$H$_5$, C$_6$H$_4$-p-CH$_3$, C$_6$H$_4$-p-CF$_3$, C$_6$H$_4$-p-NMe$_2$) have been obtained by rapidly trapping Cp*$_2$Sc-H with 2-butyne (eqs 4 and 5).

$$\text{Cp*}_2\text{Sc-CH}_2\text{CH}_2\text{R} \underset{}{\overset{k_1}{\rightleftharpoons}} \text{Cp*}_2\text{Sc-H} + \text{CH}_2\text{=CHR} \qquad (4)$$

$$\text{Cp*}_2\text{Sc-H} + \text{CH}_3\text{C≡CCH}_3 \longrightarrow E\text{-Cp*}_2\text{Sc-C(CH}_3\text{)=CH(CH}_3\text{)} \qquad (5)$$
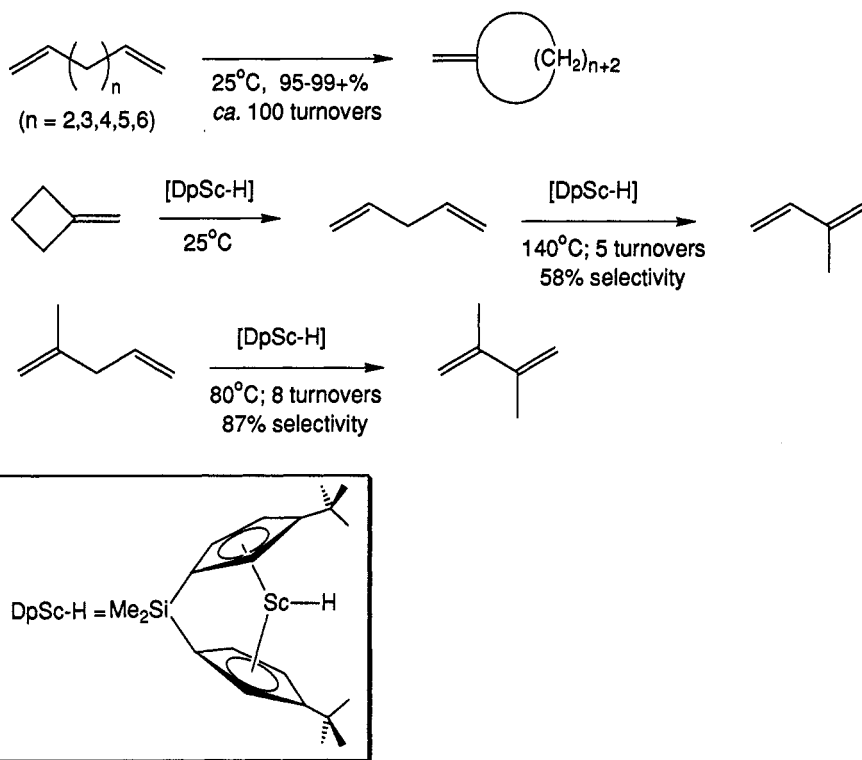
For the phenylethyl series k_1 linearly correlates with σ_p (R = 0.9967) with a slope (ρ) of -1.87(11). A transition state for the β hydrogen elimination is indicated with partial charge on the β carbon. Hydrogen is thus transferred to the scandium center as hydride in the β H elimination process.

## OLEFIN DIMERIZATION, DIOLEFIN CYCLIZATION AND SKELETAL REARRANGEMENT WITH DIMETHYLSILYL-BRIDGED SCANDOCENE HYDRIDES

Whereas Cp*$_2$ScH ultimately generates (*via* σ bond metathesis) permethylscandocene alkenyl complexes, Cp*$_2$Sc-CH=CHR, with α olefins CH$_2$=CHR, less sterically encumbered scandocene hydrides {(η^5-C$_5$Me$_4$)$_2$SiMe$_2$}ScH (OpScH) and [{(η^5-C$_5$H$_3$CMe$_3$)$_2$SiMe$_2$}ScH]$_2$ ([DpScH]$_2$) promote rapid, remarkably selective, head-to-tail dimerization of α olefins.
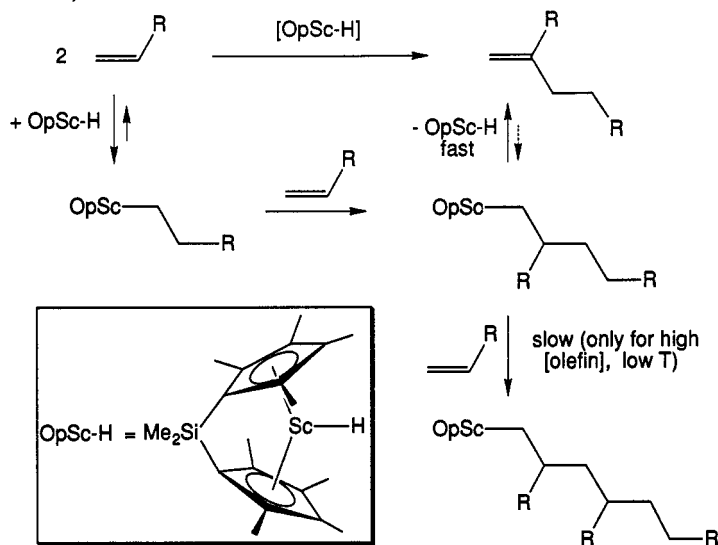
Moreover, α,ω dienes are cleanly cyclized to the corresponding methylene cycloalkane. Cyclization of 1,4-pentadiene is endothermic; hence, catalytic opening of methylene cyclobutane to 1,4-pentadiene is observed. Unexpectedly, under more forcing conditions, 1,2-dimethylallyl scandocene is obtained. At 140°C catalytic conversion of 1,4-pentadienes to the corresponding isoprenes is observed, albeit with only a moderate number of turnovers (ref 4).

(n = 2,3,4,5,6)

25°C, 95-99+%
ca. 100 turnovers

$(CH_2)_{n+2}$

[DpSc-H]
25°C

[DpSc-H]
140°C; 5 turnovers
58% selectivity

[DpSc-H]
80°C; 8 turnovers
87% selectivity

DpSc-H = Me$_2$Si

Sc—H

The (reversible) cyclization and branching of 1,4-dienes is proposed to occur via addition of Sc-H, followed by intramolecular olefin insertion to afford the (methylcyclopropylmethyl)scandium intermediate. The methyl branch is introduced by β alkyl elimination in the alternate sense. β H elimination yields isoprene, which may readd to DpScH to yield the stable branched allyl derivative.

DpSc　⇌　DpSc　⇌　DpSc-H +

DpSc-H +　⟶　DpSc　⇌　DpSc-H +

DpSc　⇌　DpSc　=　DpSc　⇌　DpSc
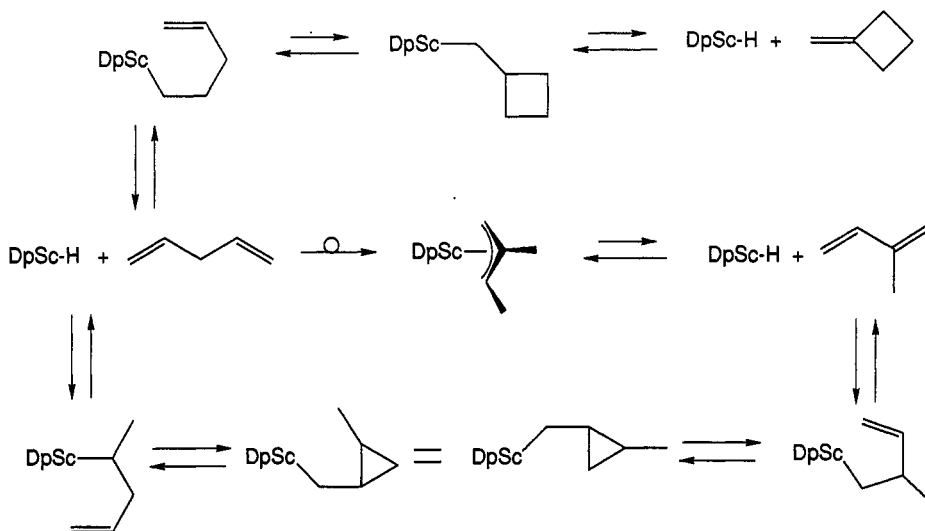
QUASI-LIVING α OLEFIN POLYMERIZATION WITH A DIMETHYLSILYL-LINKED CYCLOPENTADIENYL-AMIDE LIGAND SYSTEM

Using the hydride derivative of scandium with the dimethylsilyl-linked cyclopentadienyl-amide ligand, [{(η^5-C$_5$Me$_4$)Me$_2$Si(η^1-NCMe$_3$)(PMe$_3$)Sc(μ-H)]$_2$ ({(Cp*SiNR)(PMe$_3$)ScH}$_2$), propene, 1-butene and

1-pentene are cleanly, albeit slowly, polymerized with >99% head-to-tail coupling to produce atactic polymers with M_n = 3,000-4,000 and polydispersity indices of 1.7-2.1 (ref 5). Chain transfer is relatively slow. The molecular weight distributions for oligomers obtained at relatively low conversion of propene are adequately described by a Poisson function based on the amount of monomer consumed, *assuming all scandium centers are participating, as a "living" system.*
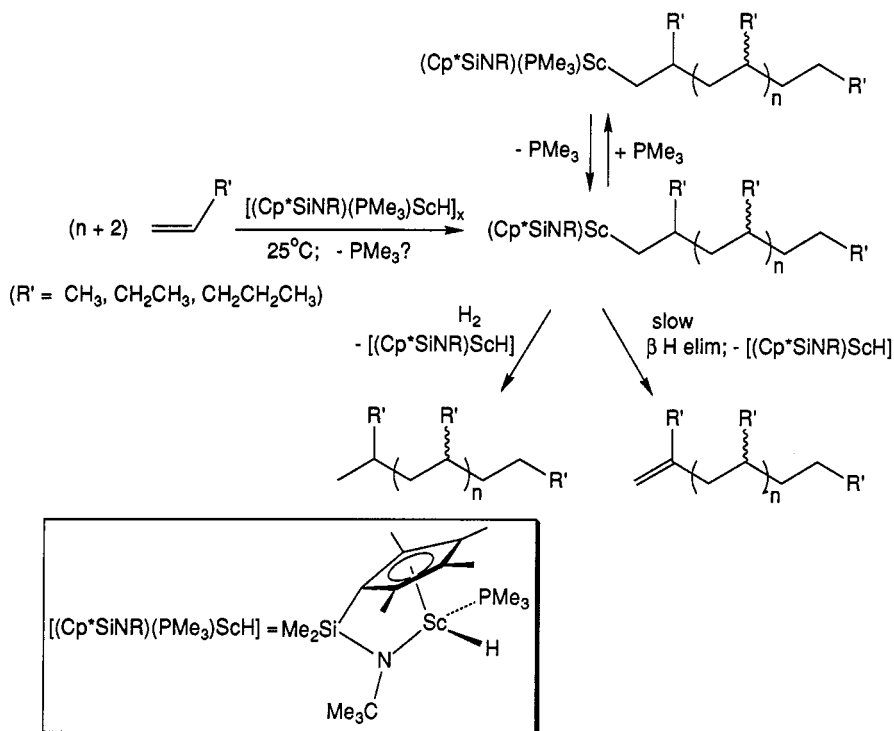
$(R' = CH_3, CH_2CH_3, CH_2CH_2CH_3)$

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