Competitive Chain Transfer by β-Hydrogen and β-Methyl Elimination for the Model Ziegler–Natta Olefin Polymerization System $[Me_2Si(\eta^5\text{-}C_5Me_4)_2]Sc\{CH_2CH(CH_3)_2\}(PMe_3)$†

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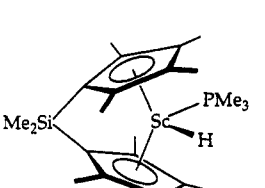
The reaction of $OpSc(H)(PMe_3)$ (Op = $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}$) with isobutene produces $OpSc(CH_3)(PMe_3)$ along with isobutene, 2-methylpentane, isobutene, 2-methyl-1-pentene, propane, and *n*-pentane. These products arise from a series of reactions involving olefin insertion, β-CH_3 and (faster) β-H elimination which proceed until only the 2-methyl-1-alkenes (C_4H_8, C_6H_{12}, *etc.*) and the predominant organoscandium product $OpSc(CH_3)(PMe_3)$ remain. A transient observed in the reaction sequence has been unambiguously characterized as $OpSc(CH_2CH_2CH_3)(PMe_3)$. Slower σ bond metathesis involving the methyl C–H bonds of PMe_3 and the Sc–C bonds of the scandium alkyls accounts for the observation of saturated alkanes (2-methylalkanes (C_4H_{10}, C_6H_{14}, *etc.*), normal alkanes (C_3H_8, C_5H_{12}, *etc.*), and a minor organoscandium product $OpScCH_2PMe_2$ in the product mixture. β-Ethyl migration is *not* observed for the closely related 2-ethylbutyl derivative, $OpSc\{CH_2CH(C_2H_5)CH_2CH_3\}(PMe_3)$, obtained from reaction of 2-ethyl-1-butene with $OpSc(H)(PMe_3)$.

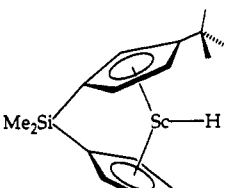
Introduction

The scientific and industrial importance of Ziegler–Natta olefin polymerization has stimulated intensive research directed toward understanding the mechanistic aspects of this remarkable catalytic process.[1] Recently, a number of research groups have developed soluble, relatively well defined Ziegler–Natta catalysts based on early transition metal metallocene derivatives.[2] These systems provide an unprecedented opportunity to understand the relationships between catalyst structure, activity and polymer microstructure.[3]

The development of Ziegler–Natta catalysts in this laboratory has concentrated largely on bis(cyclopentadienyl)scandium hydrides, alkyls, and related compounds.[4] We have found that the linked permethylscandocene complexes $OpSc(H)(PMe_3)$ (1) (Op = $\{(\eta^5\text{-}C_5Me_4)_2SiMe_2\}$) and $[DpScH]_2$ (Dp = $\{(\eta^5\text{-}C_5H_3CMe_3)_2SiMe_2\}$)[5] undergo a variety of reactions relevant to Ziegler–Natta catalysis (*e.g.*

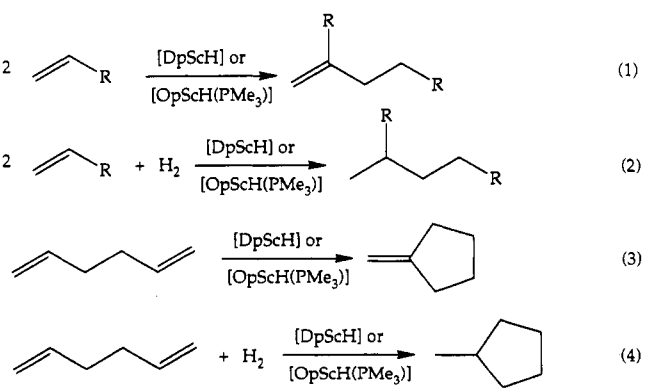


$OpScH(PMe_3)$



DpScH

olefin insertion, β-H elimination, β-alkyl elimination).[6] For example, both of these complexes are efficient catalysts for the dimerization and hydrodimerization of α-olefins, as well as the cyclization and hydrocyclization of C_6–C_{10} α,ω-dienes to methylene cycloalkanes and methylcycloalkanes (*e.g.* eqs 1–4).[7] Moreover, DpScH catalyzes ring



opening of methylenecyclobutanes and methylenecyclopropanes to the corresponding 1,4-pentadienes or 1,3-butadienes *via* sequential insertion/β-alkyl elimination

† Contribution No. 8832.

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(1) For reviews on Ziegler–Natta chemistry see: (a) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979. (b) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 857. (c) Tait, P. J. T. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Chapters 1 and 2. (d) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(2) For examples with leading references see: (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Hlatky, G. C.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (c) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *27*, 507. (d) Watson, P. L. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (e) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277. (f) Jeske, G.; Lauke, H.; Mauermann, H.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8091. (g) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

(3) Kaminsky, W.; Sinn, H. *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Springer-Verlag: Berlin, 1988.

(4) (a) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (c) Bercaw, J. E. *Pure Appl. Chem.* **1990**, *62*, 1151 and references therein. (d) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74 and references therein.

(5) Although molecular weight measurements indicate DpScH is predominantly dimeric, we assume that the reactive form is monomeric.

(6) Bunel, E. E. Ph.D. Thesis, California Institute of Technology, 1989.

(7) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74–84.

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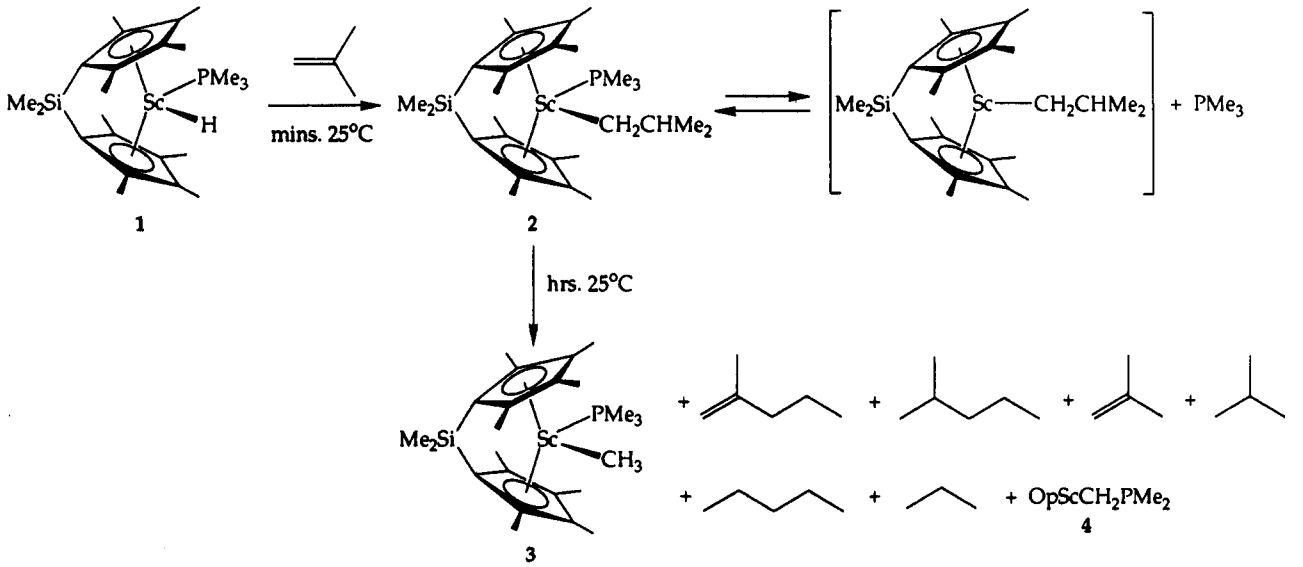
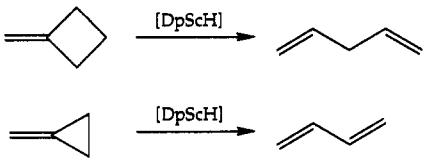
Scheme 1



pathways (*e.g.* eqs 5 and 6).[8] These reactivity patterns



have provided the basis for a variety of further experiments designed to probe mechanistic aspects of olefin insertion into M–R (R = H, alkyl) bonds.[9]

In propylene polymerization β-CH_3 elimination is now recognized as an important, and in some cases dominant, chain transfer step.[10] The organoscandium derivatives $OpScCH_2CH(CH_3)R$ offer an opportunity to examine competitive β-H, β-CH_3, and β-R elimination. Accordingly, we have examined the reactivity of $OpSc(H)(PMe_3)$ with *gem*-disubstituted olefins. These studies reveal that chain transfer by β-CH_3 elimination may be competitive with β-H elimination in this system. Significantly, [OpSc–CH_2-$CH(CH_2CH_3)_2$] shows no evidence of β-CH_2CH_3 elimination.

Results and Discussion

Reaction of $OpSc(H)(PMe_3)$ with Isobutene: Identification of Products and Proposed Reaction Scheme. Isobutene adds quickly and cleanly to $OpSc(H)(PMe_3)$ (**1**), affording $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$ (**2**). The isobutyl complex **2** then slowly decomposes to afford the previously reported methyl derivative $OpSc(CH_3)(PMe_3)$, implicating β-CH_3 elimination of propene. Free propene, however, is not detected by monitoring the process by ^1H NMR spectroscopy. Rather, careful examination of spectra and gas chromatographic analysis reveals the diverse set of products shown in Scheme 1.[11] The processes proposed to account for the formation of the major organoscandium product $OpSc(CH_3)(PMe_3)$ (**3**), the minor one $OpScCH_2PMe_2$ (**4**), and the hydrocarbons are outlined in Scheme 2. Five separate processes are invoked: (1) reversible loss of trimethylphosphine from the hydride and alkyl derivatives, (2) reversible insertions of both *gem*-disubstituted and α-olefins into the Sc–H bond of [OpScH], affording 2-methylalkyl and *n*-alkyl derivatives, respectively, (3) β-CH_3 elimination for the 2-methylalkyl derivatives, yielding α-olefin and [$OpScCH_3$], (4) insertion of α-olefin into Sc–C bonds of the *n*-alkyl derivatives, (5) σ bond metathesis[12] of a scandium–carbon bond of the scandium alkyls with a methyl C–H bond of trimethylphosphine affording alkane and $OpScCH_2PMe_2$ (**4**).[13]

The two C_6 products, 2-methylpentane and 2-methyl-1-pentene, are formed from $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$ by (i) loss of PMe_3, (ii) β-CH_3 elimination from [$OpScCH_2$-$CH(CH_3)_2$] releasing propene, (iii) addition of propene to [Op–Sc–H], which is in equilibrium with all alkyl derivatives except $OpSc(CH_3)(PMe_3)$, and (iv) a second insertion of propene to yield [$OpScCH_2CH(CH_3)CH_2CH_2CH_3$], which can then undergo (v) β-H elimination to [Op–Sc–H] and 2-methyl-1-pentene or (vi) σ bond metathesis with PMe_3 yielding 2-methylpentane and $OpScCH_2PMe_2$ (**4**).

$$OpSc\{CH_2CH(CH_3)_2\}(PMe_3) \rightleftarrows [OpScCH_2CH(CH_3)_2] + PMe_3 \quad \text{(i)}$$

$$[OpScCH_2CH(CH_3)_2] \rightleftarrows [OpScCH_3] + CH_2{=}CHCH_3 \quad \text{(ii)}$$

(8) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.

(9) (a) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (b) Krauledat, H.; Brintzinger, H. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1412. (c) Cotter, W. D.; Bercaw, J. E. *J. Organomet. Chem.* **1991**, *417*, C1.

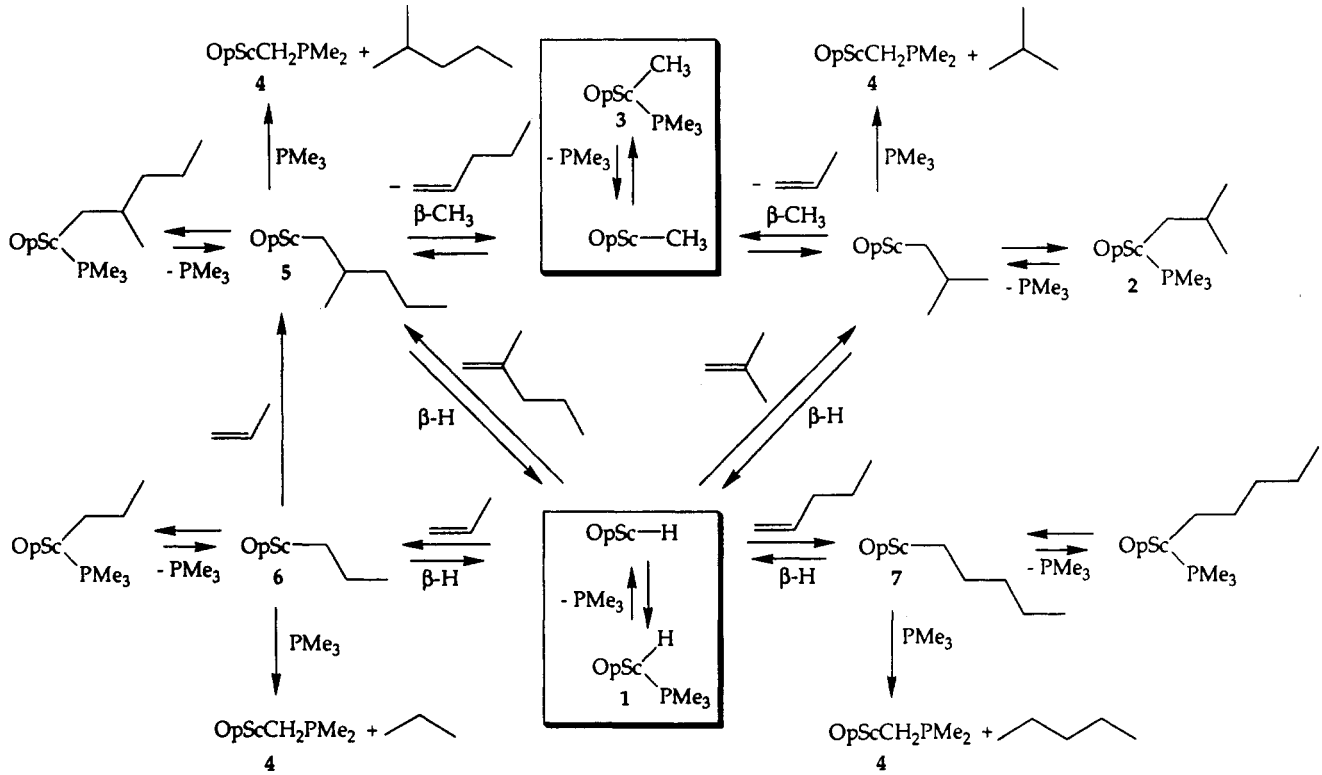
(10) (a) Roe, D. C.; Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277. (c) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.

(11) On reflection the β-CH_3 elimination of propene is almost certainly endothermic, so that conversion of $OpSc(CH_2CHMe_2)(PMe_3)$ to $OpSc(CH_3)(PMe_3)$ demands concurrent exothermic reaction(s) of propene to other reaction products (as observed).

(12) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(13) Whereas there is no definitive evidence that would rule out an intramolecular extrusion of alkane from the trimethylphosphine adducts, OpScR(PMe_3), the relative rates for formation of **4** correlate roughly inversely with trimethylphosphine affinity (*vide infra*), suggesting a bimolecular reaction between OpScR and free trimethylphosphine. The resistance of $OpSc(CH_3)(PMe_3)$ to decompose to CH_4 and **4** is in further support of this proposal. Since the methyl derivative has the highest affinity for PMe_3 and hence the alkyl with the lowest concentration of [OpScR], it would be expected to undergo the bimolecular reaction ([OpScR] + PMe_3 → **4** + RH) most slowly.

Scheme 2



$$[OpScH] + CH_2{=}CHCH_3 \rightleftarrows [OpScCH_2CH_2CH_3] \quad \text{(iii)}$$

$$[OpScCH_2CH_2CH_3] + CH_2{=}CHCH_3 \rightleftarrows [OpScCH_2CH(CH_3)CH_2CH_2CH_3] \quad \text{(iv)}$$

$$[OpScCH_2CH(CH_3)CH_2CH_2CH_3] \rightleftarrows [OpScH] + CH_2{=}C(CH_3)CH_2CH_2CH_3 \quad \text{(v)}$$

$$[OpScCH_2CH(CH_3)CH_2CH_2CH_3] + PMe_3 \rightarrow OpScCH_2PMe_2 + CH_3CH(CH_3)CH_2CH_2CH_3 \quad \text{(vi)}$$

Perhaps most surprising is the observation of *n*-pentane in the product mixture. According to the proposed scheme, it is formed by the same beginning steps (i)–(iv), followed by (vii) β-CH_3 elimination of 1-pentene from [$OpScCH_2CH(CH_3)CH_2CH_2CH_3$], which after trapping with PMe_3 (viii) leads to the major organoscandium product $OpSc(CH_3)(PMe_3)$, (ix) reaction of 1-pentene with [OpScH] to yield [$OpScCH_2CH_2CH_2CH_2CH_3$], and finally, (x) σ bond metathesis with PMe_3, yielding *n*-pentane and $OpScCH_2PMe_2$.

$$[OpScCH_2CH(CH_3)CH_2CH_2CH_3] \rightleftarrows [OpScCH_3] + CH_2{=}CHCH_2CH_2CH_3 \quad \text{(vii)}$$

$$[OpScCH_3] + PMe_3 \rightarrow OpSc(CH_3)(PMe_3) \quad \text{(viii)}$$

$$[OpScH] + CH_2{=}CHCH_2CH_2CH_3 \rightleftarrows [OpScCH_2CH_2CH_2CH_2CH_3] \quad \text{(ix)}$$

$$[OpScCH_2CH_2CH_2CH_2CH_3] + PMe_3 \rightarrow OpScCH_2PMe_2 + CH_3CH_2CH_2CH_2CH_3 \quad \text{(x)}$$

Interestingly, the only olefins present at the end of this complex reaction sequence are *gem*-disubstituted 2-methyl-1-alkenes; the α-olefins (propene, 1-pentene) reenter the sequence by addition to [OpScH] or [$OpScCH_3$], ultimately resulting in the normal C_{odd} alkane or a C_{even} 2-methyl-1-alkene or 2-methylalkane.

^{1}H NMR Observation of Reaction Intermediates and Relative Affinities for Trimethylphosphine. Although the reaction of $OpSc(H)(PMe_3)$ with isobutene is far too complex for meaningful kinetic analysis, we did follow the course of the reaction by ^{1}H NMR spectroscopy in an attempt to identify any intermediates predicted by the working mechanistic hypothesis shown in Scheme 2. Thus, 1 and isobutene were allowed to react in an NMR tube in cyclohexane-d_{12}. ^{1}H spectra were automatically acquired regularly over a period of about 12 h, spectra were analyzed in conventional 1-D form, and white-wash stacked plots of the spectra were generated. This form of presentation of the data makes following the appearance and disappearance of reactants, products, and intermediates much easier than analysis of the same data as a series of conventional 1-D spectra.

An example of the utility of these plots is shown in Figure 1, which highlights a set of resonances characteristic of one of the two equivalent[14] Op-ligand methyl groups (likely the α-methyl groups)[15] of the OpSc–alkyl complexes. As can be seen, the ^{1}H NMR resonance attributed to the isobutyl complex **2** decreases with time while that for the product methyl **3** increases. An additional resonance is clearly observed to grow in and eventually disappear. This intermediate has been identified as $OpSc(CH_2CH_2CH_3)(PMe_3)$ (**6**) by independent synthesis from $OpSc(H)(PMe_3)$ and propene (*vide infra*). Integrations reveal roughly a

(14) Whereas the four methyl groups of the {$(\eta^5\text{-}C_5(CH_3)_4)_2SiMe_2$} ligands for the trimethylphosphine adducts of the alkyl derivatives, *viz.* $OpSc(R)(PMe_3)$, are inequivalent, rapid trimethylphosphine dissociation/association results in pairwise inequivalency.

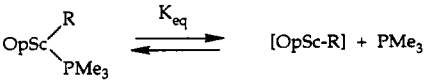
(15) The tentative assignments of $(CH_3)_\alpha$ and $(CH_3)_\beta$ are based on the observation that only the (upfield) resonance for $(CH_3)_\beta$ splits for the 2-methyl-1-pentyl derivative, {$(\eta^5\text{-}C_5Me_4)_2SiMe_2$}$Sc(CH_2CH(CH_3)CH_2CH_2CH_3)(PMe_3)$.

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

compd	assgnt	δ (ppm)
$OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$ (**2**)	$(CH_3)_2Si$	0.948 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.951 (s, 12H); 1.819 (s, 12H)
	$ScCH_2CH(CH_3)_2$	0.207 (d), $^3J_{H-H}$ = 7.55 Hz
	$ScCH_2CH(CH_3)_2$	2.22 (m)
	$ScCH_2CH(CH_3)_2$	0.715 (d), $^3J_{H-H}$ = 6.42 Hz
	$P(CH_3)_3$	0.977 (br)
$OpSc(CH_3)(PMe_3)$[b] (**3**)	$(CH_3)_2Si$	0.826 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.987 (s, 12H); 1.835 (s, 12H)
	$ScCH_3$	−1.033 (s)
	$P(CH_3)_3$	1.040 (d), $^2J_{P-H}$ = 4.14 Hz
$OpScCH_2CH(CH_3)_2$ (**2**, PMe_3-free)	$(CH_3)_2Si$	0.948 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.946 (s, 12H); 1.808 (s, 12H)
	$ScCH_2CH(CH_3)_2$	0.300 (d), $^3J_{H-H}$ = 7.81 Hz
	$ScCH_2CH(CH_3)_2$	2.243 (m)
	$ScCH_2CH(CH_3)_2$	0.705 (d), $^3J_{H-H}$ = 6.35 Hz
$OpScCH_3$ (**3**, PMe_3-free)	$(CH_3)_2Si$	0.899 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.935 (s, 12H); 1.841 (s, 12H)
	$ScCH_3$	−0.833 (s)
$OpSc\{CH_2CH(CH_3)CH_2CH_2CH_3\}(PMe_3)$ (**5**)	$(CH_3)_2Si$	0.950 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.940 (s, 12H); 1.814 (s, 6H); 1.807 (s, 6H)
	$ScCH_2CH(CH_3)(CH_2)_2CH_3$	0.147 (m)
	$ScCH_2CH(CH_3)(CH_2)_2CH_3$	0.605 (d), $^3J_{H-H}$ = 6.35 Hz
	$ScCH_2CH(CH_3)(CH_2)_2CH_3$	0.887 (t), $^3J_{H-H}$ = 7.08 Hz
	$P(CH_3)_3$	0.966 (br)
$OpSc(CH_2CH_2CH_3)(PMe_3)$ (**6**)	$(CH_3)_2Si$	0.948 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.951 (s, 12H); 1.819 (s, 12H)
	$ScCH_2CH_2CH_3$	0.207 (m)
	$ScCH_2CH_2CH_3$	0.88 (m, overlapping)
	$P(CH_3)_3$	1.018 (sl br d)
$OpSc\{CH_2CH(CH_2CH_3)_2\}(PMe_3)$ (**8**)	$(CH_3)_2Si$	0.942 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.948 (s, 12H); 1.797 (s, 12H)
	$ScCH_2CH(CH_2CH_3)_2$	0.012 (d), $^3J_{H-H}$ = 7.62 Hz
	$ScCH_2CH(CH_2CH_3)_2$	0.672 (t), $^3J_{H-H}$ = 7.18 Hz
	$P(CH_3)_3$	0.942 (br)
$OpScCH_2CH(CH_2CH_3)_2$ (**11**)	$(CH_3)_2Si$	0.948 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.945 (s, 12H); 1.794 (s, 12H)
	$ScCH_2CH(CH_2CH_3)_2$	0.034 (d), $^3J_{H-H}$ = 7.63 Hz
	$ScCH_2CH(CH_2CH_3)_2$	0.671 (t), $^3J_{H-H}$ = 7.15 Hz
$OpScCH_2PMe_2$ (**4**)	$(CH_3)_2Si$	0.948 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.946 (s, 12H); 1.808 (s, 12H)
	$ScCH_2P(CH_3)_2$	0.324 (d), $^2J_{P-P}$ = 9.09 Hz
	$ScCH_2P(CH_3)_2$	1.277 (d), $^2J_{P-H}$ = 5.96 Hz
$OpSc\{C(CH_3)=CH(CH_3)\}(PMe_3)$ (**9**)	$(CH_3)_2Si$	0.934 (s)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.888 (s, 12H); 1.755 (s, 12H)
	$ScC(CH_3)(C(H)(CH_3)$	3.690 (m), $^3J_{H-H}$ = 5.35 Hz, $^4J_{H-H}$ = 1.71 Hz
	$ScC(CH_3)C(H)(CH_3)$	1.724 (m), $^4J_{H-H}$ = 0.76 Hz
	$ScC(CH_3)C(H)(CH_3)$	1.920 (br)
	$P(CH_3)_3$	0.923 (d), $^2J_{P-H}$ = 2.73 Hz
$OpScC(CH_3)=C(CH_3)_2$ (**10**, PMe_3-free)	$(CH_3)_2Si$	0.987 (s, 3H); 0.968 (s, 3H)
	$(\eta^5\text{-}C_5(CH_3)_4)_2$	1.880 (s, 6H); 1.840 (s, 6H)
		1.830 (s, 6H); 1.789 (s, 6H)
	$ScC(CH_3)C(CH_3)_2$	1.625 (m)
	$ScC(CH_3)C(CH_3)_2$	1.245 (m), 1.180 (m)

[a] All spectra were recorded at 500 MHz in cyclohexane-d_{12} at ambient temperature. [b] NMR data for this compound in C_6D_6 have been previously reported.[6]

constant sum for these three resonances over the course of the reaction. Thus, no other organoscandium intermediates grow in to detectable levels of concentration. Close examination of the time course of the chemical shifts reveals a smooth change, and it is particularly obvious in Figure 2, where the contour plots (bottom) illustrate the dramatic chemical shift changes for the $(CH_3)_\beta$ of **2** and the transient **6**.[16] We attribute this PMe_3 chemical shift variation with time to differences in the relative PMe_3 binding constants of the various organoscandium species. Since the observed ^{1}H chemical shift represents a weighted average of that for the trimethylphosphine-bound and trimethylphosphine-free alkyl species, the average shift varies with $[PMe_3]_{free}$. Whereas we have not attempted to quantify the trimethylphosphine binding constants, simple steric arguments predict the following order:



$$(K_{eq})^{R=H} < (K_{eq})^{R=CH_3} < (K_{eq})^{R=CH_2CH_2CH_3} < (K_{eq})^{R=CH_2CHMe_2} < (K_{eq})^{R=CH_2CHMeR'}$$

Thus, as the isobutyl derivative **2**, which binds trimethylphosphine relatively weakly, proceeds to the methyl derivative **3**, which tightly binds trimethylphosphine, the $[PMe_3]_{free}$ gradually decreases. The propyl derivative **6**, with its intermediate affinity for trimethylphosphine, exhibits the greatest variation in relative concentrations for **6** and the trimethylphosphine-free species $[OpScCH_2CH_2CH_3]$.

(16) Other resonances also are observed to undergo chemical shift variations; however, for clarity only those methyl resonances shown in Figures 1 and 2 are illustrated.

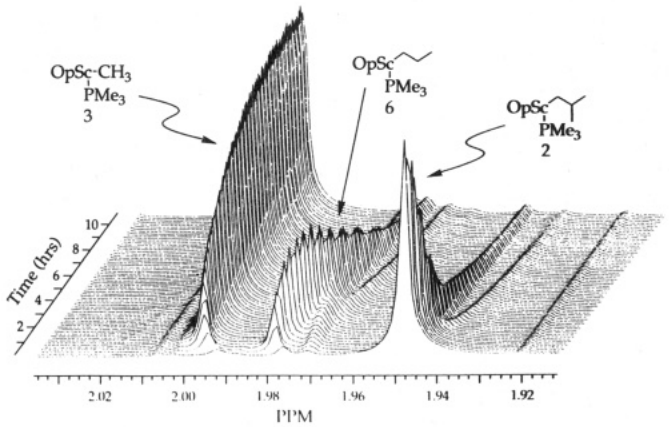


Figure 1. Reaction of **1** with isobutene: white-wash stack plots (chemical shift vs time) of characteristic (Op ligand $(CH_3)_\alpha$) resonances for the major organometallic species (**2**, **3**, and **6**) during the course of the reaction.

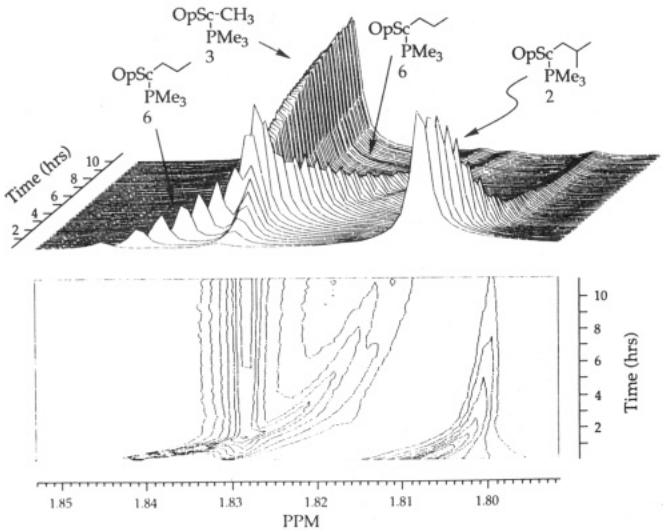
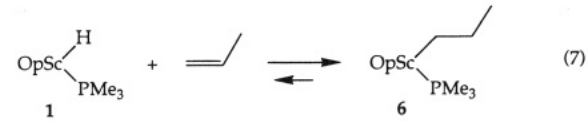


Figure 2. Reaction of **1** with isobutene: (top) white-wash stack plots (chemical shift vs time) highlighting the time dependent chemical shifts of characteristic (Op ligand $(CH_3)_\beta$) resonances for **2**, **3**, and **6** during the course of the reaction, and (bottom) contour plots of the same resonances (see text for details).

Also in support of a much larger trimethylphosphine affinity for the methyl derivative **3** *vs* the isobutyl derivative **2**, is the observation that *ca.* 80% of the trimethylphosphine can be removed with solvent cyclohexane *in vacuo* when a solution of OpSc{$CH_2CH(CH_3)_2$}(PMe_3) (**2**) is taken to dryness. By contrast, trimethylphosphine is nearly entirely retained when solutions of the methyl derivative **3** are treated similarly.[17]

Addition of an 11-fold excess of PMe_3 to solutions of **2** slow the rate of conversion to **3**, but only increase the half-time for reaction by about a factor of 3, again supporting the implication that under the conditions of the NMR experiments trimethylphosphine is substantially dissociated from **2**.[18]

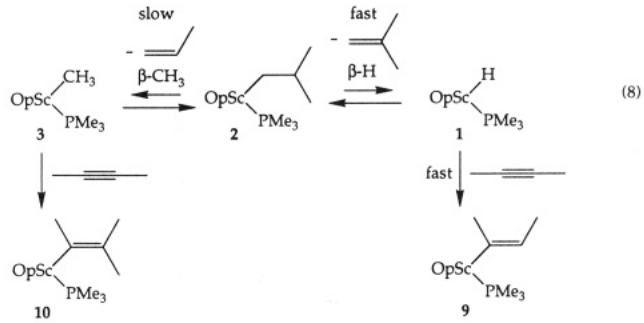
Model Reactions of Suspected Reaction Intermediates. The identity of the propyl intermediate, OpSc($CH_2CH_2CH_3$)(PMe_3) (**6**), has been confirmed by its independent synthesis (eq 7). This reaction is readily



(7)

reversed, and a number of the other reactions proposed in Scheme 2 ensue, as is apparent by monitoring the course of the reaction of **1** with 2 equiv of propene. Thus, whereas the first product is indeed **6**, it ultimately rearranges to the now familiar methyl derivative **3** and a lesser amount of $OpScCH_2PMe_2$ (**4**), along with the hydrocarbons, 2-methylpentene, and a small amount of pentane.[19] These same products are also obtained by treating OpSc(H)(PMe_3) with 2-methylpentene, again in accord with Scheme 2.

The facility of β-H elimination for the isobutyl derivative is illustrated by its rapid reaction with 2-butyne, wherein an immediate conversion to isobutene and OpSc{C(CH_3)=$CH(CH_3)$}(PMe_3) (**9**) is observed (eq 8). Moreover,



(8)

addition of a 1:1 mixture of 2-butyne and propene to **3** affords primarily OpSc{$C(CH_3)$=$C(CH_3)_2$}(PMe_3) (**10**). Since <5% of **10** is generated in the reaction of OpSc{$CH_2CH(CH_3)_2$}(PMe_3) (**2**) with $CH_3C{\equiv}CCH_3$, we may conclude that β-H elimination is faster than β-methyl elimination for **2**.[20] Moreover, alkyls such as **2** may effectively act as reservoirs for the very reactive hydride, [OpScH], capable of promoting the dimerization of α-olefins, even when both are at relatively low concentrations.

OpSc{$CH_2CH(CH_2CH_3)_2$}(PMe_3): β-Ethyl Elimination? Given the facility of β-methyl elimination for OpSc{$CH_2CH(CH_3)_2$}(PMe_3) and the 2-methyl-1-pentyl derivative, we wondered whether β elimination of higher alkyls could also proceed. Treatment of **1** with 2-ethyl-1-butene

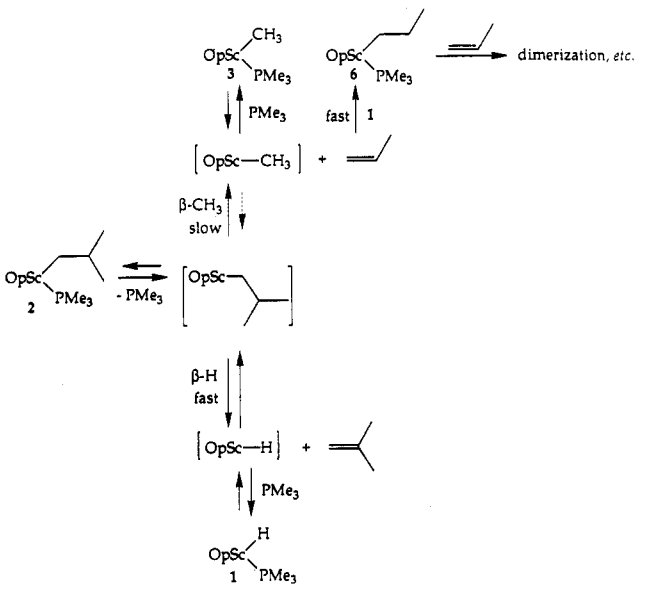
(17) Interestingly, when the (80%) phosphine-free isobutyl derivative so obtained rearranges to the methyl derivative upon redissolving in cyclohexane, large chemical shift changes accompany the Sc–CH_3 resonance for this phosphine "starved" system; the signals for the isobutyl show relatively little change in chemical shift over the course of the reaction. These observations are consistent with the relative ordering of trimethylphosphine affinity listed.

(18) Addition of 1 and 2 equiv of PMe_3 slows the reaction almost imperceptibly. Addition of a 6-fold excess of isobutene slows the conversion half-time by less than a factor of 1.5; the cause of this effect is not obvious.

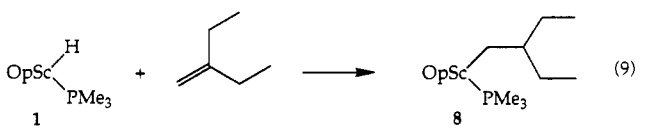
(19) Although definitive evidence for the formation of 1-pentene is lacking, there are two uncharacterized multiplets of low signal-to-noise observed at δ 4.3 and 4.7, tentatively assigned to the geminal hydrogens of the dimer that would result from [OpScH]-catalyzed dimerization of 1-pentene.

(20) A referee has pointed out that it is possible that addition of 2-butyne to the scandium hydride derivative is much faster than 2-butyne addition to the scandium methyl derivative, thus effectively funneling the reaction through the hydride, even if β-H elimination were slower than β-CH_3 elimination for **2**. We have subsequently established that faster addition of 2-butyne to **1** does, in fact, occur: addition of 0.8 equiv of 2-butyne to a mixture of 1 equiv each of **1** and **3** yields only **9**; no **10** is observed by ^1H NMR. On the other hand, the observation of **10** only, when **3** is treated with a 1:1 mixture of 2-butyne and propene, indicates that a fast prequilibrium between **2**, **3**, and propene, accompanied by slower β-H elimination, does *not* occur.

Scheme 3

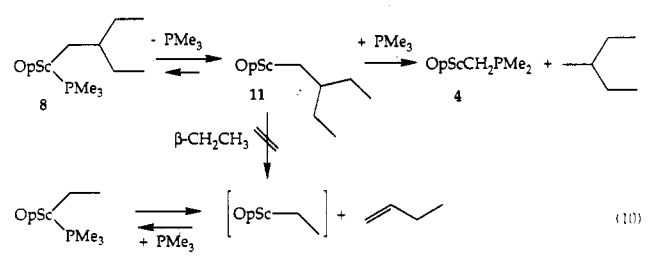


cleanly affords $OpSc\{CH_2CH(CH_2CH_3)_2\}(PMe_3)$ (8) (eq 9). Unlike the isobutyl derivative for which β-CH_3 elim-



(9)

ination begins immediately upon formation, there is no evidence for β-CH_2CH_3 elimination for 8. There is no indication (^{1}H NMR) for a new alkyl $OpSc(CH_2CH_3)(PMe_3)$, nor do any products arise from dimerization, *etc.* of 1-butene by 1. Rather, 8 only undergoes a slow decomposition to 4 and 3-methylpentane over the period of several days (eq 10).



(10)

The very low affinity of the 2-ethylbutyl derivative 8 for trimethylphosphine allows the isolation of $OpScCH_2CH(CH_2CH_3)_2$ (11) by removal PMe_3 along with solvent cyclohexane when solutions of 8 are taken to dryness. When dissolved in cyclohexane-d_{12} 11 is stable for days at 25 °C, with no evidence of reactions (*i.e.* generation of 1-butene dimer) that would be expected should β-CH_2CH_3 elimination occur.

Conclusions

The decomposition of the isobutyl derivative, $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$, proved to be rather complex, but nonetheless revealing. Whereas a facile and reversible β-H elimination of isobutene is maintained (Scheme 3), decomposition begins with the slower β-CH_3 elimination to propene and the stable methyl derivative. The further reactions of propene (dimerization, *etc.*), immediately catalyzed by [OpScH], provide the thermodynamic driving force for the undoubtedly endothermic β-CH_3 elimination from $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$. Free propene is not in evidence; rather it is immediately converted to the reactive propyl derivative by reaction with [OpScH], and a commensurate amount of free isobutene is released. As additional propene is released, further reaction with $OpSc(CH_2CH_2CH_3)(PMe_3)$ ensues (Scheme 3). This propensity for alkyls capable of β-H eliminating to provide catalytically very reactive [OpScH] is perhaps best illustrated by the observation that treatment of $OpSc(CH_3)(PMe_3)$ (3) with propene does not, in fact, result in buildup of the isobutyl derivative 2. When a small amount of 2 is formed, it immediately undergoes β-H elimination to isobutene, and the [OpScH] so generated rapidly catalyzes the dimerization, *etc.* of the remaining propene according to Scheme 2.

Formation of $OpScCH_2PMe_2$ (4) via σ bond metathesis between PMe_3 and the alkyl derivatives is especially clean for the 2-ethylbutyl derivative, since no other reaction pathways are available, apart from reversible (and nonproductive) β-H elimination. Alkane formation thus results by this previously unrecognized catalyst deactivation pathway,[21] leading to very stable 4.[22]

Competitive β-H and β-CH_3 elimination have been noted previously.[10] Both Teuben and Resconi noted that for the sterically crowded bis(pentamethylcyclopentadienyl)-zirconium and -hafnium systems, chain transfer by β-CH_3 elimination dominates. Furthermore, Resconi was able to quantify the ratio of rate constants for the two processes by NMR analysis of end groups. β-CH_3 elimination was found to be *ca.* 10 times faster for zirconium and as much as 50 times preferred for the hafnium system. Interestingly, for the less crowded $[(\eta^5\text{-}C_5H_5)_2M]$ (M = Zr, Hf) systems, β-H elimination is preferred over β-CH_3 elimination by at least a factor of 100. These findings have been rationalized on the basis that for the β,β-disubstituted alkyl intermediates, $[Cp^*_2M\text{-}CH_2CH(CH_3)R]^+X^-$, unfavorable steric interactions between the Cp* ligands and the two β-alkyl substituents destabilize the transition state for β-H elimination. Our findings that β-H elimination dominates for the more open, linked bis(cyclopentadienyl) system $OpScCH_2CH(CH_3)R$, may be accommodated by these same arguments.[23] Even though β-H elimination is dominant, β-CH_3 elimination is clearly in evidence, most convincingly demonstrated by the eventual generation of >95% $OpSc(CH_3)(PMe_3)$ from $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$. The reluctance of $OpSc\{CH_2CH(CH_2CH_3)_2\}(PMe_3)$ (8) and coordinatively even less saturated $OpScCH_2CH(CH_2CH_3)_2$ (11) to undergo β-ethyl elimination is also in accord with the findings of Resconi, who reported that for 1-butene polymerization, chain transfer

(21) This σ bond metathesis reaction with trimethylphosphine appears to be the first observation of a nonredox reaction with PMe_3, although oxidative addition of PMe_3 to electron-rich middle- and late-transition metal complexes has been previously observed: (a) Rabinovich, D.; Zelman, R.; Parkin, G. *J. Am. Chem. Soc.* **1990**, *112*, 9632. (b) Shinomoto, R. S.; Desrosiers, P. J.; Harper, T. G. P.; Flood, T. C. *J. Am. Chem. Soc.* **1990**, *112*, 704. (c) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *108*, 4856.

(22) H/D exchange between C_6D_6 and $P(CH_3)_3$ catalyzed by $[Cp^*_2ScH]_x$ has been reported. Although this exchange is almost certainly mediated by $[Cp^*_2ScCH_2PMe_2]$, it does not build up to detectable levels. Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.

(23) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, 74.

by β-C_2H_5 does not occur, even for the bis(pentamethylcyclopentadienyl)zirconium and -hafium catalysts.

Experimental Section

General Considerations. All air and/or moisture sensitive compounds were manipulated using standard high vacuum line, Schlenk, or cannula techniques or in a dry box under a nitrogen atmosphere, as described previously.[24] Argon and nitrogen gases were purified and dried by passage over columns of MnO on vermiculite and activated molecular sieves. Solvents were stored under vacuum over titanocene[25] or sodium benzophenone ketyl. ^{1}H NMR spectra were recorded on a Bruker AM500 (500.13-MHz) spectrometer in cyclohexane-d_{12} at room temperature unless otherwise specified. The preparations of OpScCl·LiCl·$2Et_2O$, $OpScCH(SiMe_3)_2$, and $OpSc(H)(PMe_3)$ were carried out as previously described.[26]

NMR Tube Reactions. Most of the reactions were carried out in sealed NMR tubes. The tubes were fitted with a 180°, concentric, Teflon needle valve which was blown directly onto the tube (the tubes employed were purchased from J. Young[27]), which could be attached to the high vacuum line by a simple adapter tube. These assemblies allow convenient loading of solids in the glovebox as well as a reversible vacuum tight seal which allows facile manipulations of volatiles into and out of the tube assembly. In a typical experiment, the NMR tube was loaded with $OpSc(H)(PMe_3)$ (*ca.* 10 mg) in the glovebox. On the vacuum line, cyclohexane-d_{12} (*ca.* 1 mL) was condensed into the evacuated tube assembly at −78 °C, to produce a solution of approximate concentration of 0.024 M, followed by the desired olefin at −196 °C. The tube was then removed from the vacuum line and warmed to room temperature with shaking. The insoluble white $OpSc(H)(PMe_3)$ was allowed to react (about 3–5 min) with the olefin to give the soluble (typically yellow-orange) alkyl derivative, and the tube was then stored at −78 °C until just prior to insertion into the NMR probe. In the cases in which the phosphine was pumped off of the reactions, this was accomplished by carefully evacuating the NMR tube after formation of the alkyl complex, and then redissolving in fresh cyclohexane-d_{12}.

Reaction of $OpSc(H)(PMe_3)$ with Isobutene: Analysis of Volatiles by Gas Chromatography. In the drybox a small volume, moderate pressure reaction vessel equipped with a Teflon needle valve was charged with $OpSc(H)(PMe_3)$ (22 mg, 0.0528 mmol). C_6D_{12} (*ca.* 1.5 mL) was vacuum transferred onto the solid at −78 °C. Isobutene (293 Torr in 3.3 mL at 25 °C, 0.0528 mmol) was condensed into the reaction vessel. The solution was allowed to warm to room temperature and the initially cloudy, white solution slowly (*ca.* 20 min) changed to a clear orange. The reaction was allowed to stir overnight, during which time a significant amount of finely divided orange/yellow precipitate was deposited. The volatiles were condensed into a NMR tube, first analyzed by ^{1}H NMR, and then by GC. Gas chromatographic analyses were carried out on a Perkin-Elmer 8410 gas chromatograph equipped with a flame ionization detector and 12-ft Chromasorb W column treated with 13% DBT (dibutyl tetrachlorophthalate). Satisfactory separation of a mixture of propane, isobutane, isobutene, *n*-pentane, 1-pentene, 2-methylpentane, 2-methylpentene, and cyclohexane was accomplished using detector and injector temperatures of 200 °C, a column temperature of 31 °C, and a helium flow rate of 20 mL/min. The reaction vessel containing the residual solid (mostly $OpSc(CH_3)(PMe_3)$) was taken back into the drybox and used for the following procedure.

Addition of Propene to the Generated $OpSc(CH_3)(PMe_3)$. In the glovebox the residual solid from the previous procedure was redissolved into *ca.* 2 mL of cyclohexane-d_{12}, and the resulting solution was divided into two NMR tubes. ^{1}H NMR spectra of the first tube indicated clean coversion of $OpSc(H)(PMe_3)$ to $OpSc(CH_3)(PMe_3)$. The second tube was taken onto the vacuum line, and into the cooled (−196 °C), evacuated tube, was condensed approximately 1 equiv of propene. The tube was warmed to ambient temperature, and ^{1}H NMR spectra were recorded after 30 min and after 90 min.

$OpSc(CH_3)(PMe_3)$ (3). In the drybox a 25-mL round bottom flask attached to a 180° Teflon needle valve was charged with $OpSc(H)(PMe_3)$ (100 mg, 0.238 mmol). Petroleum ether (*ca.* 8 mL) was vacuum transferred onto the solid at −78 °C. Isobutene (1.2 equiv) was condensed into the reaction vessel from a calibrated gas volume. The assembly was allowed to warm to room temperature and the initially cloudy, white solution slowly (*ca.* 30 min) turned orange and had a small amount of solid which remained undissolved. The solution was allowed to stir overnight after which time it was filtered and dried *in vacuo*, leaving $OpSc(CH_3)(PMe_3)$ as a slightly waxy orange-yellow solid in *ca* 85% yield. Anal. Calcd for $C_{24}H_{42}PScSi$: C, 66.31; H, 9.76. Found: C, 67.02, 66.49; H, 9.83, 9.91. ^{13}C NMR: δ 4.43, quartet, $^2J_{CH}$ = 120.3 Hz, $(CH_3)_2Si$; δ 15.10, quartet, $^2J_{CH}$ = 125.2 Hz, and δ 12.90, quartet, $^2J_{CH}$ = 125.0 Hz, $(\eta^5\text{-}C_5(CH_3)_4)_2$; δ 126.74, 121.98, and 102.62, $(\eta^5\text{-}C_5(CH_3)_4)_2$; not detected, $ScCH_3$; δ 15.26, quartet of doublets, $^2J_{CH}$ = 130.3 Hz, $^2J_{CP}$ = 6.44 Hz, $P(CH_3)_3$. ^{31}P NMR: δ 121.6.

Reaction of $OpSc(CH_3)(PMe_3)$ with 2-Butyne. $OpSc(CH_3)(PMe_3)$ (10 mg, 0.023 mmol), prepared as described above, was loaded into a sealable NMR tube. On the vacuum line, cyclohexane-d_{12} (*ca.* 1 mL) was condensed into the evacuated tube assembly at −78 °C. 2-Butyne (2 equiv) was then condensed in, at −196 °C, from a calibrated gas volume. The tube was warmed to ambient temperature, and an NMR spectrum taken after approximately 10 min was consistent with clean conversion to $OpSc\{C(CH_3)=C(CH_3)_2\}(PMe_3)$ (**10**). Removal of all volatiles followed by redissolution in fresh cyclohexane-d_{12} afforded the PMe_3-free complex $OpScC(CH_3)=C(CH_3)_2$, as indicated by its ^{1}H NMR spectrum.

Reaction of $OpSc(H)(PMe_3)$ with Isobutene: Addition of 2-Butyne to the Generated $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$. $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$ was prepared in an NMR tube as described above. 2-Butyne (4 equiv) was then condensed in, at −196 °C, from a calibrated gas volume. The tube was warmed to ambient temperature, and an NMR spectrum was taken after approximately 10 min. A spectrum taken the next day showed no change.

Competitive Reaction of $OpSc(CH_3)(PMe_3)$ with 2-Butyne and Propene. $OpSc(CH_3)(PMe_3)$ (10 mg, 0.023 mmol), prepared as described above, was loaded into a sealable NMR tube. On the vacuum line, cyclohexane-d_{12} (*ca.* 1 mL) was condensed into the evacuated tube assembly at −78 °C. 2-Butyne (1.5 equiv) and propene (1.5 equiv) were then condensed in, at −196 °C, from a calibrated gas volume. The tube was warmed to ambient temperature, and an NMR spectrum taken after approximately 30 min was consistent with >95% conversion to $OpSc\{C(CH_3)=C(CH_3)_2\}(PMe_3)$ (**10**) as the organometallic product. A spectrum taken the next day showed no change.

^{1}H NMR Monitoring of the Decomposition of $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$. The decomposition of $OpSc\{CH_2CH(CH_3)_2\}(PMe_3)$, prepared as described above, to $OpSc(CH_3)(PMe_3)$ was followed by ^{1}H NMR spectroscopy using automatic accumulation programs.[28] Spectra were recorded every 11.4 min over a period of about 12 h.

$OpScCH_2CH(CH_2CH_3)_2$ (11). In the drybox a 25-mL round bottom flask attached to a 180° Teflon needle valve was charged with $OpSc(H)(PMe_3)$ (100 mg, 0.238 mmol). Petroleum ether (*ca.* 8 mL) was vacuum transferred onto the solid at −78 °C.

(24) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.
(25) Marvich, R. H.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1971**, *93*, 2046.
(26) (a) Bunel, E. E. Ph.D. Thesis, California Institute of Technology, 1989. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74 and references therein.
(27) Purchased from Brunfelt Co. Cat. No. 1300-060-528PP-7.
(28) The automation program (for Bruker Aspect systems) is available as supplemental material.

2-Ethyl-1-butene (1.2 equiv) was condensed into the reaction vessel from a calibrated gas volume. The solution was allowed to warm to room temperature, and the initially cloudy, white solution slowly (*ca.* 30 min) turned orange and had some solid which remained undissolved. The solution was filtered and dried *in vacuo*, leaving an orange-yellow solid. Anal. Calcd for $C_{25}H_{41}ScSi$: C, 72.40; H, 9.99. Found: C, 69.73, 67.85, 68.07; H, 9.99, 9.65, 9.73. Yield: 70%. ^{13}C NMR: δ 4.40, quartet, $^2J_{CH}$ = 119.4 Hz, $(CH_3)_2Si$; δ 14.53, quartet, $^2J_{CH}$ = 125.8 Hz, and δ 12.14, quartet, $^2J_{CH}$ = 125.6 Hz, $(\eta^5\text{-}C_5(CH_3)_4)_2$; δ 131.38, 123.24, and 107.08, $(\eta^5\text{-}C_5(CH_3)_4)_2$; δ 49.64, broad triplet, $^2J_{CH}$ = 109.8 Hz, $ScCH_2CH(CH_2CH_3)_2$; δ 44.89, doublet, $^2J_{CH}$ = 120.8 Hz, $ScCH_2CH(CH_2CH_3)_2$; δ 33.90, triplet, $^2J_{CH}$ = 123.0 Hz, $ScCH_2CH(CH_2CH_3)_2$; δ 12.52, quartet, $^2J_{CH}$ = 125.6 Hz, $ScCH_2CH(CH_2CH_3)_2$.

Acknowledgment. We thank Dr. Les Field (University of Sydney) for his expert assistance in acquiring the NMR data. The work has been supported by USDOE Office of Basic Energy Sciences (Grant No. DE-FG03-85ER113431) and by Exxon Chemical Americas.

Supplementary Material Available: ^1H NMR spectra of key reactions and products, gas chromatograms, and the kinetics automation program for Bruker AM Series NMR spectrometers (13 pages). Ordering information is given on any current masthead page.

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