# "σ Bond Metathesis" for C–H Bonds of Hydrocarbons and Sc–R (R = H, alkyl, aryl) Bonds of Permethylscandocene Derivatives. Evidence for Noninvolvement of the π System in Electrophilic Activation of Aromatic and Vinylic C–H Bonds

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Abstract: A new class of coordinatively unsaturated, monomeric organoscandium compounds, Cp^*_2Sc-R ($Cp^* = (\eta^5-C_5Me_5)$; R = halide, hydride, alkyl, alkenyl, alkynyl, aryl), has been prepared. Cp^*_2Sc-Cl is obtained from reaction of $ScCl_3(THF)_3$ (THF = tetrahydrofuran) with $LiCp^*$, and Cp^*_2Sc-R (R = CH_3, C_6H_5, $C_6H_4CH_3$, $CH_2C_6H_5$) from treatment of Cp^*_2Sc-Cl with the appropriate organoalkali reagent. These organoscandium compounds react with dihydrogen rapidly to yield R–H and Cp^*_2Sc-H. The tetrahydrofuran adducts $Cp^*_2ScX(THF)$ (X = Cl, H, CH_3) are obtained upon treatment of Cp^*_2Sc-X with tetrahydrofuran. Rapid exchange of dihydrogen with the hydride ligands of Cp^*_2Sc-H and $Cp^*_2ScH(THF)$ occurs even at low temperatures. Other alkyl derivatives may be conveniently prepared by treatment of Cp^*_2Sc-H (or $Cp^*_2ScH(THF)$) with α-olefins, e.g., $Cp^*_2ScCH_2CH_3$ from Cp^*_2Sc-H and ethylene. Allene and Cp^*_2Sc-H afford $Cp^*_2Sc(\eta^3-C_3H_5)$. Cp^*_2Sc-R (R = H, CH_3, aryl) reacts with pyridine to yield $Cp^*_2Sc(C, N-\eta^2-C_5H_4N)$, which crystallizes in the orthorhombic space group $Pna2_1$ ($a = 16.297$ (4) Å, $b = 9.684$ (3) Å, $c = 14.486$ (6) Å, $V = 2286.3$ (12) Å^3, $Z = 4$). Least-squares refinement led to a goodness-of-fit of 1.74 for 1128 reflections and a value for R of 0.0362 ($I > 3\sigma$, 944 reflections). Spectroscopic and crystallographic data for $Cp^*_2Sc-CH_3$ and $Cp^*_2Sc-CH_2CH_3$ indicate that the methyl ligand is bonded in a conventional (i.e., undistorted) manner, while the ethyl ligand likely participates in a β C–H to Sc "agostic" interaction. $Cp^*_2Sc-CH_3$ crystallizes in the orthorhombic space group $P2_12_12_1$ ($a = 8.502$ (2) Å, $b = 11.095$ (4) Å, $c = 21.554$ (7) Å, $V = 2033.2$ (11) Å^3, $Z = 4$). Least-squares refinement led to a value for R of 0.072 ($F_o^2 > 3\sigma(F_o^2)$, 1143 reflections). H/D exchange between H_2, arenes, and the primary and secondary C–H bonds of alkanes is catalyzed by Cp^*_2Sc-H and $Cp^*_2ScH(THF)$. In benzene solution Cp^*_2Sc-H, $Cp^*_2Sc-C_6H_5$, and H_2 are in equilibrium ($\Delta H° = 6.7$ (3) kcal·mol^{-1}, $\Delta S° = 1.5$ (1) eu), indicating that the bond dissociation energy of the Sc–H bond for Cp^*_2Sc-H is 1.5 (4) kcal·mol^{-1} higher than the bond dissociation energy of the Sc–C bond for $Cp^*_2Sc-C_6H_5$. $Cp^*_2ScH(THF)$ is also in equilibrium with H_2, $Cp^*_2Sc-C_6H_5$, and THF in benzene solution ($\Delta H° = 18.9$ (8) kcal·mol^{-1}, $\Delta S° = 25$ (2) eu). $Cp^*_2Sc-CH_3$ reacts with a range of hydrocarbons (R–H), activating their C–H bonds to afford methane and Cp^*_2Sc-R (R–H = $^{13}CH_4$, arenes, styrenes, alkynes). The reaction of $Cp^*_2Sc-CH_3$ with styrenes is characterized by a moderate enthalpy of activation ($\Delta H^{\ddagger} = 12$ kcal·mol^{-1}) and a large negative entropy of activation ($\Delta S^{\ddagger} \approx -36$ eu). A kinetic deuterium isotope effect ($k_H/k_D = 2.8$ (2)) is observed for the reaction of $(Cp^*-d_{15})_2Sc-CH_3$ with C_6Y_6 (Y = H,D) at 80 °C. Very small differences in the rates of vinylic C–H bond activation for $(p-C_6H_4X)CH=CH_2$ (X = CF_3, OCH_3) and aryl C–H bonds of C_6H_5X (X = CF_3, H, CH_3, $N(CH_3)_2$) as well as the positional *non*selectivity for activation of the meta and para C–H bonds of toluene indicate that the scandium center does not interact substantially with the π system of these substrates in the transition states for these reactions. Thus, for these sterically encumbered organoscandium compounds, sp^2-hybridized C–H bonds are activated without formation of a π complex; rather, the electrophilic scandium center directly attacks the C–H σ bond. A general mechanism for these reactions with C–H and H–H bonds ($Cp^*_2Sc-R + R'-H \rightleftarrows Cp^*_2Sc-R' + R-H$), termed "σ bond metathesis", is proposed, which accounts for the systematic decrease in rate with decreasing s character of the reacting σ bonds (R = R' = H ≫ R = alkyl, R' = H ≫ R = alkyl, R' = sp C–H > R = alkyl, R' = sp^2 C–H > R = alkyl, R' = sp^3 C–H). Both alkyl exchange {$Cp^*_2Sc-R + R'-I \rightleftarrows Cp^*_2Sc-R' + R-I$ (R = CH_3, R' = $^{13}CH_3$; R = CH_2CH_3, R' = CH_3)} and alkyl coupling {$Cp^*_2Sc-R + R'-X \rightleftarrows Cp^*_2Sc-X + R-R'$ (R = R' = CH_3, X = I; R = CH_3, R' = $CH_2C_6H_5$, X = Cl, Br)} are observed in the reactions of Cp^*_2Sc-R with alkyl halides.

The activation of the carbon–hydrogen bonds of saturated and unsaturated hydrocarbons is a conspicuous challenge that has been actively pursued in recent years.[2] It is now generally recognized that there are two fundamentally different mechanisms for cleaving carbon–hydrogen bonds with transition-metal (or f-element) compounds: (i) oxidative addition to an extremely reactive electron-rich, coordinatively unsaturated metal center and (ii) "heterolytic" cleavage by a coordinatively unsaturated, electron-deficient and, hence, highly electrophilic metal center. The latter process typically utilizes d^0 (or d^{0}f^n) metals and is usually pictured as involving a highly charged, four-center transition state with metal abstracting carbanion and the leaving group effecting proton abstraction (eq 1). This picture closely resembles that established by Halpern[2c,3] for heterolytic activation of dihydrogen in aqueous solution.

$(R,R' = H, alkyl, alkenyl, aryl, alkynyl)$
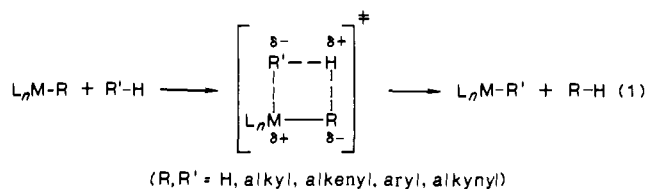
A curious feature of both types of C–H bond activating systems is that, despite their higher bond strengths, arene (sp^2-hybridized) C–H bonds are more reactive than aliphatic (sp^3-hybridized) C–H bonds. Initial formation of a π complex has been proposed to explain the greater reactivity of arenes for systems which oxidatively add C–H bonds, and, indeed, Jones and Feher[4] have developed a convincing case for an η^2-arene adduct of [Cp*-(PMe$_3$)Rh] (Cp* = η^5-C$_5$Me$_5$) mediating the reaction leading to the aryl–hydride product.[5] In view of the strongly electrophilic character of the metal center for the latter type of C–H bond

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(2) For recent reviews see, for example, (a) Crabtree, R. H. *Chem. Rev.* **1985,** *85,* 245. (b) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985,** *57,* 1897. (c) Halpern, J. *Inorg. Chim. Acta.* **1985,** *100,* 41. (d) Rothwell, I. P. *Polyhedron* **1985,** *4,* 177.

(3) (a) Halpern, J. *J. Phys. Chem.* **1959,** *63,* 348. (b) Harrod, J. F.; Ciccone, S.; Halpern, J. *Can. J. Chem.* **1961,** *39,* 1372. (c) Halpern, J. *Can. J. Chem.* **1966,** *44,* 671. (d) Brothers, P. *Prog. Inorg. Chem.* **1981,** *28,* 1.

(4) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984,** *106,* 1650. (b) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1985,** *107,* 620.
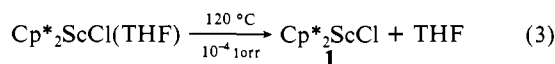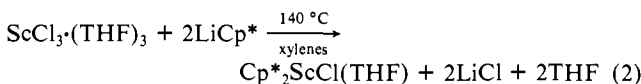
(5) On the other hand, the oxidative addition of ethylene to [Cp*(PMe$_3$)Ir] has been shown to proceed without formation of an (η^2-C$_2$H$_4$) adduct, see: Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985,** *107,* 4581.

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activating systems, initial attack at the carbon pπ orbital (cf. electrophilic aromatic substitution) could be invoked to explain the higher reactivity of arene C–H bonds with Cp*$_2$ScR,[6] Cp*$_2$LnR(Ln = Y, lanthanide),[7] and Cp*$_2$ThR$_2$.[8]

We report herein synthetic and structural studies of hydride and hydrocarbyl derivatives of permethylscandocene, together with investigations of their reactivities with H$_2$ and hydrocarbons. Experiments designed to probe the mechanisms of these processes have been carried out, and the possibility of involvement of the π system in electrophilic activation of aromatic and vinylic C–H bonds has been examined. A picture of the transition state for such "σ-bond metathesis" reactions[9] is developed, which accounts for the relative reactivities of sp-, sp^2-, and sp^3-hybridized C–H bonds with Cp*$_2$Sc–R (R = H, alkyl, aryl).
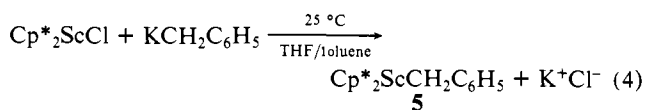
Results and Discussion

Synthesis of Alkyl, Allyl, Aryl, and Hydride Derivatives of Permethylscandocene. A useful starting material for the synthesis of a variety of derivatives of permethylscandocene is the chloride complex, Cp*$_2$ScCl (**1**). Compound **1** is obtained, together with its THF adduct (THF = tetrahydrofuran), when solvent is removed from a reaction mixture consisting of ScCl$_3$(THF)$_3$ and 2 equiv of LiCp*, which has been heated at reflux for 3 days in xylenes (eq 2). The coordinated THF is removed on sublimation of the residue under dynamic vacuum, affording pale yellow, crystalline **1** (eq 3). A solution molecular weight determination

$$\text{ScCl}_3\cdot(\text{THF})_3 + 2\text{LiCp*} \xrightarrow[\text{xylenes}]{140\ ^\circ\text{C}}$$
$$\text{Cp*}_2\text{ScCl(THF)} + 2\text{LiCl} + 2\text{THF} \quad (2)$$

$$\text{Cp*}_2\text{ScCl(THF)} \xrightarrow[10^{-4}\ \text{1orr}]{120\ ^\circ\text{C}} \underset{\textbf{1}}{\text{Cp*}_2\text{ScCl}} + \text{THF} \quad (3)$$

in benzene indicates **1** is monomeric, and mass spectral analysis shows only m/e values for ions derived from a monomer. By contrast, [(η^5-C$_5$H$_5$)$_2$ScCl]$_2$ is a robust dimer with the two chloride ligands bridging scandium centers.[10] Moreover, (η^5-C$_5$H$_5$)$_2$ScCl(THF) does not dissociate its THF ligand on sublimation.[11] Both of these differences are undoubtedly attributable to the much greater steric bulk of the pentamethylcyclopentadienyl ligand for **1**.
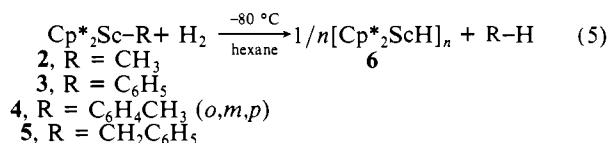
Cp*$_2$ScCl readily undergoes straightforward[12] metathetical reactions with main group organometallic compounds. Thus, Cp*$_2$ScCH$_3$ (**2**), Cp*$_2$ScC$_6$H$_5$ (**3**), Cp*$_2$Sc(o-C$_6$H$_4$CH$_3$) (**o-4**), Cp*$_2$Sc(m-C$_6$H$_4$CH$_3$) (**m-4**), and Cp*$_2$Sc(p-C$_6$H$_4$CH$_3$) (**p-4**) are obtained by treatment of **1** with the appropriate organolithium compound. The choice of solvent is sometimes critical (see Experimental Section). THF is particularly deleterious, since none of the above transformations occur in the presence of as little as 1 equiv of tetrahydrofuran; Cp*$_2$ScCl(THF) is recovered from the reaction mixture. One alkyl derivative, Cp*$_2$ScCH$_2$C$_6$H$_5$ (**5**), can be prepared, however, even in 1:1 THF–toluene (eq 4).

Presumably, KCH$_2$C$_6$H$_5$ is sufficiently potent to react even with Cp*$_2$ScCl(THF).

$$\text{Cp*}_2\text{ScCl} + \text{KCH}_2\text{C}_6\text{H}_5 \xrightarrow[\text{THF/toluene}]{25\ ^\circ\text{C}}$$
$$\underset{\textbf{5}}{\text{Cp*}_2\text{ScCH}_2\text{C}_6\text{H}_5} + \text{K}^+\text{Cl}^- \quad (4)$$
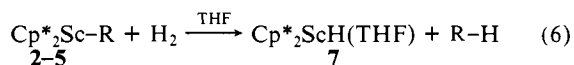
These 14-electron hydrocarbyl derivatives of permethylscandocene have very crowded coordination spheres, as illustrated by their resistance to aggregation in solution and their poor affinities for bases. Like **1**, compounds **2**, **3**, **4**, and **5** are monomeric in benzene solution. Neither trimethylphosphine nor tertiary amines form adducts with any of the above complexes. Moreover, while the phenyl, tolyl, and benzyl derivatives do not form detectable concentrations of THF adducts (^{1}H NMR), Cp*$_2$ScCH$_3$ (**2**) coordinates THF tightly enough to allow crystallization of analytically pure samples of Cp*$_2$ScCH$_3$(THF), even in the absence of excess THF, illustrating the delicate balance betwen steric and electronic factors for these permethylscandocene complexes. The ^{1}H NMR spectrum of **5** is consistent with an η^1-(rather than η^3-) coordination of benzyl to Sc; a simple A$_2$B$_2$C phenyl pattern is observed, even at −90 °C. While an η^3-(allyl-like) structure cannot be excluded, these ^{1}H NMR data indicate an upper limit of ca. 10 kcal·mol^{-1} for dissociation of the C=C π bond, if, in fact, Cp*$_2$Sc(η^3-CH$_2$C$_6$H$_5$) is more stable than Cp*$_2$Sc(η^1-CH$_2$C$_6$H$_5$).

Each of these hydrocarbyl derivatives reacts rapidly with dihydrogen to afford RH and a single permethylscandocene compound, assigned the formula [Cp*$_2$ScH]$_n$ on the basis of the data given below (eq 5). This scandium hydride is rather unstable

$$\underset{\substack{\textbf{2, R = CH}_3 \\ \textbf{3, R = C}_6\text{H}_5 \\ \textbf{4, R = C}_6\text{H}_4\text{CH}_3\ (o,m,p) \\ \textbf{5, R = CH}_2\text{C}_6\text{H}_5}}{\text{Cp*}_2\text{Sc–R}} + \text{H}_2 \xrightarrow[\text{hexane}]{-80\ ^\circ\text{C}} 1/n\underset{\textbf{6}}{[\text{Cp*}_2\text{ScH}]_n} + \text{R–H} \quad (5)$$

under reduced dihydrogen pressures, decomposing in aliphatic hydrocarbon solvents to as yet unidentified products. When several atmospheres of dihydrogen are maintained over the solution, however, **6** is quite robust. After heating to 150 °C for over a week in benzene under 4 atm H$_2$ there is no sign of decomposition. Although the kinetics of these reactions have not been examined in detail, a half-life of ca. 5 min is observed for the reaction of Cp*$_2$ScCH$_3$ (**2**) with H$_2$ (2 atm) at −78 °C in toluene (vide infra).

The characterization of unstable [Cp*$_2$ScH]$_n$ (**6**) is based on the following: (i) for R = CH$_2$C$_6$H$_5$ in reaction 5, 0.93 equiv of dihydrogen is consumed (Toepler pump analysis), and 1.0 equiv of CH$_3$C$_6$H$_5$ (^{1}H NMR) is formed; (ii) treatment with excess methyl iodide yields Cp*$_2$ScI and CH$_4$; (iii) when reaction 5 is carried out in the presence of at least 1 equiv of THF, a more stable THF adduct of **6** is obtained (eq 6). While Cp*$_2$ScH-

$$\underset{\textbf{2–5}}{\text{Cp*}_2\text{Sc–R}} + \text{H}_2 \xrightarrow{\text{THF}} \underset{\textbf{7}}{\text{Cp*}_2\text{ScH(THF)}} + \text{R–H} \quad (6)$$

(THF) does decompose slowly over a period of several days at room temperature, it appears to be indefinitely stable when stored in the dark at −10 °C. Solution molecular weight determinations for **7** show it to be monomeric. Like **6**, Cp*$_2$ScH(THF) reacts rapidly with CH$_3$I to afford methane, and, in this case Cp*$_2$ScI(THF). Infrared spectra reveal a rather low frequency for ν(Sc–H) at 1390 cm^{-1}, which shifts on deuteriation (vide infra) to 990 cm^{-1}.

Solutions of Cp*$_2$ScH catalyze rapid H/D exchange between H$_2$ and D$_2$ (eq 7). Furthermore, the room temperature ^{1}H NMR spectrum of a methylcyclohexane-d_{14} solution of Cp*$_2$ScH under 4 atm H$_2$ shows only a single resonance for the (η^5-C$_5$Me$_5$) protons; resonances for Sc*H* and *H*$_2$ are not discernible. Failure to observe

$$\text{H}_2 + \text{D}_2 \underset{}{\overset{[\text{Cp*}_2\text{ScH}]}{\rightleftharpoons}} 2\text{HD} \quad (7)$$
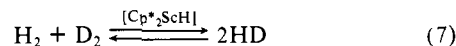
these signals could be due to broadening of the hydride resonance by the strong quadrupolar ^{45}Sc nucleus (100% abundance, $I =$

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(7) (a) Watson, P. L. *J. Am. Chem. Soc.* **1983**, *105*, 6491. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (c) Teuben, J. H. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragala, I. L., Eds.; NATO ASI Series, D. Reidel: Boston, 1985; p 195.

(8) (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (b) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425. (c) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (d) Fagan, P. J.; Manriquez, J. M.; Miatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650.
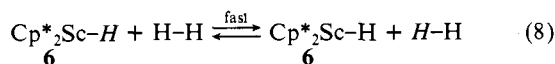
(9) In view of the apparent generality of the processes represented by eq 1, we suggest the descriptive name "σ bond metathesis" for this class of reactions involving σ bonds.

(10) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.

(11) Manzer, L. E. *J. Organomet. Chem.* **1976**, *110*, 291.

(12) With the yttrium, lutetium, and ytterbium analogues robust adducts with lithium alkyls and/or lithium halides are generated. Elegant procedures for obtaining adduct-free alkyl derivatives have been developed; see: Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, *212*, 459.
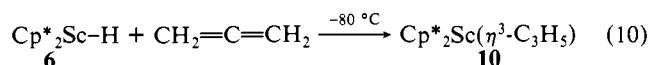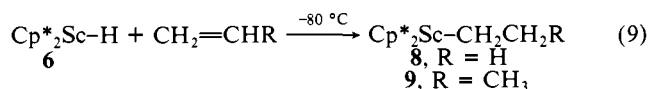
$^7/_2$, −0.22 barns) and/or rapid exchange of hydride with H_2. Since quadrupolar broadening can often be alleviated by either raising or lowering temperature,[13] variable temperature experiments were conducted. At 120 °C a broad peak at δ 6.1 (full width at half height (fwhh) = 26 Hz) is observed. This new signal must be an average resonance for Sc*H* and dissolved H_2, since the signal for dihydrogen at δ 4.5 (methylcyclohexane-d_{14}) is not observed. This averaging process (eq 8) is very fast even at lower temper-

$$Cp^*_2Sc\text{-}H + H\text{-}H \underset{}{\overset{\text{fast}}{\rightleftharpoons}} Cp^*_2Sc\text{-}H + H\text{-}H \qquad (8)$$
$$\mathbf{6} \qquad\qquad\qquad\qquad \mathbf{6}$$

atures; at −80 °C a single resonance at δ 6.2 (fwhh = 32 Hz) is observed, whereas in toluene-d_8 at −95 °C a similar resonance appears at δ 6.65 (fwhh = 33 Hz). From the estimated concentrations of dihydrogen and [6] in toluene, the simple weighted average chemical shift of δ 7.3 (3) in toluene-d_8 (−95 °C) is calculated[14] for Cp^*_2Sc*H*.

Coordination of THF slows exchange of Sc–H with H_2. Thus, in addition to resonances for (η^5-C_5Me_5) and α- and β-hydrogens of coordinated THF (Table I), a toluene-d_8 solution of Cp^*_2ScH(THF) (7) under 4 atm H_2 at −90 °C exhibits a broad resonance at δ 4.8 (fwhh = 18 Hz), attributable to Sc–H, and a sharp signal due to dissolved H_2 at δ 4.5. Above ca. −20 °C these two signals collapse to a single broad resonance. Addition of 10 equiv of THF raises the coalescence temperature to 0 °C, suggesting that exchange between Cp^*_2ScH(THF) and H_2 is preceded by dissociation of THF from 7, i.e., exchange occurs via Cp^*_2ScH (6).

Although 6 is of only marginal stability, it is, nonetheless, a valuable synthetic reagent when generated in situ. Olefins readily insert into the scandium–hydride bond, affording alkyl complexes (eq 9). It is important that these reactions be carried out at −80 °C to avoid other reactions (vida infra). With allene smooth conversion to $Cp^*_2Sc(\eta^3$-$C_3H_5)$ (10) occurs (eq 10). Variable

$$Cp^*_2Sc\text{-}H + CH_2{=}CHR \xrightarrow{-80\ ^\circ C} Cp^*_2Sc\text{-}CH_2CH_2R \qquad (9)$$
$$\mathbf{6} \qquad\qquad\qquad\qquad\qquad \mathbf{8, R = H}$$
$$\mathbf{9, R = CH_3}$$

$$Cp^*_2Sc\text{-}H + CH_2{=}C{=}CH_2 \xrightarrow{-80\ ^\circ C} Cp^*_2Sc(\eta^3\text{-}C_3H_5) \qquad (10)$$
$$\mathbf{6} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{10}$$

temperature ^{1}H NMR studies of 10 reveal a fluxional character, with coalescence of signals due to syn and anti hydrogens near room temperature. At −50 °C a spectrum indicative of a static η^3-C_3H_5 structure is observed, whereas at 90 °C rapid averaging of syn and anti hydrogens occurs (Table I).

Cp^*_2ScR (R = H, CH_3, C_6H_5, $CH_2C_6H_5$) and Cp^*_2ScH(THF) react cleanly with pyridine to afford the orthometallated (C, N-η^2) pyridine complex $Cp^*_2Sc(C, N$-η^2-$C_5H_4N)$ (11) and RH (and H_2 + THF in the case of 7). The reaction of 6 with pyridine presumably proceeds via an adduct, Cp^*_2ScH(NC_5H_5), analogous to 7. Indeed, treatment of 11 with D_2 leads to specific deuteration of the ortho position, indicative of the reversible reaction shown in eq 11. In the reaction of Cp^*_2ScCH$_3$ with pyridine, an in-
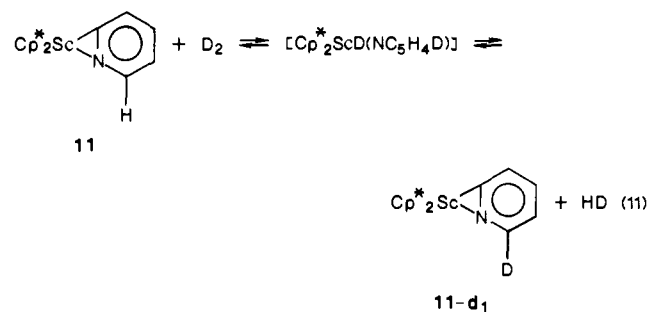
Figure 1. ORTEP drawing of $Cp^*_2Sc(C, N$-η^2-$C_5H_4N)$ (top) and skeletal view of $Cp^*_2Sc(C, N$-η^2-$C_5H_4N)$ with bond distances (Å) and angles (deg) (bottom).

termediate, presumably Cp^*_2ScCH$_3$(NC_5H_5), is observed (^{1}H NMR) prior to irreversible loss of methane to yield 11. Treatment of 11 with pyridine-d_5 affords $Cp^*_2Sc(C,N$-η^3-$C_5D_4N)$ and NC_5H_4D (at low conversions), suggesting that an ortho C–H bond of pyridine, like H_2 in reaction 11, is reactive with the Sc–C bond of 11 (eq 12).

$$Cp^*_2Sc(C, N\text{-}\eta^2\text{-}C_5H_4N) + NC_5D_5 \xrightarrow[2\ \text{days}]{25\ ^\circ C}$$
$$\mathbf{11}$$
$$Cp^*_2Sc(C, N\text{-}\eta^2\text{-}C_5D_4N) + NC_5H_4D \qquad (12)$$
$$\mathbf{11\text{-}d_4}$$

The structure of $Cp^*_2Sc(C, N$-η^2-$C_5H_4N)$ (11) was determined by single-crystal X-ray diffraction, and the results are illustrated in Figure 1. The geometry of 11 is normal with an average Sc–C (Cp*) distance of 2.50 Å, R1(ring centroid)–Sc–R2 angle of 142.1°, and coordination of the pyridyl group in the equatorial plane of the wedge. The cyclopentadienyl groups are planar within experimental error, and the average displacement of a methyl group from the ring plane is 0.1 Å.

The pyridyl group is disordered (see Experimental Section), but we can estimate a Sc–C bond length of 2.20 Å and Sc–N bond length of 2.14 Å. Thus $Cp^*_2Sc(C, N$-η^2-$C_5H_4N)$ (11) is similar to $(\eta^5$-$C_5H_5)_2Ti(C, N$-η^2-$C_5H_4N)$[15] and $Cp^*_2Lu(C, N$-η^2-$C_5H_4N)$[16] reported earlier.

Structure and Bonding of Cp^*_2ScCH$_3$ and Cp^*_2ScCH$_2$CH$_3$. Alkyl derivatives of permethylscandocene are formally 14-electron compounds and, hence, are very electron deficient. In the absence of overriding steric interactions, Lewis bases bind strongly to scandium, by using one of the two low-lying, vacant orbitals (e.g., Cp^*_2ScCH$_3$(THF) and $Cp^*_2Sc(C, N$-η^2-$C_5H_4N)$). Consideration of the possibility that the Lewis base-free alkyl derivatives could

11

11-d$_1$

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(14) With δ_{ave} = 6.65 [Cp*$_2$ScH] = 0.13 (2) M and [H$_2$] = 0.013 (3) M, δ (ScH) = 7.3 (3).
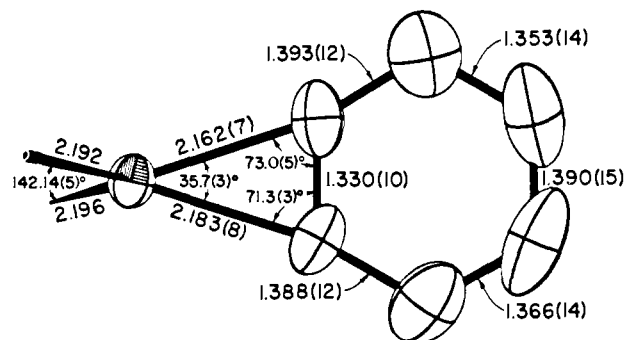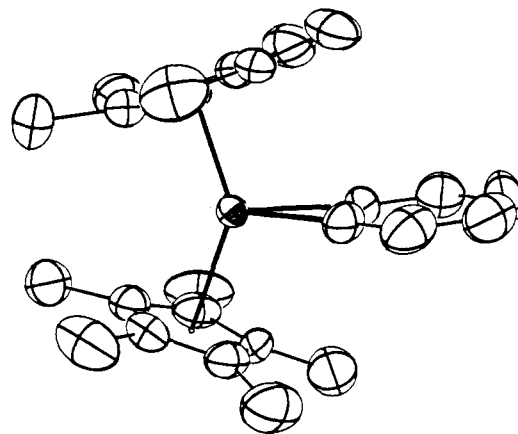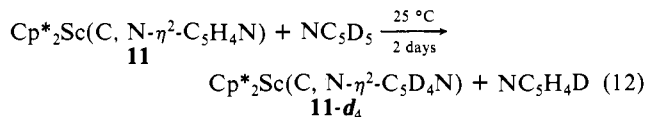
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Table I. ^{1}H and ^{13}C NMR Data[a]

compound	assignment	δ[b] (ppm)	coupling[c]
Cp*$_2$ScCl (**1**)	C$_5$(C*H*$_3$)$_5$	1.83 s	
Cp*$_2$ScCH$_3$ (**2**)	C$_5$(C*H*$_3$)$_5$	1.87 s	
	ScC*H*$_3$	0.07 s	
Cp*$_2$ScCH$_2$D (**2**-d_1)	C$_5$(C*H*$_3$)$_5$	1.87 s	
	ScC*H*$_2$D	0.013 t	$^2J_{HD} = 1.8$
Cp*$_2$Sc^{13}CH$_3$ (**2**-^{13}C)	C$_5$(C*H*$_3$)$_5$	1.87 s	
	ScC*H*$_3$	0.07 d	$^1J_{CH} = 111$
Cp*$_2$Sc(THF)CH$_3$	C$_5$(C*H*$_3$)$_5$	1.91 s	
	OC*H*$_2$CH$_2$CH$_2$C*H*$_2$	3.40 s	
	OCH$_2$C*H*$_2$C*H*$_2$CH$_2$	1.31 m	
	ScC*H*$_3$	−0.19 s	
Cp*$_2$ScC$_6$H$_5$ (**3**)	C$_5$(C*H*$_3$)$_5$	1.73 s	
	C$_6$*H*$_5$	7.0–7.4 m	
Cp*$_2$Sc(o-C$_6$H$_4$CH$_3$) (o-**4**)	C$_5$(C*H*$_3$)$_5$	1.77 s	
	C$_{(3)}$*H*	7.26 d	$J_{HH} = 6.0$[d]
	C$_{(4,5)}$*H*	7.20 m	
	C$_{(6)}$*H*	6.32 t	$J_{HH} = 5.3$[d]
	C$_5$H$_4$C*H*$_3$	2.12 s	
Cp*$_2$Sc(m-C$_6$H$_4$CH$_3$) (m-**4**)	C$_5$(C*H*$_3$)$_5$	1.77 s	
	C$_{(2)}$*H*	6.78 d	
	C$_{(4)}$*H*	7.07 d	$J_{HH} = 5.7$[d]
	C$_{(5)}$*H*	7.32 t	$J_{HH} = 5.7$[d]
	C$_{(6)}$*H*	6.85 d	$J_{HH} = 5.7$[d]
	C$_6$H$_4$C*H*$_3$	2.43 s	
Cp*$_2$Sc(p-C$_6$H$_4$CH$_3$) (p-**4**)	C$_5$(C*H*$_3$)$_5$	1.76 s	
	C$_{(2)}$*H*	7.26 d	$J_{HH} = 5.4$[d]
	C$_{(3)}$*H*	6.92 d	$J_{HH} = 5.4$[d]
	C$_6$H$_4$C*H*$_3$	2.33 s	
Cp*$_2$ScCH$_2$C$_6$H$_5$ (**5**)	C$_5$(C*H*$_3$)$_5$	1.77 s	
	C$_{(2,6)}$*H*	6.78 d	$J_{HH} = 8.0$[d]
	C$_{(3,5)}$*H*	6.95 t	$J_{HH} = 7.5$[d]
	C$_{(4)}$*H*	7.15 t	$J_{HH} = 8.5$[d]
	C*H*$_2$C$_6$H$_5$	2.23 s	
[Cp*$_2$ScH]$_n$ (**6**)	C$_5$(C*H*$_3$)$_5$	1.90 s	
	Sc*H*	7.3 (calc)[e]	
Cp*$_2$ScH(THF) (**7**)	C$_5$(C*H*$_3$)$_5$	2.08 s	
	OC*H*$_2$CH$_2$CH$_2$C*H*$_2$	3.43 m	
	OCH$_2$C*H*$_2$C*H*$_2$CH$_2$	1.25 m	
	Sc*H*	4.80 s	
Cp*$_2$ScCH$_2$CH$_3$ (**8**)	C$_5$(C*H*$_3$)$_5$	1.88 s	
	ScC*H*$_2$CH$_3$	0.97 q	$^3J_{HH} = 6.8$
	ScCH$_2$C*H*$_3$	1.18 t	$^3J_{HH} = 6.8$
Cp*$_2$Sc^{13}CH$_2$^{13}CH$_3$ (**8**-^{13}C$_2$)	C$_5$(C*H*$_3$)$_5$	1.88 s	
	Sc^{13}C*H*$_2$^{13}CH$_3$	0.91 dq	$^1J_{CH} = 122$[f]
	Sc^{13}CH$_2$^{13}C*H*$_3$	0.139 dt	$^1J_{CH} = 120$[f]
Cp*$_2$Sc^{13}CH$_2$^{13}CH$_3$ (**8**-^{13}C$_2$)	Sc^{13}C*H*$_2$^{13}CH$_3$	1.035 dq	$^1J_{CH} = 122$[g]
	Sc^{13}CH$_2$^{13}C*H*$_3$	0.077 dt	$^1J_{CH} = 120$[g]
Cp*$_2$Sc^{13}CH$_2$^{13}CH$_2$D (**8**-^{13}C$_2$,d_1)	Sc^{13}C*H*$_2$^{13}CH$_2$D	0.91 dt	$^1J_{CH} = 120$[f]
	Sc^{13}CH$_2$^{13}C*H*$_2$D	0.049 m	$^1J_{CH} = 120$[f]
Cp*$_2$Sc^{13}CH$_2$^{13}CH$_2$D (**8**-^{13}C$_2$,d_1)	Sc^{13}C*H*$_2$^{13}CH$_2$D	1.035 dt	$^1J_{CH} = 122$[g]
	Sc^{13}CH$_2$^{13}C*H*$_2$D	−0.046 m	$^1J_{CH} = 120$[g]
Cp*$_2$ScCH$_2$CH$_2$CH$_3$ (**9**)	C$_5$(C*H*$_3$)$_5$	1.88 s	
	ScC*H*$_2$CH$_2$CH$_3$	1.40 t	$^3J_{HH} = 6.6$[d]
	ScCH$_2$C*H*$_2$C*H*$_3$	0.86–1.00 m	
	C$_5$(CH$_3$)$_5$	118.6[h]	
	C$_5$(*C*H$_3$)$_5$	11.2[h]	
	Sc*C*H$_2$CH$_2$CH$_3$	45.8 (br)	$^1J_{CH} = 117$[h]
	ScCH$_2$*C*H$_2$CH$_3$	24.6[h]	
	ScCH$_2$CH$_2$*C*H$_3$	22.8[h]	
Cp*$_2$Sc(η^3-C$_3$H$_5$) (**10**)	C$_5$(C*H*$_3$)$_5$	1.90 s[j]	
	Sc(η^3-C*H*$_2$CHC*H*$_2$)	3.00 (br)	$^3J_{HH} = 12.7$[j]
	Sc(η^3-CH$_2$C*H*CH$_2$)	7.15 q	$^3J_{HH} = 12.7$[j]
Cp*$_2$Sc(η^3-C$_3$H$_5$) (**10**)	[C$_5$(C*H*$_3$)$_5$]	1.89 s[k]	
	[C$_5$(C*H*$_3$)$_5$]	1.81 s[k]	
	Sc(η^3-C*H*HCHCH*H*)	2.07 d	$^3J_{HH} = 9.8$[k]
	Sc(η^3-CH*H*CHC*H*H)	3.53 d	$^3J_{HH} = 15.6$[k]
	Sc(η^3-CH$_2$C*H*CH$_2$)	6.89 m	
Cp*$_2$Sc(η^3-C$_3$H$_5$) (**10**)	C$_5$(C*H*$_3$)$_5$	1.84 s[l]	
	Sc(η^3-C*H*$_2$CHC*H*$_2$)	2.84 d	$^3J_{HH} = 12.7$[l]
	Sc(η^3-CH$_2$C*H*CH$_2$)	6.92 q	$^3J_{HH} = 12.7$[l]
Cp*$_2$Sc(C,N-η^2-C$_5$H$_4$N) (**11**)	C$_5$(C*H*$_3$)$_5$	1.77 s	
	(C,N-η^2-C$_5$*H*HH$_3$N)	7.93 dt	$J_{HH} = 5.1, 1.5$
	(C,N-η^2-C$_5$*H*H$_3$N)	7.63 dt	$J_{HH} = 7.2, 1.5$
	(C,N-η^2-C$_5$*H*H$_3$N)	7.03 td	$J_{HH} = 7.2, 1.2$
	(C,N-η^2-C$_5$*H*H$_3$N)	6.58 m	
Cp*$_2$ScI	C$_5$(C*H*$_3$)$_5$	1.89 s	

Table I (Continued)

compound	assignment	δ^b (ppm)	coupling^c
$[(\eta^5\text{-}C_5Me_5)Sc(\eta^5\text{-}C_5Me_4CH_2)]_n$ (12)	$C_5(CH_3)_5$	1.97 s	
	$C_5(CH_3)_2(CH_3)_2CH_2$	2.08 s	
	$C_5(CH_3)_2(CH_3)_2CH_2$	1.54 s	
	$C_5(CH_3)_4CH_2$	1.39 s	
$Cp^*_2ScCH{=}CH(p\text{-}C_6H_4CH_3)$ (13)	$C_5(CH_3)_5$	1.88 s	
	$ScCH{=}CHC_6H_4CH_3$	8.07 d	$^3J_{HH} = 20$
	$ScCH{=}CHC_6H_4CH_3$	6.43 d	$^3J_{HH} = 20$
	$ScCH{=}CHC_6H_2H_2CH_3$	7.58 d	$J_{HH} = 8$
	$ScCH{=}CHC_6H_2H_2CH_3$	7.20 d	$J_{HH} = 8$
	$ScCH{=}CHC_6H_4CH_3$	2.27 s	
$Cp^*_2ScCH{=}CH(p\text{-}C_6H_4OCH_3)$	$C_5(CH_3)_5$	1.88 s	
	$ScCH{=}CHC_6H_4OCH_3$	7.90 d	$^3J_{HH} = 20$
	$ScCH{=}CHC_6OCH_3$	6.35 d	$^3J_{HH} = 20$
	$ScCH{=}CHC_6H_2H_2OCH_3$	7.51 d	$J_{HH} = 8$
	$ScCH{=}CHC_6H_2H_2OCH_3$	6.92 d	$J_{HH} = 8$
	$ScCH{=}CHC_6H_4OCH_3$	3.45 s	
$Cp^*_2ScCH{=}CH(p\text{-}C_6H_4CF_3)$	$C_5(CH_3)_5$	1.88 s	
	$ScCH{=}CHC_6H_4CF_3$	8.19 d	$^3J_{HH} = 21$
	$ScCH{=}CHC_6H_4CF_3$	6.37 d	$^3J_{HH} = 21$
	$ScCH{=}CHC_6H_4CF_3$	7.51 m	
$Cp^*_2ScCH{=}C(CH_3)_2$	$C_5(CH_3)_5$	1.90 s	
	$ScCH{=}C(CH_3)_2$	6.12 s	
	$ScCH{=}C(CH_3)(CH_3)$	2.20 s	
	$ScCH{=}C(CH_3)(CH_3)$	1.57 s	
$Cp^*_2ScCH_2CH(CH_3)_2$ (14)	$C_5(CH_3)_5$	1.84 s	
	$ScCH_2CH(CH_3)_2$	0.41 d	$^3J_{HH} = 8$
	$ScCH_2CH(CH_3)_2$	(not located)	
	$ScCH_2CH(CH_3)_2$	0.78 d	$^3J_{HH} = 6$
trans-$Cp^*_2ScCH{=}CHCH_3$ (15)	$C_5(CH_3)_5$	1.90 s	
	$ScCH{=}CHCH_3$	7.0 dq	$^3J_{HH} = 19.5,$ $^4J_{HH} = 1.5$
	$ScCH{=}CHCH_3$	5.25 dq	$^3J_{HH} = 19.5, 5.4$
	$ScCH{=}CHCH_3$	2.18 d	$^3J_{HH} = 5.4$
$Cp^*_2ScC{\equiv}CCH_3$ (16)	$C_5(CH_3)_5$	2.00 s	
	$ScC{\equiv}CCH_3$	2.07 s	
$Cp^*_2ScC(CH_3){=}C(CH_3)_2$ (17)	$C_5(CH_3)_5$	1.85 s^d	
	$ScC(CH_3){=}C(CH_3)_2$	1.89 s^d	
	$ScC(CH_3){=}C(CH_3)_2$	1.53 s^d	
	$ScC(CH_3){=}C(CH_3)_2$	1.13 s^d	
$Cp^*_2ScCH_2CH_2CH_2CH_3$	$C_5(CH_3)_5$	1.88 s^m	
	$ScCH_2CH_2CH_2CH_3$	0.90 t	$^3J_{HH} = 7.4^m$
	$ScCH_2CH_2CH_2CH_3$	0.56–0.61 m	
	$C_5(CH_3)_5$	119.3^n	
	$C_5(CH_3)_5$	11.4^n	
	$ScCH_2CH_2CH_2CH_3$	43.3^n	
	$ScCH_2CH_2CH_2CH_3$	34.5^n	
	$ScCH_2CH_2CH_2CH_3$	30.7^n	
	$ScCH_2CH_2CH_2CH_3$	14.5^n	

^{a} Unless otherwise specified, spectra were obtained in benzene-d_6 at ambient temperature, 90 MHz. ^{b} Chemical shifts are referenced to internal $Si(CH_3)_4$ or to solvent signals and indirectly referenced to $Si(CH_3)_4$. ^{c} Coupling constants are reported in Hz. ^{d} Measured in benzene-d_6 at 500 MHz. ^{e} Measured at −80 °C in methylcyclohexane-d_{14} at 90 MHz. ^{f} Measured at 25 °C in toluene-d_8 at 400 MHz. ^{g} Measured in toluene-d_8 at −80 °C, 400 MHz. ^{h} ^{13}C$\{^1H\}$ NMR spectrum in toluene-d_8 at −50 °C, 100.38 MHz. ^{j} Measured in cyclohexane-d_{12} at 25 °C, 90 MHz. ^{k} Measured in toluene-d_8 at −50 °C, 90 MHz. ^{l} Measured in cyclohexane-d_{12} at +90 °C, 90 MHz. ^{m} Measured in benzene-d_6 at ambient temperature, 400 MHz. ^{n} ^{13}C$\{^1H\}$ NMR spectrum in benzene-d_6 at ambient temperature, 100.38 MHz.

engage in "agostic",[17] three-center, two-electron bridging interactions (shown below) is warranted, especially in light of the structures established by Green, Prout, et al.[18] for the comparably

(R = H, alkyl, aryl)
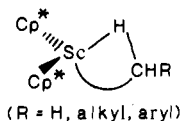
electron-deficient compounds $(Me_2PCH_2CH_2PMe_2)Cl_3TiCH_3$ and $(Me_2PCH_2CH_2PMe_2)Cl_3TiCH_2CH_3$, the former shown to have

an α C–H-to-titanium agostic interaction, the latter a β-C–H-to-titanium interaction.

The ^{1}H NMR spectrum for $Cp^*_2ScCH_3$ (2) (toluene-d_8) shows a singlet for the methyl group, even at −90 °C. The ^{13}C–H coupling constant for the methyl group of 2 is established by preparing $Cp^*_2Sc(^{13}CH_3)$ ($^1J_{C–H} = 111$ Hz). Whereas this value is significantly reduced from the ca. 125-Hz value normally associated with methyl groups, lower values may be expected for X–CH$_3$ systems where the electronegativity of X is significantly less than that of carbon. An increase in the s character of the X–C bond and a correspondingly reduced s character of the XCH$_2$–H bonds are generally held responsible.[19] Significantly, the formally 16-electron complex $Cp^*_2Sc(^{13}CH_3)$(THF) also

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(19) (a) *Isotopes in Organic Chemistry, Vol. 3. Carbon-13 NMR in Organic Chemistry*; Buncel, E., Lee, C. C., Eds.; Elsevier Scientific: New York, 1977; p 209. (b) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden and Son: New York, 1976; p 50. (c) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 323.
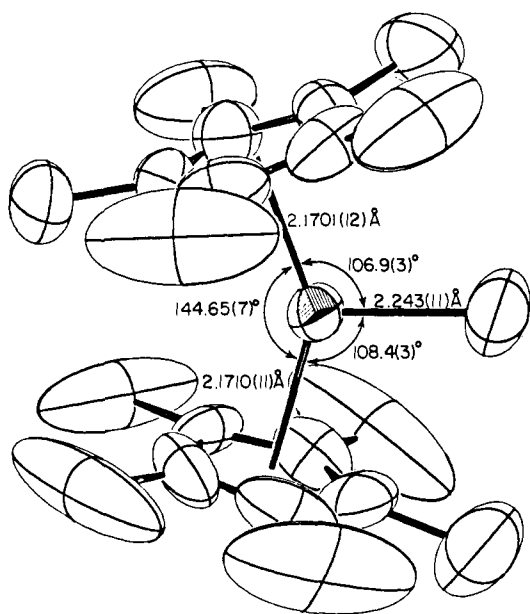
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Figure 2. ORTEP drawing of Cp*$_2$Sc–CH$_3$.

exhibits a doublet for Sc–CH_3 with $^1J_{C-H}$ = 111 Hz.

The ^{1}H NMR spectrum of Cp*$_2$ScCH$_2$CH$_3$ (**8**) exhibits a simple first-order pattern for Sc–CH_2CH$_3$ with $^3J_{H-H}$ = 6.8 Hz. Interestingly, the ^{13}C–H coupling constant for the methylene group is significantly larger than might be expected (vida infra) from the arguments presented above: $^1J_{C(\alpha)-H}$ = 122 Hz, whereas $^1J_{C(\beta)-H}$ = 120 Hz.

Since agostic structures are commonly fluxional, with terminal and bridging hydrogens undergoing rapid exchange (averaging chemical shifts and $^1J_{C-H}$'s), ^{1}H NMR data for the perprotio derivatives are often inconclusive in differentiating agostic and conventional structures.[17] Partial deuteriation of the suspected bridging position can produce significantly different ^{1}H chemical shifts and $^1J_{C-H}$'s, as compared to the perprotio compounds; however, in some cases these effects have been found to be small for both α and β agostic structures.[18c] The ^{1}H chemical shift difference between Cp*$_2$ScCH_3 and Cp*$_2$ScCH_2D amounts to only 0.057 ppm (cf., 0.047 ppm for Cp*$_2$ScCH_3(THF) vs. Cp*$_2$ScCH_2D(THF); 0.020 ppm for (η^5-C$_5$H$_5$)$_2$W(CH_3)$_2$ vs. (η^5-C$_5$H$_5$)$_2$W(CH_2D)$_2$; 0.010 ppm for CH_4 vs. CH_3D). Although the difference between Cp*$_2$ScCH$_3$ and Cp*$_2$ScCH$_2$D is the largest in the series, these data are, at best, inconclusive evidence for an α agostic structure for **2**. Comparison of the NMR data for Cp*$_2$Sc^{13}CH$_2$^{13}CH$_2$D and Cp*$_2$Sc^{13}CH$_2$^{13}CH$_3$ reveals a somewhat larger ^{1}H chemical shift difference of 0.090 ppm (0.049 vs. 0.139) for the methyl group upon monodeuteriation, but the $^1J_{C(\beta)-H}$ value of 120 Hz for Cp*$_2$Sc^{13}CH$_2$^{13}CH$_2$D is unchanged from that for Cp*$_2$Sc^{13}CH$_2$^{13}CH$_3$. Thus, these data must also be viewed as rather inconclusive as regards the structure of **8**.

8
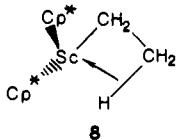
Infrared data have also been used as diagnostic for agostic interactions, since the bridging hydrogen often exhibits a low frequency "ν(C–H)".[17] No bands in the region 1600–2700 cm^{-1} are observed in the infrared spectrum of Cp*$_2$ScCH$_3$ (see Figure 2). Moreover, Cp*$_2$ScCD$_3$ exhibits two ν(C–D) bands at 2195 and 2152 cm^{-1} (cf. ν(C–D) = 2160, 2140 cm^{-1} for CD$_3$I). By contrast, three prominent, low frequency ν(C–H) bands at 2593, 2503, and 2440 cm^{-1} are noted for Cp*$_2$ScCH$_2$CH$_3$ (Figure 2). These infrared data for **8** strongly suggest a β agostic structure. Thus, despite the inconclusive ^{1}H NMR results, we presently favor an agostic structure for **8**. It should be noted that, although a β agostic structure for (Me$_2$PCH$_2$CH$_2$PMe$_2$)Cl$_3$TiCH$_2$CH$_3$ has

been unequivocally established,[18bc] insignificant ^{1}H chemical shift and $^1J_{C-H}$ differences were found for the perprotio and β-monodeuterio derivatives.[16c] With regard to the NMR data for Cp*$_2$ScCH$_2$CH$_3$ (**8**), a curiously large $^1J_{C(\alpha)-H}$ (122 Hz) is found for the methylene group as was noted for the methylene group of (Me$_2$PCH$_2$CH$_2$PMe$_2$)Cl$_3$TiCH$_2$CH$_3$.[18c] Indeed, if the structure of **8** does have the β agostic interaction and hence a small Sc–C$_\alpha$–C$_\beta$ angle shown below, a larger C–H coupling constant (vis-a-vis Cp*$_2$ScCH$_3$), like that for cyclopropane ($^1J_{C-H}$ = 161 Hz) or cyclobutane ($^1J_{C-H}$ = 134 Hz), may be anticipated. The $^1J_{C(\alpha)-H}$ of 117 Hz for Cp*$_2$ScCH$_2$CH$_2$CH$_3$, which does *not* exhibit low frequency ν(C–H) bands, suggests that an abnormally large ^{13}C$_{\alpha-H}$ coupling constant may signal a β agostic structure.[20]

Obviously, X-ray diffraction studies of the structures of Cp*$_2$ScCH$_3$ and Cp*$_2$ScCH$_2$CH$_3$ could settle these questions. Single crystals of both **2** and **8** have been obtained, and the crystal structures of the two compounds have been determined. In spite of high-quality data, it was not possible to locate the hydrogen atoms of the –CH$_3$ group for **2** or even the carbon atoms of the –CH$_2$CH$_3$ group for **8** with any precision: severe disorder in the (η^5-C$_5$Me$_5$) rings in both compounds wiped out our resolution in the rest of the molecule as well. The X-ray results for **2** do provide some evidence that the CH$_3$ group does not have an agostic interaction with the scandium, however, since the methyl carbon is found in the plane defined by the scandium atom and the centroids of the two (η^5-C$_5$Me$_5$) ligands. An agostic interaction with one (or two, but not necessarily three[18d]) C–H bond(s) would distort the carbon atom of this plane to one side. Since the methyl carbon is contained in this plane, within experimental error, we conclude that the Sc–CH$_3$ bonding is probably "conventional". It should be noted, however, a nearly symmetric[18d,21] distortion to decrease the Sc–C–H angles could also be consistent with these X-ray structural data.

We are unable to draw any conclusions regarding the structure of Cp*$_2$ScCH$_2$CH$_3$ (**8**), however, because the ethyl group as well as (η^5-C$_5$Me$_5$) ligands are disordered. The two carbon atoms are poorly defined and do not refine well; at best we can say they appear equidistant from the scandium atom. Such a geometry is compatible with an agostic interaction of a β-C–H bond, but the X-ray evidence is certainly *not* definitive.

The geometry of Cp*$_2$ScCH$_3$ (**2**) is normal. The Sc–CH$_3$ distance is 2.24 (1) Å and the average Sc–C(Cp*) distance is 2.46 (1) Å. Comparisons can be made with the structure of [Cp*$_2$LuCH$_3$]$_2$, in which there are three Lu–CH$_3$ bond distances: one terminal at 2.344 (12) Å and two for the bridging CH$_3$ group, 2.440 (9) and 2.756 (9) Å.[22] The Sc–CH$_3$ bond length we observe is therefore reasonable by comparison to these Lu–CH$_3$ bond lengths, when differences in ionic radii (0.12 Å) for Lu(III) and Sc(III) are considered. The cyclopentadienyl carbon atoms of **2** are planar, within experimental error, with the methyl groups nearly in the same plane. The ring C–C distances range from 1.284 (18) Å to 1.463 (15) Å, with an average of 1.36 (6) Å; the ring methyl–carbon distances range from 1.425 (24) to 1.601 (20) Å with an average of 1.50 (5) Å. Because of large U_{ij}'s in the (η^5-C$_5$Me$_5$) groups, these latter distances are highly imprecise.

H/D Exchange Reactions Catalyzed by Cp*$_2$ScH (6) and Cp*$_2$ScH(THF) (7). Permethylscandocene hydride derivatives catalyze H/D exchange for a variety of C–H bonds. As with other catalysts,[23] H/D exchange is rapid for arenes. Exchange between Cp*$_2$Sc–H and the aryl or methyl C–D bonds of toluene-d_8 is slow at –80 °C, but at room temperature exchange between Cp*$_2$Sc–D and C$_6$H$_6$ is >95% complete within 5 min as shown in eq 13. The
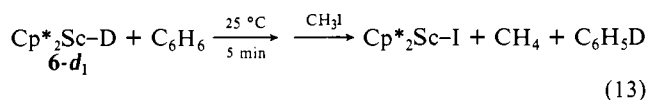
(20) Admittedly, these differences in C$_\alpha$–H coupling constant are rather small for the permethylscandocene series [Cp*$_2$Sc–R, R = CH$_3$ (111 Hz), CH$_2$CH$_3$ (122 Hz), CH$_2$CH$_2$CH$_3$ (117 Hz)], so that caution should be exercised in extrapolating from these results. The lack of an agostic β C–H interaction with scandium for Cp*$_2$ScCH$_2$CH$_2$CH$_3$ may be attributed to an unfavorable steric interaction of the C$_\beta$ methyl group with a pentamethylcyclopentadienyl group which is imposed upon coordination of a β C–H bond.
(21) Eisenstein, O.; Jean, Y. *J. Am. Chem. Soc.* **1985,** *107,* 1177.
(22) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985,** *18,* 51.
(23) (a) Parshall, G. W. *Chemtech* **1984,** 628. (b) Parshall, G. W. *Acc. Chem. Res.* **1975,** *8,* 113.

σ Bond Metathesis for Hydrocarbons

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complementary reaction, **6** + C_6D_6 + CH_3I, yields $Cp*_2ScI$, C_6D_5H, and CH_3D (only). An upper limit of ca. 100 s is thus established for the half life of the exchange reaction at 25 °C (k > ca. 10^{-3} s⁻¹·M⁻¹).

$$Cp*_2Sc\text{-}D + C_6H_6 \xrightarrow[5\ min]{25\ °C} \xrightarrow{CH_3I} Cp*_2Sc\text{-}I + CH_4 + C_6H_5D$$
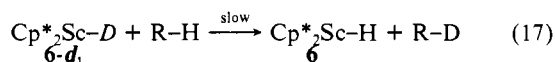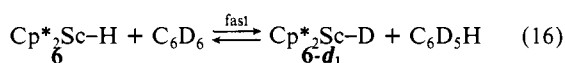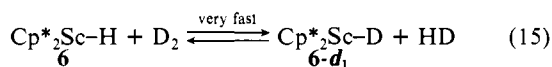$$\mathbf{6\text{-}d_1}$$
(13)

H/D exchange for $Cp*_2ScH(THF)$ (**7**) and benzene-d_6 is much slower. After 1.5 h at 25 °C, treatment of a solution of $Cp*_2Sc\text{-}H(THF)$ in C_6D_6 with excess CH_3I yields only $CH_4(<5\%$ CH_3D, k < ca. 10^{-5} s⁻¹·M⁻¹ at 25 °C). Onset of exchange occurs at elevated temperatures (>50 °C), but like exchange with H_2 (vida supra), dissociation of the THF ligand very likely precedes reaction of **7** with benzene.

With toluene the progress of H/D exchange was monitored by ¹H NMR spectroscopy. Multiple exchanges are achieved by treating toluene-d_8 with $Cp*_2Sc\text{-}H$ and H_2 (4 atm) in a sealed NMR tube (eq 14). The positional preference (ortho, meta, para,

$$toluene\text{-}d_8 \xrightarrow[H_2\ (4\ atm)]{[Cp*_2Sc\text{-}H]} toluene\text{-}d_n$$
(14)
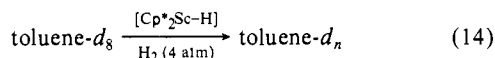
CH_3) is of particular interest as regards the mechanism of exchange (vida infra). After 2-3 turnovers the meta and para positions show roughly equal extents of proton incorporation, exchange into the ortho positions being much slower. An unchanging ratio (39:41:20) of integrations, ortho:meta:para (¹H NMR, 500 MHz), is obtained after 48 h at 80 °C. Hydrogen incorporation into the methyl group occurs at a rate 60-70 times slower than for the aryl positions. On prolonged heating the amount of hydrogen in the methyl position gradually increases, eventually equilibrating at an aryl:methyl ratio of 5.0:4.0 (slightly less than statistical incorporation of H in the aryl and hence slightly greater incorporation of D in the aryl positions relative to the methyl positions, as expected on the basis of the relative zero-point energy differences). The relative amounts of hydrogen incorporated among the aryl positions does not change.

A series of substrates was examined for H/D exchange with $Cp*_2Sc\text{-}D$ by using ¹H NMR spectroscopy. In order to effect extensive deuteration of the C-H positions of these substrates, $Cp*_2Sc\text{-}D$ and excess substrate were dissolved in benzene-d_6 under 4 atm of D_2. The pool of deuterium in the solvent thus serves as the principal source for exchange, since reaction of $Cp*_2Sc\text{-}H$ with benzene-d_6 and D_2 is considerably faster than H/D exchange with substrates (eq 15-17). Under these conditions **6** is thermally

$$Cp*_2Sc\text{-}H + D_2 \underset{}{\overset{very\ fast}{\rightleftharpoons}} Cp*_2Sc\text{-}D + HD$$
$$\mathbf{6} \qquad\qquad\qquad \mathbf{6\text{-}d_1}$$
(15)

$$Cp*_2Sc\text{-}H + C_6D_6 \underset{}{\overset{fast}{\rightleftharpoons}} Cp*_2Sc\text{-}D + C_6D_5H$$
$$\mathbf{6} \qquad\qquad\qquad \mathbf{6\text{-}d_1}$$
(16)

$$Cp*_2Sc\text{-}D + R\text{-}H \xrightarrow{slow} Cp*_2Sc\text{-}H + R\text{-}D$$
$$\mathbf{6\text{-}d_1} \qquad\qquad\qquad \mathbf{6}$$
(17)

quite stable. By using this standard procedure, intramolecular H/D exchange is observed for the methyl groups of the (η^5-C_5Me_5) ligands of **6** (ca. 2 turnovers·h⁻¹ at 80 °C) and for the α-C-H positions of the THF ligand and the methyl positions of the (η^5-C_5Me_5) ligands for **7** (h at 80 °C); the β-C-H positions of the THF ligand remain unreactive even after several days at this temperature. In light of the reactivity of $Cp*_2ScH$ with pyridine (eq 11 and 12), the α-C-H bonds of the THF almost certainly react reversibly and intramolecularly with the Sc-D bond of **7**. Moreover, free and coordinated THF are in rapid equilibrium so that **7** acts as a catalyst for the selective α-deuteration of THF.

Intermolecular H/D exchange is observed for the primary C-H bonds of a variety of molecules. In addition to the methyl group of toluene (vida supra), a moderate rate of H/D exchange is noted for CH_4, $Si(CH_3)_4$, $P(CH_3)_3$,[21] and remarkably, at 80 °C for *only* the methyl groups of propane. $Cp*_2ScH(THF)$ (**7**) also catalyzes these H/D exchange reactions; however, in all cases the rates are

Table II. Equilibrium Constants for Reaction of $Cp*_2ScH$ with Benzene To Yield $Cp*_2ScC_6H_5$ and H_2[a]

| temp	K_{eq} ($\times 10^6$ M⁻¹)	$\Delta G°$ (kcal·mol⁻¹)
6	2.8 (4)	7.09 (8)
25	5.6 (7)	7.16 (9)
47	13 (2)	7.15 (10)
66.5	23 (4)	7.20 (13)
80	36 (5)	7.18 (13)

[a] Equation 18.

much lower. Methane and tetramethylsilane exhibit similar rates of exchange, the predominant products at low conversions being CH_3D and $Si(CH_3)_n(CH_2D)_{4-n}$. Thus, incorporation of deuterium occurs in a one-at-a-time manner, in contrast to H/D exchange catalysts based on $[PtCl_4]^{2-}$ [25] and zirconium alkoxides,[23] which have been reported to effect multiple deuterations per interaction with the catalyst.

Hydrogen/deuterium exchange is also observed for 2° C-H bonds, but the rates are generally very slow compared with intramolecular exchange or intermolecular exchange with 1° or aryl C-H bonds. For example, a rate of only 0.06 turnovers·h⁻¹ at 120 °C is observed for cyclopentane.[24] The large difference in the rates of 1° vs. 2° C-H exchange suggests that this catalyst system may be used generally in the synthesis of aliphatic hydrocarbons with only primary deuteration (e.g., $CD_3(CH_2)_nCD_3$) or aromatic hydrocarbons with only 1° and aryl deuteration (e.g., $CD_3CH_2C_6D_5$). Moreover, the low rates of 2° C-H bond activation may be used to advantage in providing inert solvents (e.g., cyclohexane and cyclooctane) for the mechanistic studies described in the next sections. The C-H bonds of cyclopropane are exceptionally reactive and are readily exchanged under the standard reaction conditions described above, at a rate comparable to methane and tetramethylsilane; no ring opening is apparent under these conditions.

The qualitative scale of reactivity toward H/D exchange shown below clearly indicates that sterics (and s character of the C-H bond, vida infra) correlate more closely with reactivity than does the C-H bond dissociation energy of the substrate: *decreasing rate of H/D exchange with* $Cp*_2\overline{Sc\text{-}D \rightarrow H\text{-}H} \gg$ aryl C-H > (η^5-C_5Me_5), $\overline{O\text{-}CH_2}CH_2CH_2CH_2$, PMe_3 > $\overline{CH_4}$, $Si(CH_3)_4$, cyclopropane, $C_6H_5\overline{CH_3}$ > $\overline{CH_3}CH_2CH_3 \gg O\text{-}CH_2\overline{CH_2CH_2}CH_2$, cyclopentane, cyclohexane, cyclooctane, $CH_3\overline{CH_2}CH_3$.

Thermochemistry of Equilibration of $Cp*_2Sc\text{-}H$, C_6H_6, $Cp*_2Sc\text{-}C_6H_5$, **and** H_2. During the course of our studies of the H/D exchange reactions between $Cp*_2ScH$ (**6**) and benzene-d_6, we discovered that **6** reacts in a cleanly reversible manner with benzene to afford $Cp*_2ScC_6H_5$ (**3**) and dihydrogen (eq 18). Thus,

$$Cp*_2ScH + C_6H_6 \overset{K_{eq}}{\rightleftharpoons} Cp*_2ScC_6H_5 + H_2$$
$$\mathbf{6} \qquad\qquad\qquad \mathbf{3}$$
(18)
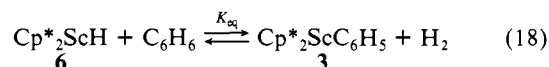
if isolation of $Cp*_2ScH$, prepared in benzene solution (for example, by hydrogenation of $Cp*_2ScCH_3$), is attempted by removing the benzene in vacuo, the product obtained is largely $Cp*_2ScC_6H_5$, together with minor amounts of **6**. Dissolution of this product mixture in benzene, followed by admission of 1 atm of H_2, drives the equilibrium almost completely back to **6** (¹H NMR).

Measureable concentrations of both **3** and **6** in benzene solution are obtained by dissolving **6** in benzene in a sealed NMR tube. The determination of the concentration of dihydrogen in solution using ¹H NMR spectroscopy is, of course, not possible, since exchange with the hydride ligand of **6** is rapid, and the ⁴⁵Sc quadrupolar broadening obscures the average signal. The concentration of H_2 may be calculated, however, by assuming the

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(24) The molecularity of the H/D exchange with PMe_3 has not been determined. Detectable concentrations of a PMe_3 adduct of **6** do not build up, even in the presence of several equivalents of phosphine (presumably due to unfavorable steric interactions with the bulky Cp* ligands); however, H/D exchange with the methyl groups of PMe_3 is faster than with the methyl groups of the (η^5-C_5Me_5) ligands of **6** and faster than exchange with the 1° C-H positions of hydrocarbons.
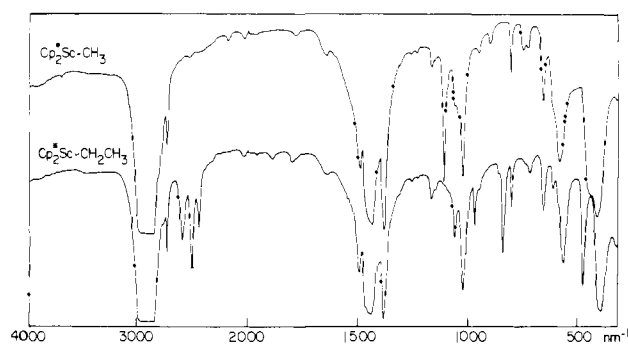
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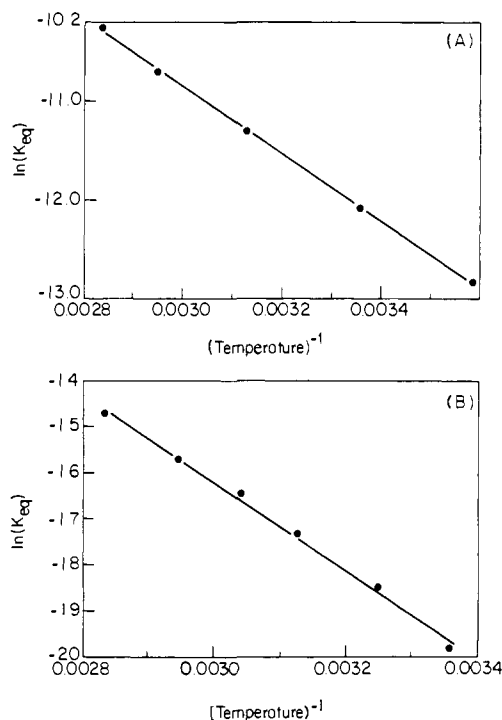**Figure 3.** IR spectra (Nujol mull) of Cp*$_2$Sc–CH$_3$ (top) and Cp*$_2$Sc–CH$_2$CH$_3$ (bottom).

Figure 4. (A) van't Hoff plot for the equilibrium between Cp*$_2$ScH, H$_2$, and Cp*$_2$ScC$_6$H$_5$ in C$_6$H$_6$ solution. (B) van't Hoff plot for the equilibrium between Cp*$_2$Sc(THF)H, H$_2$, THF, and Cp*$_2$ScC$_6$H$_5$ in C$_6$H$_6$ solution.

number of molar equivalents of dihydrogen is precisely equal to the molar equivalents of Cp*$_2$ScC$_6$H$_5$ (eq 18) and that Henry's Law is followed (see Experimental Section). The consistent values of K_{eq} obtained, when samples are cycled back and forth in temperature between 6 and 80 °C, give us confidence in this procedure (see Table II). A van't Hoff plot of these data (Figure 4A) reveals $\Delta H° = 6.7$ (3) kcal·mol^{-1} and $\Delta S° = -1$ (1) eu.

The small value of $\Delta S°$ for equilibrium 18, although not entirely expected for an equilibrium involving reagents both in solution and in the gas phase, supports the assumptions of others[28] that the free energy change accompanying an equilibrium is a good approximation of the enthalpy change and thus useful in estimating relative bond dissociation energies (BDEs). For equilibrium 18, the relative Sc–H and Sc–C$_6$H$_5$ BDEs may be estimated from the C–H bond strength for benzene (110.9 kcal·mol^{-1})[29] and the

(25) Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725.

(26) Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1982**, *2*, 161.

(27) This H/D exchange process was not monitored by ^{1}H NMR spectroscopy; rather, the deuterium incorporation after heating at 120 °C for 36 h was measured by mass spectrometry (see Experimental Section).

(28) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. submitted for publication in *J. Am. Chem. Soc.* (b) Janowicz, A. H.; Periana, R. A.; Buchanan, J. M.; Kovac, C. A.; Stryker, J. M.; Wax, M. J.; Bergman, R. G. *Pure Appl. Chem.* **1984**, *56*, 13.
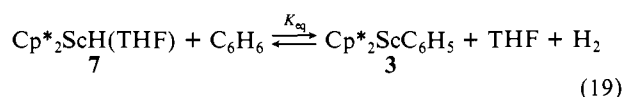
Table III. Equilibrium Constants for Reaction of Cp*$_2$ScH(THF) with Benzene To Yield Cp*$_2$ScC$_6$H$_5$, THF, and H$_2$[a]

temp	K_{eq} (×10^8 M^{-1})	$\Delta G°$ (kcal·mol^{-1})
25	0.25 (3)	11.7 (1)
35	0.9 (1)	11.3 (1)
47	2.9 (4)	11.0 (1)
56	7.2 (9)	10.8 (1)
66.5	15 (2)	10.6 (1)
80	41 (6)	10.3 (1)

[a] Equation 19.

H–H bond strength (104.2 kcal·mol^{-1}),[30] including the heat of solution for H$_{2(g)}$ in benzene (1.5 kcal·mol^{-1}).[31] Thus, the Sc–H BDE in **6** is greater than the Sc–C$_6$H$_5$ BDE in **3** by 1.5 (4) kcal·mol^{-1} {= (6.7 + 1.5 + 104.2) − (110.9) kcal·mol^{-1}}. Although bond strength data are limited, especially for early transition-metal compounds, the small value for this difference is in accord with the findings of others.[28] For example, by using reaction calorimetry Bruno, Marks, and Morss[32] found that the average Th–H BDE for [Cp*$_2$ThH$_2$]$_2$ is ca. 7 kcal·mol^{-1} greater than the Th–C$_6$H$_5$ BDE for Cp*$_2$Th(C$_6$H$_5$)$_2$.

The tetrahydrofuran adduct of Cp*$_2$ScH also equilibrates cleanly with benzene (eq 19). By using a similar procedure for determining the concentration of H$_2$, together with the ^{1}H NMR integrations for [**7**], [**3**], and [THF],[33] the temperature variation of the equilibrium constant for eq 19 was determined (Table III).

$$\text{Cp*}_2\text{ScH(THF)} + \text{C}_6\text{H}_6 \underset{}{\overset{K_{eq}}{\rightleftharpoons}} \text{Cp*}_2\text{ScC}_6\text{H}_5 + \text{THF} + \text{H}_2$$

7   **3**

$$(19)$$

Again, a linear van't Hoff fit is obtained (Figure 4B) with $\Delta H° = 18.9$ (8) kcal·mol^{-1} and $\Delta S° = 24$ (2) eu. The much larger $\Delta S°$ for equilibrium 19 is expected, since three molecules are generated from two. If one makes the (doubtful) assumption that the Sc–H bond strength for Cp*$_2$ScH(THF) is unchanged from that for Cp*$_2$ScH, comparison of the values for $\Delta H°$ for equilibria 18 and 19 indicates a 12 (1) kcal·mol^{-1} dative bond strength for the tetrahydrofuran ligand (eq 20).

$$\text{Cp*}_2\text{ScH(THF)} \overset{K_{eq}}{\rightleftharpoons}$$

7

$$\text{Cp*}_2\text{ScH} + \text{THF} \qquad (\Delta H° = 12 \text{ (1) kcal·mol}^{-1}) \quad (20)$$

6
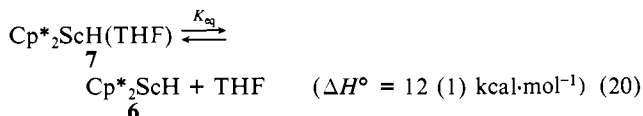
Thermal Decomposition of Cp*$_2$ScCH$_3$. Heating Cp*$_2$ScCH$_3$ (**2**) in cyclohexane at 80 °C for several days produces CH$_4$ and a pale yellow, crystalline compound which has defied complete characterization. Its solubility in aliphatic hydrocarbons is very low, precluding an accurate molecular weight determination; however, the low solubility does suggest an oligomeric structure. The ^{1}H NMR spectrum (benzene-d_6) exhibits four singlets at δ 2.08, 1.96, 1.54, and 1.39 with relative intensities 6:15:6:2, indicative of one (η^5-C$_5$Me$_5$) and one metallated (or "tucked-in") ring [(η^5-C$_5$Me$_5$)Sc(η^5-C$_5$Me$_4$CH$_2$)]$_n$ (**12**).

Treatment of a benzene slurry of **12** with H$_2$ (1 atm) results in dissolution of the solid and exclusive generation of Cp*$_2$ScH (**6**) (eq 21). Addition of H$_2$ across the metal–carbon bond of such "tuck-in" complexes is commonly facile.[34] When heated with

(29) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

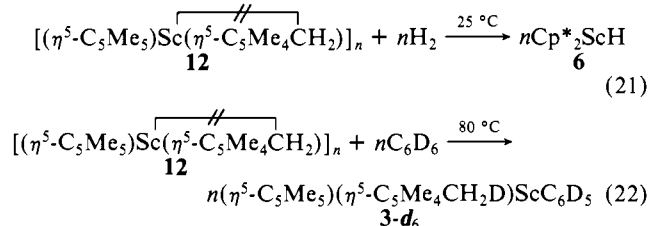(30) Gingerich, K. A. *J. Phys. Chem.* **1971**, *54*, 3720.

(31) Cook, M. W.; Hanson, D. N.; Adler, B. J. *J. Phys. Chem.* **1957**, *26*, 748.

(32) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824.

(33) The concentration of benzene was calculated from its density at temperature = $T(°C)$, $d_T = d_{25°C} + 10^{-3}$ (−1.0636) ($T − 25$ °C). *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*; Washburn, E. W., Ed.; McGraw-Hill: New York, 1928; Vol. 3, p 27.

(34) (a) Bercaw, J. E. *Adv. Chem. Ser.* **1978**, *167*, 36. (b) Bulls, A. R.; Parkin, G.; Bercaw, J. E., manuscript in preparation.

benzene-d_6, **12** cleanly affords $Cp^*(Cp^*-d_1)ScC_6D_5$ (**3-d_6**) (^1H and ^2H NMR) (eq 22).

$$[(\eta^5\text{-}C_5Me_5)Sc(\eta^5\text{-}C_5Me_4CH_2)]_n + nH_2 \xrightarrow{\text{25 °C}} nCp^*_2ScH$$
$$\textbf{12} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \textbf{6}$$

$$\text{(21)}$$

$$[(\eta^5\text{-}C_5Me_5)Sc(\eta^5\text{-}C_5Me_4CH_2)]_n + nC_6D_6 \xrightarrow{\text{80 °C}}$$
$$\textbf{12}$$

$$n(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5Me_4CH_2D)ScC_6D_5 \quad \text{(22)}$$
$$\textbf{3-}d_6$$

When $Cp^*_2ScCH_3$ (**2**) is heated with benzene, methane is generated along with $Cp^*_2ScC_6H_5$ (**3**) (eq 23). In pure benzene solution reaction 23 follows clean first-order kinetics. When

$$Cp^*_2ScCH_3 + C_6H_6 \xrightarrow{\text{80 °C}} Cp^*_2ScC_6H_5 + CH_4 \quad \text{(23)}$$
$$\textbf{2} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{3}$$
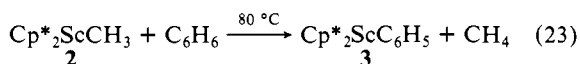
treated with benzene-d_6, a mixture of CH_4 and CH_3D is obtained, the relative amounts varying with temperature from 24:76 (respectively) at 60 °C, 40:60 at 80 °C, 47:53 at 98 °C, to 50:50 at 125 °C. These results are indicative of competitive bimolecular reaction of benzene-d_6 with **2** to yield CH_3D and $Cp^*_2ScC_6D_5$ (**3-d_5**) and intramolecular decomposition of **2** to CH_4 and **12**, followed by faster reaction (eq 22) of **12** with benzene-d_6 to yield $Cp^*(Cp^*-d_1)ScC_6D_5$ (**3-d_6**) as shown in eq 24. The kinetics thus
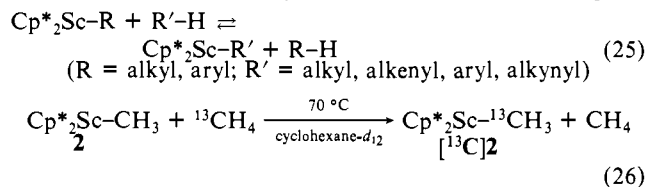

$$\text{(24)}$$
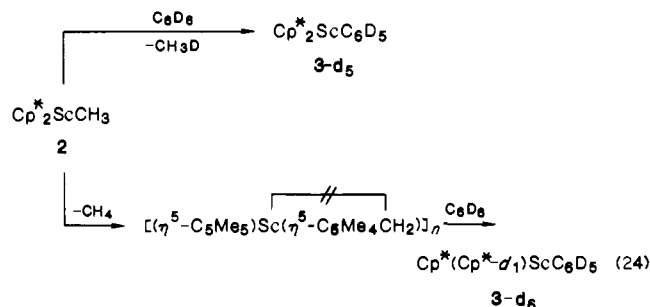
reflect two parallel processes: a second-order step for the direct reaction of **2** with benzene-d_6 and a first-order (vida infra) one for the decomposition of **2** to the monomeric precursor to **12**. The mechanism for the former is discussed in the following section. With regard to the latter, examination of the kinetics for the decomposition of **2** to **12** in an inert solvent (e.g., cyclohexane) under a variety of conditions revealed the following complications: (i) whereas different starting concentrations of **2** in cyclohexane-d_{12} produce similar initial rates of decomposition ($k \approx 6$ (1) $\times 10^{-6}$ s^{-1}), nonlinear, autocatalytic behavior is observed, with the final rate of decomposition typically quadrupling the initial rate; (ii) rate acceleration accompanies precipitation of microcrystalline **12**; (iii) addition of small amounts of nearly insoluble **12** produces a greater initial rate of decomposition of **2**, but nonlinear first-order plots are still obtained; (iv) Toepler pump measurements after complete conversion of **2** to **12** indicate only 0.80 equiv of methane are evolved. In view of the unknown structure of **12** and the complications encountered in studying the mechanism(s) of its formation, the (η^5-C_5Me_5) ligands of **2** have been deuteriated (via treatment of Cp^*_2ScH with several portions of excess benzene-d_6 under D_2 at 125 °C, conversion to **1** with CH_2Cl_2, and treatment of **1-d_{30}** with $LiCH_3$) to minimize this side reaction in the mechanistic studies presented in the following section. Although $(Cp^*-d_{15})_2ScCH_3$ shows the same complex kinetic behavior in decomposing to CH_3D and **12-d_{29}**, a moderate kinetic deuterium isotope effect ($k_H/k_D = 1.6$ (2)) for the initial rates of decomposition obtains. Moreover, ^1H and ^2H NMR spectroscopy of the methanes evolved provides a reliable quantitative measure of the extent of (η^5-C_5Me_5) involvement in reactions of **2-d_{30}** with (undeuteriated) substrates R–H.

Carbon–Hydrogen Bond Activation with Cp^*_2ScR (R = Alkyl, Aryl) Complexes. The slowest reactions in the series are those involving σ bond metathesis between alkyl or aryl derivatives of permethylscandocene and the carbon–hydrogen bonds of alkanes

	p-(CH_3O)- $C_6H_4CH{=}CH_2$	p-(CF_3)- $C_6H_4CH{=}CH_2$
k ($\times 10^4$ s^{-1}·M^{-1})	12.5 (7)	8.5 (5)
E_a (kcal·mol^{-1})	12.1 (3)	13.2 (3)
log A	4.9 (2)	5.7 (2)
$\Delta H^{\ddagger}$ (kcal·mol^{-1})	11.5 (3)	12.6 (3)
$\Delta S^{\ddagger}$ (eu)	−38 (3)	−34 (3)

(eq 25). The primary example, that between $Cp^*_2ScCH_3$ (**2**) and methane, is demonstrated by treatment of **2** with $^{13}CH_4$ (eq 26).

$$Cp^*_2Sc\text{-}R + R'\text{-}H \rightleftharpoons$$
$$Cp^*_2Sc\text{-}R' + R\text{-}H \qquad \text{(25)}$$
$$\text{(R = alkyl, aryl; R}' = \text{alkyl, alkenyl, aryl, alkynyl)}$$

$$Cp^*_2Sc\text{-}CH_3 + {}^{13}CH_4 \xrightarrow[\text{cyclohexane-}d_{12}]{\text{70 °C}} Cp^*_2Sc\text{-}{}^{13}CH_3 + CH_4$$
$$\textbf{2} \qquad\qquad\qquad\qquad\qquad\qquad\qquad [{}^{13}C]\textbf{2}$$

$$\text{(26)}$$

The activation of the C–H bonds of methane with soluble metal complexes has been observed thus far only with $[PtCl_4]^{2-}$ in D_2O/CH_3COOD solution,[35] with some electron-rich group 8 complexes,[36] by some closely related compounds, $Cp^*_2YCH_3$ and $Cp^*_2LuCH_3$,[7a] and by some thoracyclobutane derivatives, $Cp^*_2ThCH_2XCH_2$ (X = CMe_2, $SiMe_2$).[37] Reaction 26 is rather slow, the second-order rate constant being 1 $\times$ 10^{-5} s^{-1}·M^{-1} ($[^{13}CH_4] = 0.5$–1.5 M, $[2] = 0.06$ M), approximately 50 times slower than reaction of CH_4 with $Cp^*_2LuCH_3$ and 250 times slower than reaction of CH_4 with $Cp^*_2YCH_3$.[38]

Ethylene is rapidly polymerized by alkyl and aryl derivatives of permethylscandocene;[6,39] however, σ bond metathesis rather than olefin insertion commonly occurs with substituted olefins. For example, $Cp^*_2ScCH_3$ (**2**) reacts readily with p-methylstyrene in cyclohexane-d_{12} to afford *trans*-$Cp^*_2ScCH{=}CHC_6H_4CH_3$ (**13**) (eq 27). The trans arrangement of $[Cp^*_2Sc]$ and tolyl

$$Cp^*_2ScCH_3 + CH_2{=}CHTol \xrightarrow[\text{cyclohexane-}d_{12}]{\text{60 °C}}$$
$$\textbf{2}$$

$$\textit{trans-}Cp^*_2ScCH{=}CHTol + CH_4 \quad \text{(27)}$$
$$\textbf{13}$$
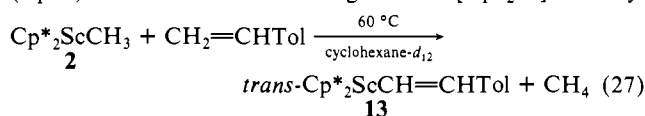
is based on the large coupling constant ($^3J_{HH} = 20$ Hz) for $Cp^*_2ScCH{=}CHC_6H_4CH_3$. The rates of reaction with two para substituted styrenes $\{p$-$(CH_3O)C_6H_4CH{=}CH_2$ and p-$(CF_3)C_6H_4CH{=}CH_2\}$ were examined to establish the effect of electron-donating and electron-withdrawing groups on the rate of vinylic C–H bond metathesis with $Cp^*_2Sc\text{-}CH_3$ (**2**). Convenient rates at 40–70 °C are obtained, it the reaction is conducted with $[2] \approx 0.1$ M in benzene-d_6 and 2–4 molar equiv of styrene. Good fits to second-order plots were obtained in both cases.[40] Measurements over a ca. 40 °C range provide the second-order rate constants and activation parameters shown in Table IV. The difference in the rate between the electron-rich and electron-poor styrenes is insignificant, being barely outside the limits of uncertainty. The activation parameters are also revealing, particularly the very large, negative entropies of activation observed. Thus, the reaction of $Cp^*_2ScCH_3$ with the vinylic C–H bond of styrene is characterized as having a rather small enthalpy of

(35) Gol'dehleger, N. F.; Tybain, M. B.; Shilov, A. E.; Shteinman, A. A. *Russ. J. Phys. Chem.* **1969**, *43*, 1222.

(36) (a) Wax, A. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121. (b) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190.

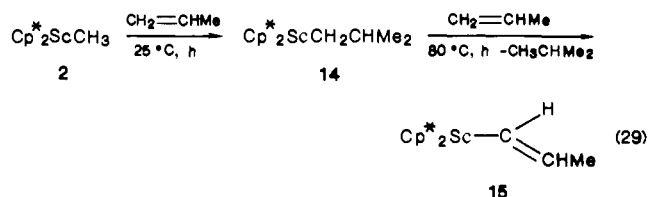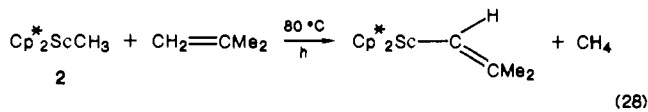(37) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214.

(38) The rates of reaction of $Cp^*_2MCH_3$ (M = Sc, Y, Lu) with methane are sufficiently slow so that involvement of the (η^5-C_5Me_5) C–H bonds (i.e., intermediate tuck-in species) appears likely, at least in part. Indeed, Watson has commented on a competitive bimolecular and unimolecular nature of these reactions for = Y, Lu (ref 7a). With scandium, a set of parallel pathways analogous to the reaction of **2** with benzene (eq 24) appears likely.

(39) Burger, B. J.; Bercaw, J. E., unpublished results.

(40) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*; Wiley-Interscience: New York, New York, 1981; pp 22–26.
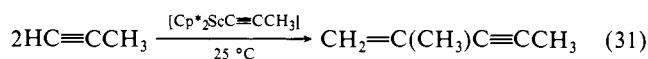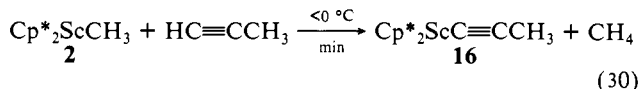
activation and a nonpolar, highly ordered transition state.[41]

Isobutylene reacts with $Cp^*_2ScCH_3$ (**2**) in the same manner as does styrene (eq 28), and propene undergoes insertion[42] to afford the isobutyl derivative $Cp^*_2ScCH_2CHMe_2$ (**14**) and then σ bond metathesis with the trans *vinylic* C–H bond of excess propene, yielding isobutane and *trans*-$Cp^*_2ScCH=CHMe$ (**15**) (eq 29).
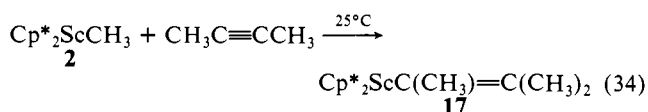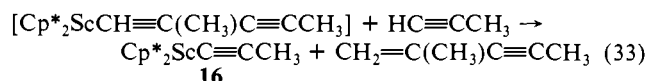
$$Cp^*_2ScCH_3 + CH_2{=}CMe_2 \xrightarrow[h]{80\ ^\circ C} Cp^*_2Sc{-}C\overset{H}{\underset{CMe_2}{<}} + CH_4$$

2

(28)

$$Cp^*_2ScCH_3 \xrightarrow[25\ ^\circ C,\ h]{CH_2{=}CHMe} Cp^*_2ScCH_2CHMe_2 \xrightarrow[80\ ^\circ C,\ h\ -CH_3CHMe_2]{CH_2{=}CHMe}$$

2   **14**

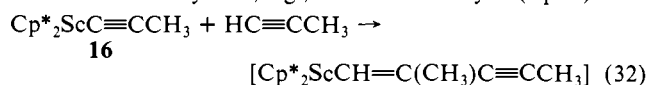$$Cp^*_2Sc{-}C\overset{H}{\underset{CHMe}{<}} \quad (29)$$

15

These observations are significant in at least two regards: (i) unlike the permethylyttrocene and permethyllutetocene analogues, which undergo several insertions of propene,[43] the permethylscandocene system described here terminates completely (by vinylic C–H bond metathesis) after one insertion into the Sc–CH$_3$ bond and (ii) the σ bond metathesis processes for reactions 28 and 29 appear to involve the much stronger vinylic C–H bonds in preference to the ca. 20 kcal·mol^{-1} weaker allylic C–H bonds. In order to ascertain whether the propenyl derivative, *trans*-$Cp^*_2ScCH=CHMe$ (**15**), is indeed the kinetic product of reaction 29, i.e., to exclude the possibility that the allyl complex **10** is initially generated but rearranges rapidly to more stable **15**, $Cp^*_2Sc(\eta^3$-$C_3H_5)$ (**10**) was subjected to the reaction conditions for extended periods. No interconversion of **10** and **15** was found, thus confirming that vinylic C–H bond activation is kinetically preferred.

While vinylic carbon–hydrogen bonds are more reactive than aryl C–H bonds, the much higher reactivity of the terminal C–H bonds of alkynes is striking. For example, $Cp^*_2ScCH_3$ (**2**) reacts rapidly with propyne to afford methane and the propynyl complex $Cp^*_2ScC{\equiv}CCH_3$ (**16**), even at low temperatures (eq 30). Compound **16** efficiently and selectively catalyzes the dimerization of propyne to the *gem*-enyne $CH_2{=}C(CH_3)C{\equiv}CCH_3$ (eq 31).

$$Cp^*_2ScCH_3 + HC{\equiv}CCH_3 \xrightarrow[min]{<0\ ^\circ C} Cp^*_2ScC{\equiv}CCH_3 + CH_4$$
2   **16**

(30)

$$2HC{\equiv}CCH_3 \xrightarrow[25\ ^\circ C]{[Cp^*_2ScC{\equiv}CCH_3]} CH_2{=}C(CH_3)C{\equiv}CCH_3 \quad (31)$$

A likely mechanism, sequential σ bond metathesis and alkyne insertion into Sc–propynyl bonds, is given in eq 32 and 33. Insertion of alkynes into scandium–carbon bonds is, indeed, observed with internal acetylenes, e.g., for **2** and 2-butyne (eq 34).
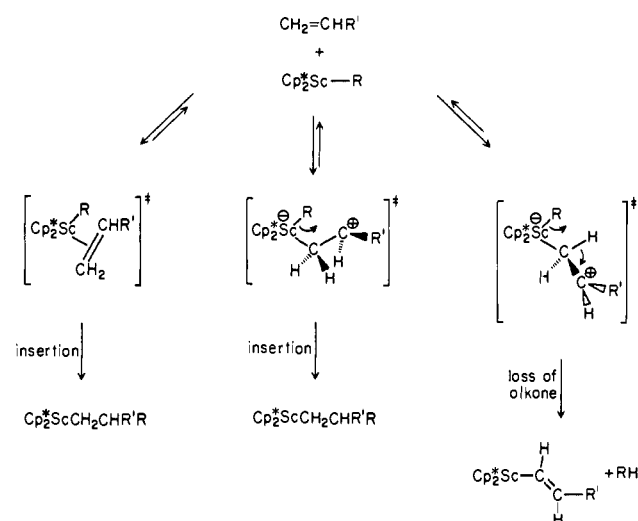
$$Cp^*_2ScC{\equiv}CCH_3 + HC{\equiv}CCH_3 \rightarrow$$
16

$$[Cp^*_2ScCH{=}C(CH_3)C{\equiv}CCH_3] \quad (32)$$

$$[Cp^*_2ScCH{=}C(CH_3)C{\equiv}CCH_3] + HC{\equiv}CCH_3 \rightarrow$$
$$Cp^*_2ScC{\equiv}CCH_3 + CH_2{=}C(CH_3)C{\equiv}CCH_3 \quad (33)$$
16

$$Cp^*_2ScCH_3 + CH_3C{\equiv}CCH_3 \xrightarrow{25^\circ C}$$
2

$$Cp^*_2ScC(CH_3){=}C(CH_3)_2 \quad (34)$$
17

(41) Other C–H bond activating systems, particulary those based on d^0 metals, also exhibit moderate to large, negative entropies of activation. See: Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.

(42) When **2** is treated with only 1 or 2 equiv of propene, or if the reaction is carried out at 80 °C even with excess propene, the reaction is not as straightforward as indicated by eq 29. In addition to the products listed in eq 29, isobutene and $Cp^*_2ScCH_2CH_2CH_3$ (**9**) are also observed. A reasonable explanation is that β-H elimination from the isobutyl complex may compete with σ bond metathesis. Insertion of propene into the Sc–H bond of Cp^*_2ScH (generated by β-H elimination) is, in fact, rapid (eq 9).

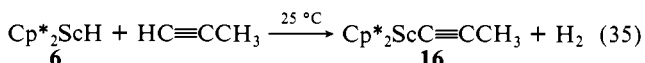(43) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

Scheme I

Scheme II
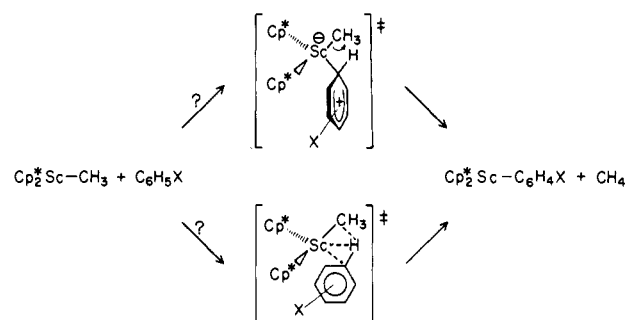
The preference for σ bond metathesis over insertion for terminal acetylenes with Sc–R (R = H, alkyl) is further illustrated by the rapid reaction of Cp^*_2ScH with propyne to afford $Cp^*_2ScC{\equiv}CCH_3$ and H_2 (eq 35). By contrast, zirconium and hafnium

$$Cp^*_2ScH + HC{\equiv}CCH_3 \xrightarrow{25\ ^\circ C} Cp^*_2ScC{\equiv}CCH_3 + H_2 \quad (35)$$
6   **16**

hydrides rapidly insert propyne, yielding the trans propenyl derivatives.[44] Curiously, whereas *trans*-$Cp^*_2ScCH=CHMe$ (**15**) is, indeed, stable, it is not formed, even after prolonged heating of the product mixture from reaction 35.

As noted in the previous section, $Cp^*_2ScCH_3$ (**2**) reacts cleanly with benzene to yield $Cp^*_2ScC_6H_5$ (**3**) (eq 24). The strongly electrophilic nature of the scandium center of **2**, evidenced by its high affinity for Lewis bases, and the insertion reactions with ethylene, propene, and 2-butyne, which undoubtedly proceed by interaction of scandium with the π orbitals of these substrates, suggest that the enhanced reactivity of permethylscandocene derivatives with sp^2- and sp-hybridized C–H bonds might well be attributable to initial attack of scandium at the π orbitals of these substrates. As suggested earlier[6] by two of us (M.E.T. and J.E.B.), vinylic C–H bond activation could be viewed as arising from attack of scandium at the terminal carbon of substituted olefins to produce a zwitterionic intermediate or transition state, which collapses to product via abstraction of the proton α to the substituted carbenium ion by the methyl "carbanion" (Scheme I).[45] The activation of aryl C–H bonds would then resemble electrophilic aromatic substitution (of $[Cp^*_2Sc^+]$ for H$^+$), proceeding via a similar phenonium intermediate (or transition state) (Scheme II). The analogue in organic chemistry for the rapid reactions of the terminal C–H bonds of alkynes with $Cp^*_2ScCH_3$ is not as

(44) McDade, C.; Bercaw, J. E. *J. Organomet. Chem.* **1985**, *279*, 281.

(45) The insensitivity of the rate constant for reaction of the para substituted styrenes is not consistent with this type of mechanism, however. See Conclusion section.
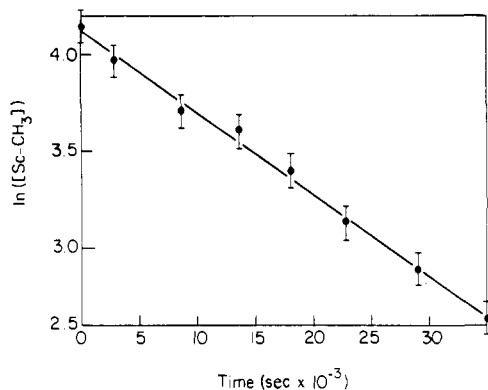
Figure 5. First-order plot of the data from the reaction of $Cp*_2ScCH_3$ with $C_6H_5N(CH_3)_2$.

Table V. Rate Constants for Reaction of $(Cp*_2-d_{15})_2ScCH_3$ (2) with Monosubstituted Arenes[a]

arene	$k_2(\times 10^5 \cdot s^{-1} \cdot M^{-1})$
$C_6H_5N(CH_3)_2$	3.2 (1)
$C_6H_5CH_3$	3.4 (1)
C_6H_6	3.3 (1)
$C_6H_5CF_3$	1.4 (1)

[a] Equation 36 at 80 °C, cyclohexane-d_{12} with [2] = 0.12 M, [arene] = 1.3 M.

obvious; however, the higher acidity of these sp-hybridized C–H bonds would once again be generally in accord with such heterolytic carbon–hydrogen bond cleavage mechanisms.

Although attack of an electrophile at the highest occupied molecular orbital of an unsaturated substrate (i.e., at the π orbitals) is entirely plausible, interaction of the frontier orbitals of scandium[46] with the π orbitals of alkenes or arenes does impose very unfavorable steric interactions of the arene ring or the β substituents of the alkene with the bulky (η^5-C_5Me_5) ligands in the intermediate (or transition state). Direct attack of scandium at the C–H σ bond (perpendicular to the π system) is considerably less crowded as shown in Schemes I and II.

In order to experimentally probe these issues, the mechanism of reaction of $(Cp*-d_{15})_2ScCH_3$ with (perprotio) arenes was more closely examined. As noted above, deuteration of the pentamethylcyclopentadienyl ligands reduces the complications from competing unimolecular decomposition to $[(\eta^5-C_5Me_5)-Sc(\eta^5-C_5Me_4CH_2)]_n$, the $CH_3D:CH_4$ ratio providing a reliable indication of the amount of (η^5-C_5Me_5) ring involvement in the σ bond metathesis reaction. The dependence of the rate of reaction of $Cp*_2ScCH_3$ (2) with arenes, monosubstituted with electron-donating or electron-withdrawing substituents, has been investigated (eq 36). Good first-order kinetics (Figure 5) were observed

$$(Cp*-d_{15})_2ScCH_3 + \text{[arene]}-X \xrightarrow{k_2} (Cp*-d_{15})_2Sc-\text{[arene]}-X + CH_4 \quad (36)$$

2-d_{30}

$$X = N(CH_3)_2, CH_3, H, CF_3$$
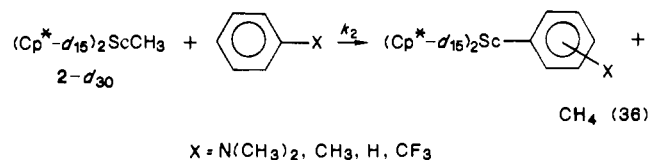
in all cases (cyclohexane-d_{12}, 80 °C, $[(Cp*-d_{15})_2ScCH_3]$ = 0.12 M, [arene] = 1.3 M), with CH_3D amounting to less than 5% in each case. Although several of the arenes possess other C–H bonds (e.g., $C_6H_5N(CH_3)_2$, $C_6H_5CH_3$) or other potentially reactive σ bonds (e.g., $C_6H_5CF_3$), clean conversion to CH_4 and the aryl derivative of permethylscandocene are observed in all cases. The activation parameters for the reaction of 2-d_{30} with C_6H_6, determined over the temperature range 42–67 °C, are $\Delta H^\ddagger$ = 18.9 (2) kcal·mol^{-1} and $\Delta S^\ddagger$ = –23 (2) eu. The rates at 80 °C are listed in Table V. Indeed, the rate of reaction of $Cp*_2ScCH_3$ with $C_6H_5CF_3$ is the lowest in the series; however, it differs only by

(46) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

Table VI. Isomer Ratios for the Product Mixtures Obtained by Reaction of $Cp*_2ScCH_3$ (2), $Cp*_2ScCH_2C_6H_5$ (5), $Cp*_2Sc(o-C_6H_4CH_3)$ (o-4), and $Cp*_2Sc(p-C_6H_4CH_3)$ (p-4) with Toluene

entry no.	reactant (condtns)[a] (°C, h)	product ratios[b] (relative tolyl %)			
		ortho	meta	para	benzyl
1	2 (80, 2)[c]	6 (7)	57 (66)	23 (27)	14
2	2 (80, 7.5)[d]	9 (11)	52 (67)	23 (27)	16
3	5 (80, 7.5)	3 (5)	3 (5)	14 (23)	39
4	o-4 (80, 7.5)	>95			
5	p-4 (80, 7.5)			>95	
6	2 (115, 12)	13	61	26	
7	o-4 (115, 36)	15	60	25	

[a] All reactions were carried out in sealed NMR tubes in toluene solvent; [Cp*$_2$ScR] = ca. 0.10 M. [b] Relative percentages were determined by cutting and weighing the tolyl-CH_3 and benzylic-CH_2 peaks from ^1H NMR spectra. The ratios are accurate to ca. ±3%. Numbers in parentheses represent the relative percentage of tolyl isomer, when detectable concentrations of 5 are present. [c] Reactions ca. 40% complete. [d] Reaction ca. 75% complete.

a factor of two from the other arenes, which are indistinguishable from each other.

The positional preferences (ortho, meta, para as well as benzylic) for σ bond metathesis between the C–H bonds of toluene and $Cp*_2Sc-CH_3$ (2) have also been examined. High field ^1H NMR spectroscopy (500 MHz) allows ready differentiation of $Cp*_2Sc(o-C_6H_4CH_3)$ (o-4), $Cp*_2Sc(m-C_6H_4CH_3)$ (m-4), $Cp*_2Sc(p-C_6H_4CH_3)$ (p-4) and $Cp*_2ScCH_2C_6H_5$ (5). Thermodynamic and kinetic ratios of the tolyl and benzyl derivatives of permethylscandocene derived from reaction of 2 with neat toluene (eq 37) are given in Table VI. The first three entries represent
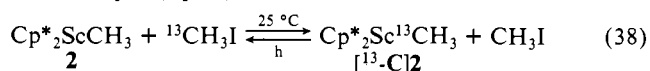
$$Cp*_2ScCH_3 + C_6H_5CH_3 \xrightarrow{80-115\,°C} Cp*_2Sc-\text{[arene]}-CH_3 +$$

2

$$(o-, m-, p-4)$$

$$Cp*_2ScCH_2C_6H_5 \quad (37)$$

5
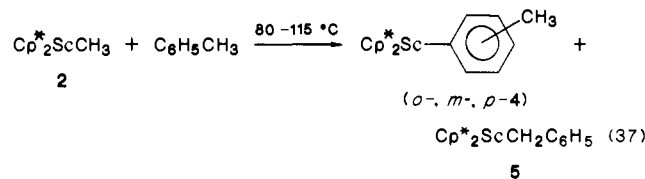
the kinetic ratios for the reactions of 2 and 5 with toluene, since authentic samples of o-4 and p-4 do *not* isomerize on the time scale of these experiments (80 °C, <8 h, entry 4). The kinetic and thermodynamic ratios of the tolyl isomers appear to be the same (±3%), since prolonged heating of $Cp*_2Sc(o-C_6H_4CH_3)$ eventually gives an unchanging ratio of tolyl isomers (entry 7), which is the same as the kinetic ratio, within experimental error. Significantly, $Cp*_2ScCH_2C_6H_5$ (5) is a kinetic product of the reaction of 2 with $C_6H_5CH_3$ (eq 37); however, as shown by entry 3, 5 eventually reacts further to afford the thermodynamically more stable mixture of tolyl isomers. Furthermore, the kinetic ratio of meta-tolyl:para-tolyl products is nearly statistical (i.e., the rates of σ bond metathesis for meta and para positions are roughly equal), whereas the ortho-tolyl product is formed more slowly and is thermodynamically less stable, presumably for steric reactions.

The results of these experiments are clearly inconsistent with σ bond metathesis mechanisms involving attack of scandium at the p π orbitals of olefins or arenes (Schemes I and II). The following observations are particularly definitive in this regard: (i) hydrogen incorporation into toluene-d_8 and H_2 and $Cp*_2Sc-H$ (eq 14) proceeds at the same rate for para and meta positions (ortho being lower); (ii) there are no appreciable resonance effects on the second-order rate constants for reaction of $Cp*_2ScCH_3$ with the trans vinylic C–H bonds of p-$XC_6H_4CH=CH_2$ (X = OCH_3, CF_3) (Table IV) indicative of a relatively nonpolar transition state for formation of the trans styrenyl complex, inconsistent with the zwitterionic one proposed in Scheme I; (iii) the rate of reaction of $Cp*_2ScCH_3$ with substituted arenes is insensitive to the (π) donating or withdrawing character of the substituent (Table V), in contrast to very large rate differences commonly observed for electrophilic aromatic substitution; $C_6H_5NMe_2$ and $C_6H_5CF_3$

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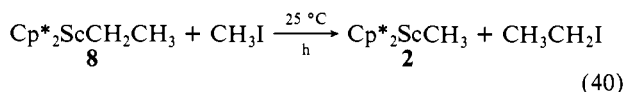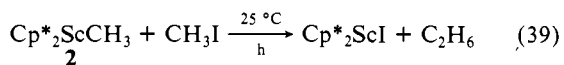
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differ by as much as 10^8–10^{10},[47] rarely less than 10^3–10^6;[48] and perhaps most convincing (iv) the (ortho-) para preference characteristic of electrophilic aromatic substitution reactions of toluene is *not* observed for a σ bond metathesis between $C_6H_5CH_3$ and $Cp*_2ScCH_3$ (**2**) (Table VI). Large rate differences among various substituted benzenes are usually characteristic of electrophilic aromatic substitution; however, the absence of such effects may not be diagnostic, particularly for extremely reactive electrophiles.[49] A more definitive test for electrophilic attack is the positional selectivity of the substitution. For example, nitration of toluene proceeds with >95% ortho–para selectivity; the electrophile, [NO_2^+] attacks <5% at the two meta positions. All electrophiles, even very active ones, show a high ortho–para:meta preference.[50] Moreover, electrophilic transition-metal complexes show the same strong preference; e.g., [$Cp*Re(NO)(CO)$]$^+$ and [$PtCl_5$]$^-$ attack toluene electrophilically with $2k_{para}/k_{meta}$ = 32 and 18, respectively.[51] Competitive attack at the benzylic C–H bonds of toluene is never observed.

None of these characteristics of electrophilic aromatic substitution are exhibited in the reaction of $Cp*_2ScCH_3$ with toluene. Indeed, significant amounts of the benzyl tautomer **5** are observed early in the reaction, and significantly, $2k_{para}/k_{meta} \approx 1.0$. Rate-determining homolysis of the Sc–CH_3 bond to produce free [$Cp*_2Sc^•$] and [$CH_3^•$] radicals appears inconsistent with the general reactivity patterns for $Cp*_2ScCH_3$ (**2**) with substrates: (i) cleavage of the *strongest* C–H bonds of substrates (e.g., H—CH=CHCH_3, H—C≡CCH_3, in addition to H–$C_6H_4CH_3$, etc.), (ii) pyrolysis of **2** in cyclohexane-d_{12} affords only CH_4(<3% CH_3D), and (iii) very large negative entropies of activation for the σ bond metathesis between $Cp*_2Sc$–CH_3 and H—CH=CHPh (ca. -35 eu), indicative of an associative rate-limiting step. An estimate of the kinetic deuterium isotope effect can be made from the rate differences for $(Cp*$-$d_{15})_2ScCH_3$ with C_6H_6 and C_6D_6 at 80 °C: 1.29 (5) × 10^{-5} s^{-1}·M^{-1} and 4.7 (1) 10^{-6} s^{-1}·M^{-1}, respectively (k_H/k_D = 2.8 (2)), suggestive of moderate arene C–H bond weakening in the transition state. A mechanistic model which accommodates these experimental results is presented in the Conclusions section below.

Reaction of Alkyl Derivatives of Permethylscandocene with Alkyl Halides. σ bond metathesis is also observed for $Cp*_2Sc$–CH_3 (**2**) and $^{13}CH_3$–I (eq 38), reminiscent of the reaction of **2** with

$$Cp*_2ScCH_3 + {}^{13}CH_3I \underset{h}{\overset{25\ °C}{\rightleftharpoons}} Cp*_2Sc^{13}CH_3 + CH_3I \qquad (38)$$
$$\textbf{2} \qquad\qquad\qquad [^{13}\text{-}C]\textbf{2}$$

$^{13}CH_3$–H (eq 26). An additional, irreversible reaction proceeds at a comparable rate: coupling of the methyl groups with formation of $Cp*_2ScI$ and ethane (eq 39). The latter reaction is undoubtedly thermodynamically preferred, in view of the strong Sc–I bond (vis-a-vis CH_3I bond) generated. Alkyl exchange also precedes coupling in the reaction of $Cp*_2ScCH_2CH_3$ (**8**) with methyl iodide (eq 40). Eventual formation of ethane in the

$$Cp*_2ScCH_3 + CH_3I \xrightarrow[h]{25\ °C} Cp*_2ScI + C_2H_6 \qquad (39)$$
$$\textbf{2}$$

$$Cp*_2ScCH_2CH_3 + CH_3I \xrightarrow[h]{25\ °C} Cp*_2ScCH_3 + CH_3CH_2I \qquad (40)$$
$$\textbf{8} \qquad\qquad\qquad\qquad\qquad \textbf{2}$$

presence of excess methyl iodide suggests that reaction 39 is much preferred over coupling reactions between ethyl iodide and either **2** or **8**, presumably for steric reasons. Steric control may also be

invoked to explain the reactivity of benzyl bromide and benzyl chloride with **2** (eq 41). Alkyl exchange to afford sterically more crowded $Cp*_2ScCH_2C_6H_5$ (**5**) and methyl halide does not proceed to a detectable level prior to coupling to ethyl benzene and permethylscandocene halide.

$$Cp*_2ScCH_3 + C_6H_5CH_2X \xrightarrow{25\ °C} Cp*_2ScX + C_6H_5CH_2CH_3$$
$$\textbf{2} \qquad\qquad X = Cl,\ Br$$
$$(41)$$
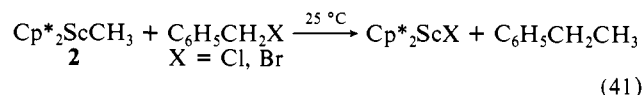
Conclusions

The hydride, alkyl, and aryl derivatives of permethylscandocene reported in the preceding section are extremely reactive toward a variety of σ bonds. The general reaction (eq 42) illustrates the

$$Cp*_2Sc\text{-}R + A\text{-}B \rightleftharpoons Cp*_2Sc\text{-}A + R\text{-}B \qquad (42)$$
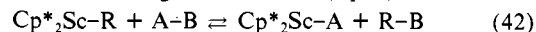
(R = H, alkyl, aryl; A–B =
H–H, sp C–H, sp^2 C–H, sp^3 C–H, C–X, X–C; X = halide)

broad scope of these σ bond metathesis processes, several of which have been utilized as convenient syntheses for some of the derivatives reported herein. The mechanisms of these reactions are fundamental to an understanding of the reaction chemistry of other oxidatively inert, electron-deficient compounds, particularly d^0 and many d$^0f^n$ systems.

Our evidence relevant to the mechanisms of σ bond metathesis with the permethylscandocene system points to a concerted, rather than stepwise, process. An appropriate model for the transition states of such σ bond metathesis reactions must accommodate the observed order of reactivity of R–H bonds with $Cp*_2Sc$–R′ bonds (R = R′ = H ≫ R = H, R′ = alkyl ≫ R–H = sp C–H, R′ = alkyl > R–H = sp^2 C–H, R′ = alkyl > R–H = sp^3 C–H, R′ = alkyl). These rate differences are striking, e.g., $Cp*_2Sc$–H + H–H, k_2 > 10^3 s^{-1}·M^{-1} (-95 °C); $Cp*_2Sc$–CH_3 + H–H, $k_2 \approx 4 × 10^{-1}$ s^{-1}·M^{-1} (-78 °C); $Cp*_2Sc$–CH_3 + H–C_6H_5, $k_2 \approx 3 × 10^{-5}$ s^{-1}·M^{-1} (80 °C); $Cp*_2Sc$–CH_3 + H–CH_3, $k_2 \approx 1 × 10^{-5}$ s^{-1}·M^{-1} (80 °C). Clearly, the rate decreases systematically with decrease in the s character of the reacting σ bonds. The simplest possible picture, namely a four-center transition state, is indeed consistent with this feature.

$$(43)$$
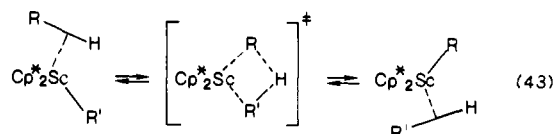
The stability of the transition state should depend critically upon the s character of the valence orbitals of the atoms comprising the four centers: nondirectional orbitals provide better overlap, hence more bonding and more stability to the transition state.

Steigerwald and Goddard[52] have carried out calculations on a model system, Cl_2Sc–H + H–H. Two of their findings are of particular interest in the present discussion: (i) The nodal properties of the scandium d orbitals are ideally suited to provide good overlap in the transition state with all three hydrogen atoms (4 centers, 4 electrons). Since the Cl atoms (and by extension, the Cp* ligands for permethylscandocene derivatives) bond principally via the Sc 4s valence orbitals, the Sc–H bonding for Cl_2ScH is largely Sc(3d)–H(1s) in character. Hence, the σ bond metathesis, a formal 2s + 2s process, is orbitally allowed and energetically quite favorable due to the excellent bonding characteristics of the transition state. (ii) The optimal geometry for the transition state was found to be distinctly "kite-shaped" rather than square. As a consequence, the H atom occupying the central (β) position relative to scandium bonds to both lateral hydrogen atoms but not to scandium.[53] Similar arguments have been
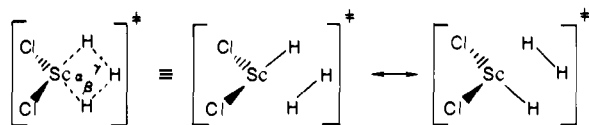
(47) Johnson, C. D. *The Hammett Equation*; Cambridge University: Cambridge, England, 1973.

(48) (a) Aoyama, T.; Yoshida, K.; Sakurai, K.; Hogoshi, H. *J. Chem. Soc., Chem. Commun.* **1983**, 478. (b) Shulpin, G. B.; Kitaigorodskii, A. N. *Zh. Fiz. Khim.* **1981**, *55*, 266.

(49) Olah, G. A.; Kuhn, S. J.; Flood, S. H. *J. Am. Chem. Soc.* **1961**, *83*, 4571.

(50) Olah, G. A. *Acc. Chem. Res.* **1971**, *4*, 240 and references cited therein.

(51) (a) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *2*, 135. (b) Shul'pin, G. B.; Nizova, G. V.; Nikitaev, A. T. *J. Organomet. Chem.* **1984**, *276*, 115.
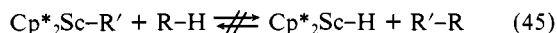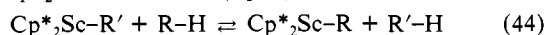
(52) Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308.

(53) The d(Sc–H) distances are, in fact, identical (see ref 52); however, frontier orbital considerations reveal that no formal bond between the Sc and the β-H exists: the four electrons (one each from the three hydrogens and one from Sc) occupy the orbitals of 1a$_1$ and b$_2$ symmetry; the remaining orbital, of 2a$_1$ symmetry (that which is bonding with respect to Sc and the β-H) is thus empty.

σ Bond Metathesis for Hydrocarbons

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α = 62°
β = 75°
γ = 149°

developed and further elaborated by Rappe and Upton.[54] Moreover, these authors point out that an electron-deficient metal center with one or more vacant orbitals would provide a low-energy means of approach for the H–H or C–H bond to the Sc–R bond, a distinct advantage in accessing the Steigerwald–Goddard transition state.
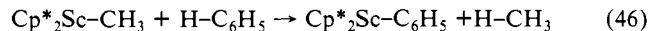
The picture which emerges for the mechanisms of these concerted, σ bond metathesis reactions involving electron-deficient metallocene derivatives is thus (i) approach of the H–H or C–H bond to the vacant $1a_1$ orbital of $Cp*_2Sc-R$,[46] (ii) formation of the transition state described above (eq 43) with H occupying the central (β) position in all cases, and (iii) departure of the new H–H or C–H σ bond from the opposite side of the $1a_1$ orbital.

The preference for H to occupy the central (β) position in the transition state is easily reconciled by the model presented above. The bond angle to the lateral atoms is largest for this position in the transition state (the top of the "kite"), and, accordingly, the preference for s (nondirectional) orbital character is maximum. The resultant preference for [R] and [R'] exchange between [$Cp*_2Sc$] and [H] (eq 44) as opposed to coupling of [R] and [R'] to afford $Cp*_2Sc-H$ and R–R' (eq 45) can thus be attributed to

$$Cp*_2Sc-R' + R-H \rightleftarrows Cp*_2Sc-R + R'-H \qquad (44)$$

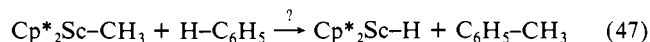$$Cp*_2Sc-R' + R-H \not\rightleftarrows Cp*_2Sc-H + R'-R \qquad (45)$$

$$(R',R = alkyl, aryl)$$

the relative energies of the transition states, i.e., a strong kinetic preference for the former. The equilibration of $Cp*_2Sc-H$, benzene, $Cp*_2Sc-C_6H_5$, and H–H (eq 18) allows an estimate of the thermodynamics accompanying reactions 44 and 45 for R' = alkyl and R = C_6H_5. Since the $Cp*_2Sc-H$ bond strength is 1.5 (4) kcal·mol^{-1} stronger than the $Cp*_2Sc-C_6H_5$ bond strength (vide supra), the thermodynamics of the two processes can be approximated. For the reaction of $Cp*_2Sc-CH_3$ with benzene, the two possible outcomes (eq 46 and 47) involve breaking the

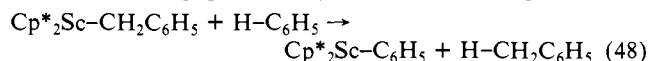$$Cp*_2Sc-CH_3 + H-C_6H_5 \rightarrow Cp*_2Sc-C_6H_5 + H-CH_3 \qquad (46)$$

$$BDE = x \qquad 105 \text{ kcal·mol}^{-1}$$

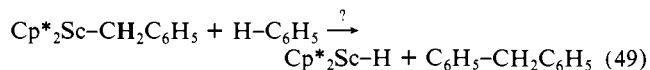$$Cp*_2Sc-CH_3 + H-C_6H_5 \overset{?}{\rightarrow} Cp*_2Sc-H + C_6H_5-CH_3 \qquad (47)$$

$$BDE = x + 1.5 \qquad 101 \text{ kcal·mol}^{-1}$$

same two σ bonds and making two new σ bonds whose relative BDEs are known. Thus, in this case the observed products are also the (slightly) thermodynamically more favored ones, so that it could be argued that thermodynamics govern the selectivity (although by only 2.5 (5) kcal·mol^{-1}). A similar treatment for the reaction of $Cp*_2Sc-CH_2C_6H_5$ with benzene (eq 48 and 49)

$$Cp*_2Sc-CH_2C_6H_5 + H-C_6H_5 \rightarrow$$
$$Cp*_2Sc-C_6H_5 + H-CH_2C_6H_5 \qquad (48)$$

$$BDE = x \qquad 88 \text{ kcal·mol}^{-1}$$

$$Cp*_2Sc-CH_2C_6H_5 + H-C_6H_5 \overset{?}{\rightarrow}$$
$$Cp*_2Sc-H + C_6H_5-CH_2C_6H_5 \qquad (49)$$

$$BDE = x + 1.5 \qquad 87 \text{ kcal·mol}^{-1}$$

leads to the opposite thermodynamic prediction, however, since the $C_6H_5CH_2-H$ and $C_6H_5CH_2-C_6H_5$ BDEs are roughly equal.[55]

Treatment of $Cp*_2ScCH_2C_6H_5$ with benzene at 80 °C yields $Cp*_2ScC_6H_5$ (3) and toluene (no diphenylmethane and $Cp*_2ScH$ (6)), despite the fact that the latter (eq 49) is slightly favored by 0.5 (5) kcal·mol^{-1}. Thus, kinetic control (i.e., a transition state energy difference) does indeed appear to be governing the selectivities of these σ bond metathesis reactions.[56] Despite the apparent steric preference for the transition states for reactions 47 and 49, the much poorer overlap provided by the sp^3 C orbital of R (vis-a-vis the s orbital of H) in the crucial center (β) position results in an overriding, unfavorable electronic effect.
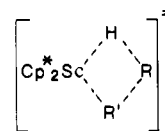
The mechanism(s) for reaction of alkyl halides with alkyl derivatives of permethylscandocene are not yet understood. Radical pathways are likely alternatives to the concerted, four-center process outlined above, considering the prevalence of radical chain reactions between transition-metal complexes and alkyl halides.[57] If the same concerted, four-center mechanism is, in fact, applicable, the two possible orientations of the C–X bond would appear to lead to comparable transition-state energies, since the alkyl exchange and alkyl–alkyl coupling reactions occur at approximately the same rates. The lone electron pairs on the halogen

A$^+$ B$^+$
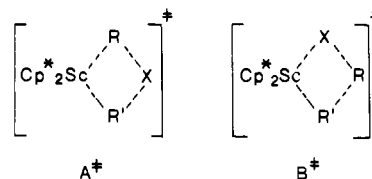
undoubtedly contribute to stability of both of these transition states, with the C–X moiety providing two orbitals and four electrons. Transition state A$^+$, with X occupying the central bridging position, thus bears close similarity to commonly encountered halogen-bridged structures. Transition-state B$^+$, although suffering from placement of the poorly bridging sp^3-hybridized carbon in the central position, gains considerably in stability from the Sc–X interaction. The latter four-center, six-electron arrangement would thus compare with the transition states for activation of the C–H bonds α to an oxygen or nitrogen donor atom (e.g., the α C–H bonds of THF and the ortho C–H bonds of pyridine).
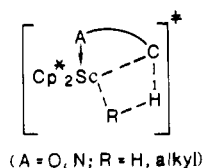
(A = O, N; R = H, alkyl)

The higher reactivity of sp^2- and sp-hybridized C–H bonds is attributed to increased bonding (i.e., lower transition-state energy) in the transition state for these reactions, summarized in eq 43. Implicit in this explanation is that the π systems of these substrates do not interact with the frontier orbitals of $Cp*_2Sc-R$ along the reaction coordinate for σ bond metathesis. The two bulky pentamethylcyclopentadienyl ligands likely block approach of the π orbitals for substituted olefins. Indeed, when the olefin is sufficiently small to allow interaction of its π system with $Cp*_2Sc-R$, insertion, rather than σ bond metathesis appears to occur, as in the polymerization of ethylene or the insertion of propene (eq 29).

(54) Upton, T. H.; Rappe, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206.

(55) The bond dissociation energy for $C_6H_5-CH_2C_6H_5$ was calculated from the heats of formation of [C_6H_5·] and [·$CH_2C_6H_5$] (ref 29) and group equivalent heat of formation for $C_6H_5CH_2C_6H_5$: Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley and Sons: New York, 1976.

(56) Although alkyl–alkyl coupling of alkanes to higher alkanes and dihydrogen is slightly endothermic, it is apparently very much disfavored kinetically: no homogeneous system which effects this transformation has been reported to our knowledge. An equally conspicuous challenge is the (exothermic) reverse: cleavage of carbon–carbon single bonds with dihydrogen to afford lower molecular weight hydrocarbons.

(57) (a) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635. (b) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.

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The attack of Cp*$_2$Sc–R at the C–H bonds of arenes perpendicular to the π system has been convincingly demonstrated experimentally. Once again, sterics may be invoked to explain preferential attack of the Lewis acidic scandium center at the (lower energy and less extensive) C–H α orbital, since approach of the arene along this reaction coordinate places the arene ring in a much less crowded, nearly parallel orientation relative to the two (η^5-C$_5$Me$_5$) rings.

Steric interactions of substrate substituents with the bulky (η^5-C$_5$Me$_5$) ligands may also be invoked to explain the striking preference for primary C–H bonds in H/D exchange reactions catalyzed by Cp*$_2$ScH (vide supra). With primary C–H bonds the lone substituent may be placed in the equatorial plane of the bent sandwich [Cp*$_2$Sc], whereas with secondary or tertiary C–H bonds, one or two unfavorable steric interactions between (η^5-C$_5$Me$_5$) ligands and alkyl substituent(s) necessarily accompany the transition states of these σ bond metathesis reactions.

(R, R', R'' = H, alkyl)
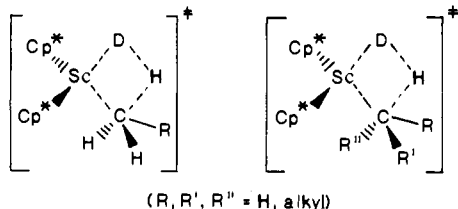
A significant and interesting question concerns the polarity of the transition states for these σ bond metathesis reactions. In view of the electropositive character of the metals which effect these transformations, a highly polar transition state has normally been invoked.[58] On the other hand, the facility of these reactions is
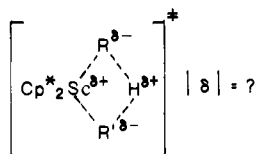
nonpolar media (e.g., aliphatic and aromatic hydrocarbons) and the Mulliken populations obtained by Goddard and Steigerwald for Sc and the H atoms in the transition state[52] suggest a relatively nonpolar character. The insensitivity of the second-order rate constants for the reaction of Cp*$_2$ScCH$_3$ with substituted arenes (eq 36) to the electron-withdrawing or electron-donating nature of the substituents might be taken to support the latter view; however, the effect of these substituents on the polarity of the ortho, meta, and para C–H bonds is only minimal. Indeed, an alternative explanation for the order of reactivity (sp-C–H > sp^2-C–H > sp^3-C–H) could invoke a highly polar transition state, since hydrocarbon acidity[59] does indeed follow precisely this same order.[60] Since both explanations invoke higher reactivity with higher s character, a distinction between the two and, hence, a decision concerning the polarity of the transition states for σ bond metathesis must await further experiments. At present, we favor a relatively nonpolar concerted process with the electrophilic scandium attacking the reacting σ bond in a relatively symmetric fashion. We admit, however, that our experimental results do not require this interpretation.

Experimental Section

General Considerations. All manipulations were performed by using glovebox and high-vacuum line techniques. Gas evolution measurements were performed by using standard Toepler techniques, and the gases were identified by mass spectrometry or NMR. Xylene was distilled from CaH$_2$ under dinitrogen. THF was purified by vacuum transfer from sodium benzophenone. All other solvents were dried over LiAlH$_4$ and stored over titanocene.[61] NMR solvents: benzene-d_6, cyclohexane-d_{12}, toluene-d_8 (Stohler Inc.), and methylcyclohexane-d_{14} were dried over activated 4-Å molecular sieves. Argon and hydrogen were purified by passage over MnO on vermiculite[62] and activated 4-Å molecular sieves.

NMR spectra were recorded on Varian EM-390 (^{1}H, 90 MHz), JEOL FX 90Q (^{1}H, 89.56 MHz; ^{13}C, 22.50 MHz; ^{19}F, 84.26 MHz), JEOL GX400Q (^{1}H, 399.78 MHz; ^{13}C, 100.38 MHz) and Bruker WM500 (^{1}H, 500.13 MHz) spectrometers. Infrared spectra were measured as Nujol mulls on KBr plates and recorded on a Beckman IR-4240 spectrometer. Mass spectra were recorded by using Kratos MS25 and Dupont 4592 mass spectrometers. Analyses were performed by Bernhardt Analytical Laboratories and by Larry Henling of the Caltech Analytical Laboratory. Molecular weights were determined by using the vapor phase osmometry techniques developed by Signer and described by Clark.[63]

Procedures. Cp*$_2$ScCl (1). An orange slurry of ScCl$_3$(THF)$_3$ (10.0 g, 27 mmol) and LiCp* (9.0 g, 63 mmol) in 250 mL of xylene was refluxed over 3 days. Periodically (ca. once per day) approximately 30 mL of solvent was removed in vacuo. After 3 days the volatiles were removed in vacuo to give an orange solid. Sublimation over 4 days at 120 °C (10^{-4} torr) afforded 8.0 g of bright yellow crystalline 1 (80%): mol wt in benzene, 365 (calcd 350); IR (Nujol) 2715, 1030, 800, 430, 360 cm^{-1}. Anal. Calcd for C$_{20}$H$_{30}$ClSc: C, 68.47; H, 8.77; Cl, 10.10. Found: C, 68.05; H, 8.77; Cl, 10.12.

Cp*$_2$ScCH$_3$ (2). Compound 1 (5.0 g, 14 mmol) was dissolved in 75 mL of toluene. An 8.01-mL portion (14.2 mmol) of LiCH$_3$ (1.78 M in diethyl ether) was added slowly by syringe to the solution. The reaction mixture was stirred for 30 min at room temperature. The volatiles were removed under reduced pressure. The residue was washed with 30 mL of petroleum ether, and the resulting solution was filtered. The filtrate was concentrated to 10 mL and cooled to –78 °C, precipitating pale yellow 2 (2.6 g, 55%), which was isolated by cold filtration. Solid samples of 2 were stored at 10 °C to prevent decomposition: IR (Nujol) 2730, 1490, 1114, 1028, 800, 605, 580, 420 cm^{-1}. Anal. Calcd for C$_{21}$H$_{33}$Sc: C, 76.33; H, 10.07. Found: C, 76.02; H, 9.98.

Cp*$_2$Sc(o-C$_6$H$_4$CH$_3$) (o-4). Compound 1 (0.420 g, 1.2 mmol) and *ortho*-tolyllithium (0.18 g, 1.8 mmol) were dissolved in 15 mL of toluene. The mixture was stirred for 12 h. The volatiles were removed under reduced pressure. The resulting solid was washed with 10 mL of petroleum ether and filtered. The filtrate was concentrated to ca. 30 mL and cooled to –78 °C to afford 0.285 g (59%) of off-white o-4. The same procedure was followed for the preparation of Cp*$_2$Sc(m-C$_6$H$_4$CH$_3$) and Cp*$_2$Sc(p-C$_6$H$_4$CH$_3$): IR (Nujol for o-4) 2715, 1578, 1300, 1252, 1222, 1208, 1160, 1140, 1079, 1053, 1030, 1016, 793, 774, 720, 549, 480, 417 cm^{-1}. Anal. Calcd for C$_{27}$H$_{37}$Sc: C, 79.77; H, 9.17. Found: C, 79.79; H, 9.08.

Cp*$_2$ScCH$_2$C$_6$H$_5$ (5). Compound 1 (2.0 g, 5.7 mmol) was dissolved in 20 mL of toluene. A solution of 0.820 g (6.3 mmol) of KCH$_2$C$_6$H$_5$ dissolved in 20 mL of cold THF was added slowly by cannulation. When addition was complete, volatiles were removed under reduced pressure. The resulting solid was washed with 20 mL of petroleum ether, and the resulting solution was filtered. The filtrate was concentrated to 5 mL and cooled to –78 °C, precipitating bright yellow 5 (1.34 g, 58%). Solid samples of 5 were stored at –10 °C to prevent decomposition: mol wt in benzene, 460 (calcd 407); IR (Nujol) 3050, 2710, 1595, 1490, 1200, 1030, 935, 790, 740, 705, 660 cm^{-1}. Anal. Calcd for C$_{27}$H$_{37}$Sc: C, 79.76; H, 9.17. Found: C, 79.67; H, 9.12.

Cp*$_2$Sc(THF)H (7). Compound 2 (1.0 g, 3.0 mmol) was dissolved in 20 mL of THF. One atmosphere of H$_2$ was introduced into the reaction vessel, and the solution was stirred for 5 h. The THF was removed under reduced pressure and replaced with 7 mL of petroleum ether. Cooling the solution to –78 °C precipitated pale yellow 7 (0.82 g, 70%): mol wt in cyclohexane, 408 (calcd 388); IR (Nujol) 2710, 1390, 1155, 1140, 1020, 855, 730, 655, 510, 365 cm^{-1}. Anal. Calcd for C$_{24}$H$_{39}$OSc: C, 74.19; H, 10.12. Found: C, 74.08; H, 10.14.

Cp*$_2$ScCH$_2$CH$_3$ (8). Compound 2 (0.280 g, 0.85 mmol) was dissolved in 10 mL of toluene in a thick-walled glass bomb. The solution was placed under 4 atm of H$_2$ and stirred for 10 minutes at 25 °C and then cooled to –78 °C. The hydrogen was removed, and 1 equiv of ethylene (375 torr in 42.2 mL) was condensed into the reaction mixture at –196

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°C. After slowly warming to 25 °C, the solution was transferred to a flask attached to a swivel frit assembly in an N_2-filled glovebox. The toluene was removed under reduced pressure and replaced with 10 mL of petroleum ether. The solution was filtered, and the filtrate was concentrated to ca. 3 mL. The solution was cooled to −78 °C, precipitating yellow **8** (0.160 g, 55%): IR (Nujol) 2714, 2593, 2503, 2440, 1493, 1172, 1066, 1025, 973, 844, 807, 722, 660, 618, 568, 480 cm⁻¹. Anal. Calcd for $C_{22}H_{35}Sc$: C, 76.71; H, 10.24. Found: C, 76.66; H, 10.22.

Cp*₂ScCH₂CH₂CH₃ (9). The procedure used for the preparation of **8** was followed by using 500 mg of compound **2** (1.5 mmol) and 1.5 mmol of propene. Because **9** is too soluble in nonreactive solvents to be precipitated, it was isolated by removing the solvent under reduced pressure (90–95% pure (¹H NMR), 440 mg, 80%): IR (Nujol) 2735, 1306, 1160, 1060, 1028, 862, 805, 720, 723, 666, 618, 580, 505, 412 cm⁻¹.

Cp*₂Sc(η³-C₃H₅) (10). The procedure used for the preparation of **8** was followed by using allene in place of ethylene; 0.220 g of compound **1** afforded 0.160 g (67%) of **10**: IR (Nujol) 3090, 2725, 1554, 1258, 2155, 1085, 1028, 785, 755, 705, 635, 618, 595 cm⁻¹. Anal. Calcd for $C_{23}H_{35}Sc$: C, 77.49; H, 9.90. Found: C, 77.25; H, 10.00.

Cp*₂Sc(C,N-η²-C₅H₄N) (11). Compound **2** (1.0 g, 3.0 mmol) was dissolved in 25 mL of benzene, and 0.25 mL (3.1 mmol) of pyridine was added. The solution was heated to reflux for 30 min and cooled to room temperature, and the solvent was removed under reduced pressure. Recrystallization from diethyl ether afforded 0.71 g (60%) of **11**: IR (Nujol) 2720, 1573, 1535, 1414, 1252, 1216, 1150, 1020, 985, 757, 720, 405 cm⁻¹. Anal. Calcd for $C_{25}H_{34}NSc$: C, 76.31; H, 8.71; N, 3.56. Found: C, 76.53; H, 8.69; N, 3.38.

Reaction of Cp*₂Sc(C,N-η²-C₅H₄N) with Pyridine-d₅. An NMR tube containing 0.025 g of **11** (0.064 mmol) and 0.026 mL of pyridine-d_5 (0.32 mmol, 5 equiv) dissolved in 0.35 mL of benzene-d_6 was sealed with a torch. After 2 days at room temperature the pyridyl ligand had been converted to o-pyridine-d_1 (¹H NMR), while the Cp* resonance remained unchanged.

H/D Exchange between Cp*₂Sc-D and C₆H₆ (eq 13). Compound **5** (33 mg, 0.081 mmol) was dissolved in 0.3 mL of benzene-d_6 and placed under 2 atm of D_2. The solution was stirred for 10 min and then cooled to −78 °C. Benzene-d_6 was sublimed from the reaction under reduced pressure as the solid was allowed to warm. The resulting solid was dissolved in 0.4 mL of C_6H_6 and transferred to an NMR tube. After 5 min at room temperature the tube was cooled to −78 °C and charged with 0.098 mmol of CH_3I. The tube was sealed and warmed to room temperature. The ¹H NMR spectrum showed resonances assignable to Cp*₂ScI and CH_4; CH_3D was not observed. A small amount of Cp*₂ScC₆H₅ (5% relative to Cp*₂ScI) was observed.

H/D Exchange for Cyclopentane. A 5-mm NMR tube was charged with 8 mg of **1** (0.024 mmol), 50 μL of cyclopentane (0.53 mmol), 0.35 mL of benzene-d_6, and 700 torr of H_2 (3.6 atm at 25 °C). The entire tube (open to the 700 torr H_2 source) was cooled to −196 °C and sealed with a torch. The tube was heated at 120 °C for 26 days, and the reaction solution was examined by GC/MS. Comparison with the mass spectrum of a cyclopentane standard indicated 17% monodeuteriation, corresponding to a turn over rate of ca. 0.06 turnovers/day.

Equilibration of Cp*₂ScH or Cp*₂ScH(THF), C₆H₆, Cp*₂ScC₆H₅, and H₂ (eq 18 and 19). The sample used in equilibrium studies between Cp*₂ScH and Cp*₂ScC₆H₅ (eq 18) was prepared in an NMR tube fused to a Kontes Teflon stoppered valve, which was fitted with a standard taper joint for attaching to a vacuum line. The tube was charged with 18 mg of **2** (0.054 mmol) and 0.5 mL of C_6H_6. The entire NMR tube was cooled to −196 °C. H_2 (700 torr) was introduced into the tube, and 10 minutes was allowed for the gas to come to thermal equilibrium. The Kontes valve was closed, and the tube was warmed to 25 °C. The tube was removed from the vacuum line and shaken for 5 min to ensure formation of Cp*₂ScH. The tube was connected to the vacuum line and cooled to −196 °C, the hydrogen was removed in vacuo, and the tube was sealed with a torch.

To study the equilibration between Cp*₂Sc(THF)H and C₆H₆ (eq 19) a C₆H₆ solution of an isolated sample of Cp*₂Sc(THF)H was sealed in an NMR tube.

The experiments at 25 °C and higher temperatures were carried out in a constant temperature oil bath (±0.1 °C), which was heated with a Precision Scientific Co. thermostated water circulator. The samples were fully submerged in the bath and agitated to facilitate the equilibration of H_2 between the solution and gas phases. The experiments carried out at 6 °C were performed in a cold room at this temperature.

The equilibrium constant for eq 18 was evaluated as follows

$$K_{eq} = \frac{[Cp*_2ScC_6H_5][H_2]}{[Cp*_2ScH][C_6H_6]}$$

At a given temperature, the volume of the solution (measured from the depth of the solution in the tube) and the ratio of the two equilibrating

scandium species (¹H NMR) were determined. The concentration of benzene was calculated from its density.[33] The concentration of dihydrogen was calculated by using Henry's law and the standard concentration[31] of H_2 at the temperature of the experiment. The equilibrium concentration of dihydrogen, $[H_2]_{equil}$, was derived from two simultaneous equations

$$(mmol\ H_2)_{tot} = \frac{p(V_1)}{RT} + [H_2]_{equil}(V_2) \tag{50}$$

$$[H_2]_{equil} = \frac{p([H_2]_{std})}{1\ atm} \tag{51}$$

where p is the pressure of H_2 above the solution, V_1 is the volume of gas space above the solution, R is the gas constant, T is the temperature, V_2 is the volume of the solution, and $[H_2]_{std}$ is the concentration of H_2 in C_6H_6 at temperature T when the pressure of H_2 is 1 atm. The expression for $[H_2]_{equil}$ is thus

$$[H_2]_{equil} = \frac{(total\ mmol\ H_2)([H_2]_{std}RT)}{V_1 + V_2\ ([H_2]_{std}RT)} \tag{52}$$

where (total mmol H_2) = (mmol H_2)_init + (mmol Cp*₂ScC₆H₅). The (mmol H_2)_init was calculated from eq 51, assuming that only the amount of H_2 frozen in benzene, prior to sealing the NMR tube, remained after evacuation of the tube. The equilibrium constants for eq 19 were determined by using analogous equations.

[(η⁵-C₅Me₅)Sc(η⁵-C₅Me₄CH₂)]ₙ (12). Compound **2** (0.50 g, 1.5 mmol) was dissolved in 5 mL of cyclohexane, and the solution was heated at 80 °C for 4 days. Yellow crystals of **12** were filtered off and washed several times with petroleum ether, yielding 0.40 g (85%). Anal. Calcd for $C_{20}H_{29}Sc$: C, 76.40; H, 9.30. Found: C, 75.42; H, 9.04.

Preparation of (Cp*-d₁₅)₂ScCH₃. A 50-mL, thick-walled glass bomb with a fused Teflon needle valve was charged with 4 g of Cp*₂ScCH₃ (**2**) (12 mmol), 10 mL of benzene-d_6 (>99.5% D), and 2 atm of D_2. The bomb was heated at 80 °C for 1 day. The gas (H_2, HD, D_2, and CH_3D) was removed, and 1 atm of D_2 was admitted. After heating at 115 °C for 24 h, the gas mixture and benzene were removed in vacuo, and benzene-d_6 (20 mL) and D_2 (1 atm) were added. After heating an additional 24 h at 115 °C, the cycle was repeated one more time with fresh benzene-d_6 (35 mL) and D_2 (1 atm). The bomb was cooled to −78 °C, 12 mmol of CH_2Cl_2 were condensed in, 1 atm of H_2 was added, and the mixture was allowed to warm slowly to room temperature. After 5 min, volatiles were removed in vacuo. The residue was recrystallized at −78 °C from diethyl ether/petroleum ether to afford 2.73 g (62%) of yellow (Cp*-d_{15})₂ScCl (**1-d_{30}**). The amount of proton impurity was determined (¹H NMR integration vs. ferrocene) to be <0.2%. (Cp*-d_{15})₂ScCH₃ was prepared from **1-d_{30}** as described previously.

Kinetic Measurements of Intramolecular C–H and C–D Activation. Compound **2** (25 mg, 0.076 mmol), 3 μL of cyclooctane, and 0.40 mL of cyclohexane-d_{12} were loaded into an NMR tube, and the tube was sealed under 1 atm of N_2. The sample was heated at 80 °C. The kinetics of intramolecular C–H activation were followed by ¹H NMR, monitoring the decrease in integrated intensity of the Sc–CH₃ resonance relative to internal cyclooctane. The kinetics of intramolecular C–D activation were examined in the same manner substituting **2-d_{30}** in place of **2**.

Kinetic Measurements for the Reaction of Cp*₂ScCH₃ with ¹³CH₄ (eq 26). Compound **2** (10 mg, 0.03 mmol), cyclohexane-d_{12} (0.5 mL), and 0.6–5.0 mmmol of ¹³CH₄ were sealed in 5-mm medium-walled NMR tubes (Wilmad Inc., 524-p). At 70 °C approximately 20% of the CH_4 was in solution; accurate (±5%) concentrations were obtained with cyclooctane as an internal integration standard. Plots of −ln[Sc–CH₃] vs. time were linear over 2–5 half-lives (depending on the ratio of ¹²C:¹³C in the system) with excess ¹³CH₄. Only data from the first 20–30% of the reaction was considered. In roughly 20% of these experiments k_{obsd} was 3–4 times larger than expected. Repeating the experiment generally gave a value of k_{obsd} consistent with those observed at other concentrations of methane. We attribute this rate increase to a small amount of some (unidentified) catalyst promoting the reaction. The reaction chemistry exhibited by the tucked-in complex **12** (vide supra) suggests that it may be the catalyst. This apparent catalysis was most common in aged samples of **2**, for which some thermal decomposition could have given rise to a small amount of **12**.

trans-Cp*₂ScCH=CH(p-C₆H₄CH₃). Scandium styrenyl complexes made with para methoxy or para CF₃ styrene were not successfully isolated as crystalline compounds. Cp*₂ScCH=CH(p-C₆H₄CH₃) was isolable, and its synthesis is described here. Compound **2** (256 mg, 0.77 mmol) and p-methylstyrene (91 μL, 1.01 equiv) were dissolved in 4 mL of petroleum ether. The solution was heated to 63 °C for 12 h and then concentrated to 2 mL. Cooling the solution to −78 °C precipitated 99

mg (30%) of pale yellow product: IR (Nujol) 2710, 1503, 1193, 1138, 1102, 1055, 1020, 981, 835, 754, 656, 608, 585, 480, 365 cm⁻¹. Anal. Calcd for $C_{29}H_{39}Sc$: C, 80.52; H, 9.09. Found: C, 80.29; H, 9.20.

Kinetic Measurements of the Reactions of Cp*₂ScCH₃ with H₂C= CH(p-C₆H₄X) (X = CF₃; OCH₃). Samples were prepared in septum-capped NMR tubes containing 25 mg (0.076 mmol) of compound **2**, 0.4 mL of C_6D_6, and 0.16–0.30 mmol of the appropriate styrene compound. The kinetics of the reaction of **2** with H₂C=CH(p-C₆H₄OCH₃) were followed by ¹H NMR (90 MHz) by monitoring the disappearance of the Sc–CH₃ signal and the appearance of the methoxy resonance of Cp*₂ScCH=CHC₆H₄OCH₃ relative to internal FeCp₂ (sublimed twice). The kinetics of the reaction of Cp*₂ScCH₃ with H₂C=CH(p-C₆H₄CF₃) were followed by ¹⁹F NMR (84.26 MHz), monitoring the disappearance of the CF₃ resonance of H₂C=CH(p-C₆H₄CF₃) relative to internal $C_6H_5CF_3$. This reaction was followed by ¹H NMR as well to verify that only Cp*₂ScCH=CH(p-C₆H₄CF₃) was produced. The reactions of Cp*ScCH₃ with both of these styrenes obey second-order kinetics, giving linear second-order plots for over 3 half-lives.

Reaction of Cp*₂ScCH₃ with Isobutylene (eq 28). Compound **2** (275 mg, 0.83 mmol) was dissolved in 5 mL of petroleum ether in a thick-walled glass bomb. Approximately 1 mL of isobutylene was condensed into the bomb. The mixture was heated to 80 °C for 20 h. After the bomb was cooled to room temperature, the isobutylene was slowly removed in vacuo. The solution was concentrated to 2 mL and cooled to −78 °C, precipitating a white solid Cp*₂ScCHC(CH₃)₂ (eq 28) (230 mg, 75%): IR (Nujol) 2715, 2695, 1584, 1498, 1260, 114, 1080, 1060, 1022, 790, 615, 589, 500, 447, 420 cm⁻¹. Anal. Calcd for $C_{24}H_{37}Sc$: C, 77.80; H, 10.07. Found: C, 77.49; H, 10.01.

Reaction of Cp*₂ScCH₃ with Propene. A sealed NMR tube was prepared containing 20 mg of compound **2** (0.06 mmol), 0.4 mL of cyclohexane-d_{12}, and 0.64 mmol of propene. The reaction was monitored at room temperature by ¹H NMR (90 MHz). The isolation of a pure sample of trans-Cp*₂ScCH=CHCH₃ was attempted by using the same procedure as for Cp*₂ScCH=C(CH₃)₂ at 25 and 80 °C. In both cases only an impure oil (80–90%, ¹H NMR) was obtained [IR 2660, 1565, 1530, 1250, 1150, 1020, 985, 795, 680, 660, 435 cm⁻¹]. The NMR spectrum of trans-Cp*₂ScCH=CHCH₃ is very similar to those reported[44] for the analogous zirconium and hafnium complexes trans-Cp*₂M-(CH=CHCH₃)₂ (M = Zr, Hf).

Cp*₂ScC≡CCH₃ (16). Compound **2** (234 mg, 0.71 mmol) was dissolved in 10 mL of petroleum ether, and the solution was cooled to −78 °C. Propyne (0.78 mmol) was condensed into the solution from a gas bulb, and the reaction vessel was slowly warmed to room temperature. The reaction mixture was concentrated to 4 mL and cooled to −78 °C, precipitating white solid **16** (15 mg, 62%): IR (Nujol) 2720, 2090, 1165, 1060, 1022, 965, 800, 700, 655, 440, 370 cm⁻¹. Anal. Calcd for $C_{23}H_{33}Sc$: C, 77.93; H, 9.38. Found: C, 77.83; H, 9.42.

Dimerization of Propyne. A sealed NMR tube was prepared with 26 mg of compound **2** (0.079 mmol), 0.4 mL of benzene-d_6, and 0.55 mmol of propyne (7 equiv). Within 30 min at room temperature, all of the propyne had been consumed. 2-Methyl-1-penten-3-yne, **16**, and methane were the only compounds observed in the NMR spectrum. The 2-methyl-1-penten-3-yne was identified by comparison of its NMR to that of an authentic sample.

Kinetics of the Reactions of (Cp*-d_{15})₂ScCH₃ with C₆H₅R (R = N-(CH₃)₂, CH₃, H, CF₃). Sealed NMR tubes containing 15 mg of (Cp*-d_{15})₂ScCH₃ (0.041 mmol), 0.35 mL of cyclohexane-d_{12}, 0.52 mmol of the appropriate substituted benzene, and 2.5 µL of cyclooctane were heated at 80 ± 0.5 °C. The reaction was followed by ¹H NMR spectroscopy, monitoring the decrease in integrated intensity of the Sc–CH₃ resonance relative to cyclooctane. In all cases, the only new compounds observed were the aryl complexes, and the kinetics were pseudo first order for over 3 half-lives. CH₃D accounted for 5% or less of the total methanes produced.

Structure Determination for (η^5-C₅Me₅)₂Sc(C, N-η^2-C₅H₄N). Single crystals, grown from a toluene solution at −80 °C over 2 days, were mounted in glass capillaries under N₂. Oscillation and Weissenberg photographs indicated orthorhombic symmetry (a = 16.297 (4) Å, b = 9.684 (3) Å, c = 14.486 (6) Å, V = 2286.3 (12) Å³, Z = 4). The crystals decomposed rapidly upon X-ray exposure. After 8–10 h the reflection intensities began to decrease, and after 24 h, no diffraction was observed. Intensity data were collected on a locally modified Syntex P2₁ diffractometer with graphite monochromator and Mo Kα radiation at a fast scan speed (8.37°·min⁻¹ in 2θ), and an entire quadrant (+h,+k,±l) to 2θ = 30° was collected in 8.5 h with θ–2θ scans (Δ2θ = 2.8° plus dispersion); no observable deterioration was indicated. Systematic absences in the intensity data indicated space group Pna2₁ or Pnam; Pna2₁ was chosen. The intensities were reduced to F_o^2. Variances, $\sigma^2(I)$, were assigned the intensities on the basis of counting statistics plus an additional term, $(0.02I)^2$, to account for additional errors proportional to the

Table IX. Atom Coordinates (×10⁴) and U_{eq}'s (×10⁴) for Cp*₂Sc(pyr) (**11**)

atom	x	y	z	U_{eq}
Sc	2858 (1)	−181 (1)	0	374 (3)
C1	1756 (4)	−1039 (8)	603 (5)	471 (18)
C2	1895 (4)	158 (8)	1024 (5)	497 (21)
C3	1356 (6)	683 (9)	1678 (6)	698 (28)
C4	653 (5)	−31 (13)	1870 (6)	839 (33)
C5	510 (5)	−1300 (12)	1451 (8)	847 (35)
C6	1054 (6)	−1791 (9)	827 (6)	666 (25)
C11	3026 (5)	453 (8)	−1663 (5)	502 (21)
C12	3100 (4)	1674 (8)	−1164 (5)	478 (21)
C13	2340 (5)	1964 (7)	−749 (6)	461 (20)
C14	1787 (5)	906 (9)	−1004 (6)	462 (23)
C15	2217 (5)	−50 (8)	−1561 (5)	504 (21)
C21	3651 (6)	−107 (11)	−2360 (6)	813 (29)
C22	3825 (5)	2682 (9)	−1142 (7)	759 (25)
C23	2135 (5)	3222 (7)	−186 (7)	744 (25)
C24	882 (5)	869 (10)	−820 (7)	803 (30)
C25	1864 (6)	−1297 (9)	−2004 (7)	836 (28)
C31	4366 (4)	−703 (7)	83 (8)	482 (19)
C32	4158 (4)	48 (8)	905 (6)	539 (22)
C33	3634 (5)	−945 (9)	1402 (5)	479 (22)
C34	3509 (4)	−2118 (7)	863 (6)	490 (22)
C35	3951 (4)	−1973 (6)	43 (8)	502 (18)
C41	5042 (5)	−247 (10)	−588 (7)	842 (28)
C42	4513 (6)	1301 (9)	1233 (8)	925 (29)
C43	3354 (6)	−685 (12)	2386 (7)	888 (34)
C44	3056 (5)	−3401 (9)	1154 (8)	905 (29)
C45	4035 (6)	−3061 (9)	−677 (8)	949 (30)

intensity; the form factors for Sc were corrected for anomalous dispersion.[66]

The coordinates of the scandium atom were derived from the Patterson map; a series of Fourier maps was used to determine the coordinates of the remaining non-hydrogen atoms. Hydrogen atom positions were determined by assuming idealized geometry and by locating peaks in the difference map.

The pyridyl ligand is disordered and results in the complete superposition of two pyridyl groups of equal population. To model this, all atoms in the pyridyl group were given full populations, except for the two atoms bound to Sc, which were each modeled as 50% carbon and 50% nitrogen atom. Least-squares refinement of the coordinates of all non-hydrogen atoms with anisotropic Gaussian displacement parameters, U_{ij}'s, anisotropic secondary extinction parameter, and hydrogen atoms with fixed coordinates and isotropic U's (U = 0.09 Å²) resulted in S (goodness-of-fit) $\{\Sigma w[F_o^2 - (F_c/k)^2]^2/(n - p)\}^{1/2}$ = 1.74 (n = 1128 reflections, p = 244 parameters), R $(\Sigma||F_o| - |F_c||/\Sigma|F_o|$ for I > 0) = 0.045 (1092 reflections), and R' (R for I > 3σI) = 0.036 (944 reflections); final shift/error < 0.01. Crystal data are given in Table VII and VIII, and final atom coordinates are given in Tables IX and X, U_{ij}'s in Table XI, hydrogen atom coor-

(64) Duchamp, D. J. Presented at the National Meeting of the American Crystallographic Association, 1974; Paper no. B19, 29.

(65) Johnson, C. D. "ORTEP, a Fortran Thermal Ellipsoid Plot Program"; Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN 1965.

(66) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 72.

Table X. Atom Coordinates and U_{eq} for Cp*$_2$ScCH$_3$ (2)

atom	x^a	y	z	$U_{eq}{}^b$
Sc	2029 (2)	495 (1)	1131 (1)	53 (0.3)
C1	249 (8)	−913 (8)	579 (6)	72 (3)
C2	1362 (17)	−602 (10)	175 (4)	78 (3)
C3	2718 (14)	−1018 (11)	353 (6)	94 (4)
C4	2615 (17)	−1597 (9)	867 (7)	100 (4)
C5	1060 (19)	−1602 (9)	1061 (5)	90 (4)
C6	−1500 (11)	−856 (14)	576 (10)	313 (11)
C7	1113 (29)	100 (10)	−404 (5)	334 (10)
C8	4244 (19)	−919 (13)	−79 (8)	241 (7)
C9	4009 (22)	−2203 (13)	1168 (11)	315 (10)
C10	451 (38)	−2361 (14)	1537 (6)	367 (11)
C11	65 (11)	1859 (10)	1569 (5)	82 (3)
C12	1416 (13)	2489 (7)	1568 (4)	72 (3)
C13	2458 (10)	1959 (12)	1982 (5)	84 (4)
C14	1604 (17)	951 (10)	2239 (4)	93 (4)
C15	169 (15)	977 (9)	1965 (6)	92 (4)
C16	−1359 (12)	2274 (10)	1200 (6)	155 (4)
C17	1792 (14)	3624 (8)	1190 (5)	151 (4)
C18	4001 (14)	2394 (15)	2178 (6)	218 (6)
C19	2175 (26)	151 (12)	2729 (4)	284 (9)
C20	−1291 (15)	263 (11)	2165 (6)	183 (5)
C21	4259 (13)	1293 (9)	757 (5)	156 (4)

^{a} x, y, and z have been multiplied by 10^4. ^{b} $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33}) \times 10^3$; $\sigma U_{eq} = 6^{-1/2} \langle \sigma U_{ii}/U_{ii} \rangle U_{eq}$.

dinates in Table XIII, and bond lengths and angles in Table XV. (Tables XI, XIII, XV are found in the Supplementary Material.) The final value of the secondary extinction parameter is 1.55 (16) × 10^{-6}. The atoms numbered 1 and 2 are the pyridyl atoms bound to scandium. Atoms C3–C6 are the remaining atoms (carbons) of the pyridyl ring. C11–C15 and C31–C35 are the (η^5-C$_5$Me$_5$) inner ring carbons, and C21–C25 and C41–C45 are the methyl groups associated with them, respectively.

Structure Determination for (η^5-C$_5$Me$_5$)$_2$ScCH$_3$. A crystal approximately 0.3 × 0.3 × 0.2 mm, that appeared satisfactory from an oscillation photograph, was centered on a Syntex P2$_1$ diffractometer equipped with graphite-monochromated Mo Kα radiation. An orthorhombic cell was found, and cell dimensions were obtained from a least-squares fit to the setting angles of 15 reflections (various forms of six independent reflections) with 20° < 2Θ < 26°. Systematic absences observed in the data of h00, $h = 2n + 1$, $0k0$, $k = 2n + 1$, and $00l$,$l = 2n + 1$ are unique for the space group no. 19, $P2_12_12_1$. Five octants of data (hkl, $h\bar{k}l$, $\bar{h}\bar{k}l$, $h\bar{k}l$, and $\bar{h}k\bar{l}$) were collected with 4° < 2Θ < 40° and one octant, hkl, with 40° < 2Θ < 50°, a total of 6684 reflections. The data were merged (goodness of fit = 1.04) to give 2076 independent reflections, of which

1859 had $F_o > 0$ and 1143 had $(F_o{}^2) > 3\sigma(F_o{}^2)$. Three check reflections monitored every 97 reflections showed linear decay of 1.5% in F over the 230 h required to collect the data. The data were corrected for this decay and reduced to $F_o{}^2$; variances were assigned as described above. The least-squares refinement used all 2076 data and minimized the quantity $\Sigma w(F_o{}^2 - F_c{}^2)^2$, where $w = 1/\sigma^2(F_o{}^2)$. No absorption correction was made because of the small value of μr_{max}. A Patterson map gave scandium coordinates, and successive structure factor-Fourier calculations located the remaining atoms. Hydrogen atoms on the Cp* methyl groups were introduced, based on difference maps calculated in the planes where they were expected, and included in the subsequent calculations as constant contributions to the structure factors, with isotropic B of 10.0 Å^2. Six cycles of full matrix least squares, the hydrogen atoms being repositioned two times, concluded the refinement; the final $R = 0.113$ for all the data with $F_o{}^2 > 0$ and 0.072 for data with $F_o{}^2 > 3\sigma(F_o{}^2)$. The goodness of fit was $S = 2.98$, where n = number of data = 2076 and p = number of parameters. In the final refinement no parameter shifted more than one-half its standard deviation. A final difference map showed no excursion greater than ±0.44 e/Å^3. Crystal data are given in Table VIII and atom coordinates in Table X. Calculations were done by using the programs of the CRYRM crystallographic computing system^{64} on a VAX 11/780 computer; the final drawing was done by using ORTEP.^{65}

Kinetic and Thermodynamic Studies of the Thermal Electrocyclic Interconversions of Perfluorinated Dienes and Cyclobutenes

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Abstract: Detailed kinetic and thermodynamic analyses were carried out for the thermal interconversions of (*Z,Z*)- and (*E,E*)-perfluoro-2,4-hexadienes with *trans*-perfluoro-3,4-dimethylcyclobutene, (*E,Z*)-perfluoro-2,4-hexadiene with perfluoro-*cis*-3,4-dimethylcyclobutene, (*Z,Z*)- and (*E,E*)-perfluoro-3,5-octadienes with *trans*-perfluoro-3,4-diethylcyclobutene, and (*Z*)- and (*E*)-perfluoro-1,3-pentadiene with perfluoro-3-methylcyclobutene. In each case the (*Z,Z*)- or (*Z*)-dienes exhibited substantial kinetic advantage over the (*E,E*)- or (*E*)-dienes in their cyclization processes.

The elegant stereochemical studies of Criegee in 1959 on the ring opening of *cis*- and *trans*-1,2,3,4-tetramethylcyclobutenes^1 were the first to demonstrate unambiguously the conrotatory

nature of the cyclobutene–butadiene electrocyclic interconversion. It wasn't until 1965, of course, that the classic papers of Woodward

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(1) Criegee, R.; Noll, K. *Liebigs Ann. Chem.* **1959**, *627*, 1; *Chem. Ber.* **1965**, *98*, 2339.