

## SOME ASPECTS OF THE CHEMISTRY OF ALKYL AND HYDRIDE DERIVATIVES OF PERMETHYLSCANDOCENE

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**Abstract** - The use of two bulky pentamethylcyclopentadienyl groups has allowed the preparation of highly coordinatively unsaturated monomeric derivatives of scandium. The chloride, methyl, benzyl, and phenyl derivatives are described. An unstable hydride derivative is obtained via hydrogenation of the alkyls. Spectral data for the methyl derivative together with the results of an X-ray structure determination suggest that the methyl group is bonded to scandium in a conventional manner; in particular, no agostic Sc-H-C interaction is indicated. H-D exchange between H<sub>2</sub>, benzene, [ $\eta^5$ C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>], Si(CH<sub>3</sub>)<sub>4</sub>, P(CH<sub>3</sub>)<sub>3</sub>, CH<sub>4</sub>, and the  $\alpha$ -CH bonds of tetrahydrofuran is catalyzed by the hydride derivative. The C-H bonds of cyclohexane and the  $\beta$ -CH bonds of tetrahydrofuran are unreactive. With pyridine an  $\alpha$ -metallated pyridine derivative is obtained, whose structure is reported. These hydride and methyl derivatives rapidly polymerize ethylene, whereas propene and isobutene undergo insertion to yield first n-alkyl scandium derivative followed by insertion into the vinylic C-H bonds of additional olefin to afford alkane and scandium alkenyls. Some speculation on the mechanisms of these unusual transformations is presented.

### INTRODUCTION

The organometallic chemistry of the elements of the first transition series (Ti  $\rightarrow$  Cu) has been extensively investigated during the past three decades. The remaining member, scandium, has been virtually ignored. Its classification as a true transition element is somewhat debatable, and scandium has been traditionally grouped with yttrium, and lanthanum, and the lanthanide elements (Ce  $\rightarrow$  Lu). On the other hand, the ionic radius of Sc<sup>3+</sup> is closer to those of some of the early transition metal ions (1) in some of their common oxidation states:

III	IV	V
Sc <sup>3+</sup> 0.81 Å	Ti <sup>4+</sup> 0.68 Å	V <sup>3+</sup> 0.78 Å
Y <sup>3+</sup> 0.93 Å	Zr <sup>4+</sup> 0.80 Å	Nb <sup>3+</sup> 0.86 Å
La <sup>3+</sup> . . . Lu <sup>3+</sup> 1.15 Å 0.93 Å	Hf <sup>4+</sup> 0.81 Å	Ta <sup>3+</sup> 0.86 Å

Thus, the organometallic chemistry of scandium may be expected *a priori* to be intermediate between that of the early transition elements and that of yttrium and the later lanthanide elements.

Our research group has a longstanding interest in the organometallic chemistry of the group IV transition elements. We have found that monomeric, coordinatively unsaturated alkyls and hydrides may be obtained with two bulky pentamethylcyclopentadienyl groups as ancillary ligands, i.e.

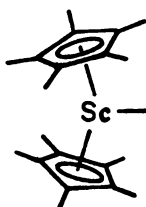


(M = Ti, Zr, Hf; R, R' = H, alkyl)

The high reactivity of these toward CO, olefins, H<sub>2</sub>, and C-H bonds is attributed in large part to the fact that the formally d<sup>0</sup>, 16-electron metal center is a strong Lewis acid; entering substrates interact strongly with the vacant 1a<sub>1</sub> orbital (2) of the bent sandwich complex. It occurred to us that monomeric hydride and alkyl derivatives of scandocene may exhibit even greater Lewis acidity; scandium is more electropositive and Cp<sub>2</sub>Sc-R (R = H, alkyl) derivatives are d<sup>0</sup>, 14-electron species with two low-lying vacant orbitals.

Organoscandium compounds are commonly polymeric (e.g., [Sc(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>x</sub> (3), [Sc(C≡CC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>x</sub> (3), and [Sc(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>]<sub>x</sub> (4)), dimeric (e.g., [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ScCl]<sub>2</sub> (5)) or are associated with a main group III compound (e.g., (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sc(μ-CH<sub>3</sub>)<sub>2</sub>Al(CH<sub>3</sub>)<sub>2</sub> (6) and {η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>Sc(μ-H)<sub>2</sub>BH<sub>2</sub> (7)). Monomeric species may be obtained as adducts with Lewis bases (e.g., (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Sc(CH<sub>3</sub>)(B), B = THF, pyridine) (8). Hence, highly coordinatively unsaturated organoscandium compounds are indeed voracious Lewis acids which tightly bind bases, or, in their absence, oligomerize with bridging halide or alkyl groups. In these regards, organoscandium compounds resemble organic compounds of the main group III element aluminum.

Bulky ancillary ligands often impede oligomerization of coordinatively unsaturated species and render them more soluble. Recently Lappert and co-workers have adopted this strategy in the preparation of hydrocarbon soluble bis(cyclopentadienyl)scandium derivatives (e.g., [{η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>ScCl]<sub>2</sub> (9) and {η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>Sc(μ-H)<sub>2</sub>BH<sub>2</sub>). In order to obtain monomeric, base-free organoscandium we have undertaken the syntheses of derivatives containing two sterically more demanding pentamethylcyclopentadienyl groups as ancillary ligands:



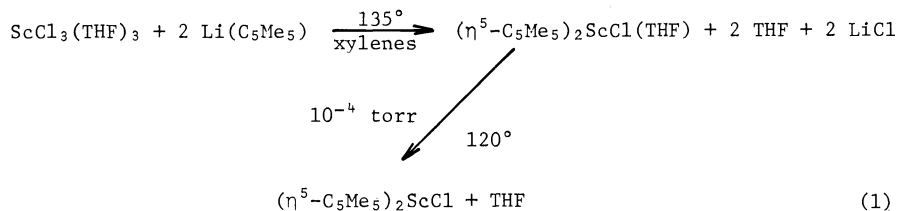
(R = hydride, alkyl, aryl, etc.)

These formally d<sup>0</sup>, 14-electron compounds are extremely reactive, undergoing facile reactions with olefins, H<sub>2</sub>, and C-H bonds\*. We report herein the preparation and characterization of these compounds and some aspects of their chemistry.

## RESULTS AND DISCUSSION

### Preparation of Alkyl and Hydride Derivatives of Permethylscandocene

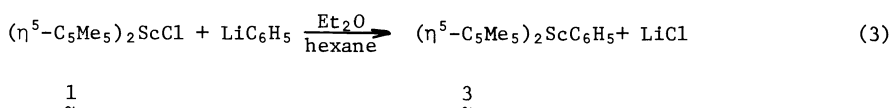
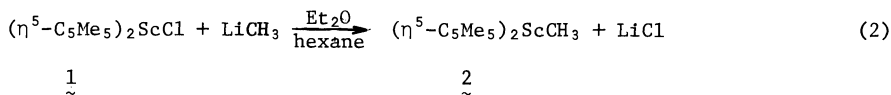
The requisite starting material, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ScCl (1), is prepared straightforwardly from ScCl<sub>3</sub>(THF)<sub>3</sub> (THF = tetrahydrofuran) and Li(C<sub>5</sub>Me<sub>5</sub>) in refluxing xylenes (eq 1). The product is obtained in 75% yield by direct sublimation from the residue following removal of solvent



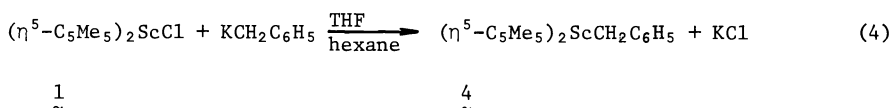
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\*One of the authors (M.E.T.) feels the chemistry reported herein is best described as a veritable bonanza.

in vacuo. Mass spectral analysis and an ebulliometric molecular weight determination in benzene indicate  $\underline{1}$  is monomeric, unlike  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ScCl}]_2$  (5) and  $[(\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2)_2\text{ScCl}]_2$  (7). Moreover, whereas  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ScCl}(\text{THF})$  sublimes without dissociation of THF,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCl}(\text{THF})$  is converted to  $\underline{1}$  on sublimation under dynamic vacuum. The methyl and phenyl derivatives are readily obtained as shown in eqs 2 and 3. If these reactions are carried out in the presence of tetrahydrofuran; however, neither  $\underline{2}$  nor  $\underline{3}$  are obtained,

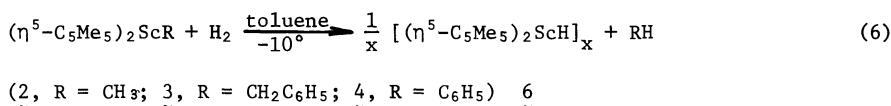


rather,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCl}(\text{THF})$  is isolated, which is unreactive towards  $\text{LiCH}_3$  and  $\text{LiC}_6\text{H}_5$ . With benzyl potassium  $\underline{1}$  is converted to the benzyl derivative, even when a mixture of hexane and tetrahydrofuran is used as solvent (eq 4). Ebulliometric molecular weight determinations for  $\underline{2}$ ,  $\underline{3}$  and  $\underline{4}$  indicate that all three compounds are monomeric in benzene. The propensity for the methyl derivative  $\underline{2}$  but not the benzyl derivative  $\underline{4}$  to reversibly bind THF (eq 5) further points up the severe steric constraints imposed on the scandium center by the two bulky  $(\eta^5\text{-C}_5\text{Me}_5)$  ancillary ligands. The THF adduct  $\underline{5}$  is sufficiently stable to

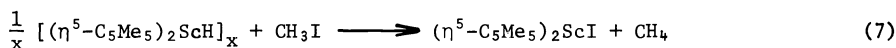


allow crystallization as an analytically pure material.

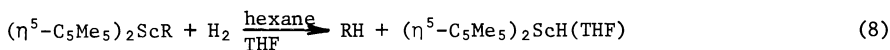
The monomeric derivatives  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScR}$  ( $\text{R} = \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5, \text{C}_6\text{H}_5$ ) react readily with  $\text{H}_2$  (2 atm) with release of  $\text{RH}$  (eq 6). Since 0.93 equivalent of  $\text{H}_2$  is consumed and 1.0



equivalent of  $\text{CH}_3\text{C}_6\text{H}_5$  is released in the hydrogenation of  $\underline{3}$ , we presume that the product is the hydride derivative  $\underline{6}$ . This formulation is further supported by the stoichiometry of its reaction with methyl iodide (eq 7). Unfortunately, its extreme reactivity (vide infra)



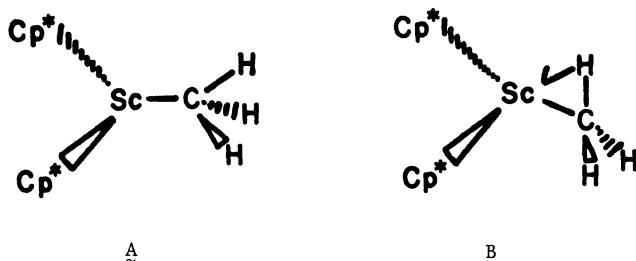
and instability at  $25^\circ\text{C}$  under hydrogen pressures below 2 atmospheres has precluded its full spectral characterization and determination of its molecular weight. The  $^1\text{H}$  NMR spectrum for  $\underline{6}$  exhibits a single resonance at  $\delta$  1.93 (benzene- $d_6$ ) attributable to the pentamethylcyclopentadienyl groups; however, no resonance has been observed thus far which may be assigned to  $\text{ScH}$ . The strong electric quadrupole moment ( $-0.22$  barns) of the  $^{45}\text{Sc}$  nucleus ( $I = 7/2$ , 100% abundance) may be expected to broaden this signal considerably. Hydrogenation of the alkyls in a mixture of hexane and tetrahydrofuran affords a more stable hydride complex, the tetrahydrofuran adduct  $\underline{7}$  (eq 8).



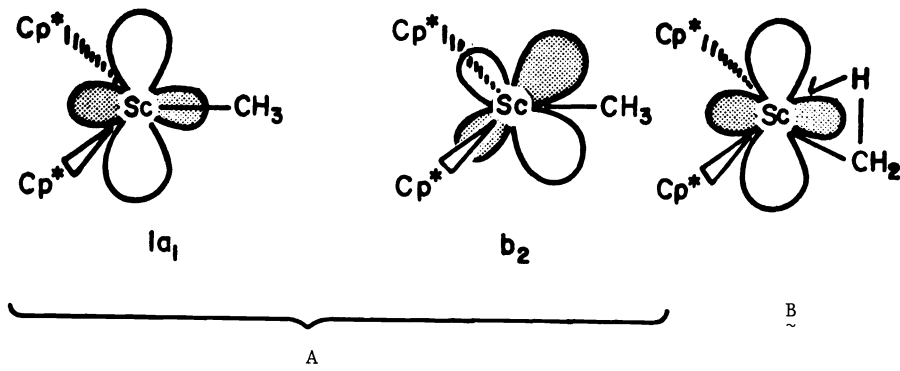
Although  $\zeta$  is moderately stable in solution in the absence of  $H_2$ , it does decompose in the solid state after several days at room temperature. A prominent feature of its infrared spectrum is a band of moderate intensity at  $1390\text{ cm}^{-1}$ , which shifts to  $990\text{ cm}^{-1}$  when  $\zeta$  is prepared from  $D_2$  according to eq 8, and thus assigned to  $\nu(\text{Sc-H})$ . The  $^1\text{H}$  NMR spectrum exhibits resonances attributable to  $(\eta^5\text{-C}_5\text{Me}_5)_2$  and coordinated THF, but no signal which may be assigned to ScH (*vide supra*).

#### Structure and Bonding for $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3$

$(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3$  ( $\zeta$ ) is monomeric in solution and thus very electron deficient. As discussed recently by Brookhart and Green (10), one may suspect one hydrogen of the methyl group to participate in 2-electron 3-center bonding in such circumstances. Hence two structures\* for  $\zeta$  must be considered: the conventional structure  $\tilde{A}$  and the more coordinatively



saturated structure  $\tilde{B}$  with an "agostic" methyl group. There are two (essentially) non-bonding metal-centered orbitals for  $\tilde{A}$ , whereas for  $\tilde{B}$  one of these, the  $b_2$  orbital, is used in the 2-electron 3-center  $\text{Sc}\leftarrow\text{H-C}$  interaction. Hence for  $\tilde{B}$  only one nonbonding orbital



$(1a_1)$  remains, so that structure  $\tilde{B}$  may be considered somewhat analogous to the tetrahydrofuran adduct  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3(\text{THF})$ . An "agostic"  $\text{Ti}\leftarrow\text{H-C}$  interaction has been established by an X-ray structure determination for the related compound  $(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{TiCl}_3\text{CH}_3$  (11).

A single resonance at  $\delta = 0.07$  (toluene- $d_8$ ) is observed for all three hydrogens of the Sc- $\text{CH}_3$  moiety even at  $-90^\circ\text{C}$ ; for  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc}(^{13}\text{C})\text{CH}_3$  a doublet with  $^1J_{13\text{CH}} = 111\text{ Hz}$  is observed. These data are consistent with either of two situations:  $\zeta$  has structure  $\tilde{A}$  or a fluxional structure  $\tilde{B}$  obtains such that the  $^1\text{H}$  chemical shift and  $^1J_{13\text{CH}}$  values are averaged. A comparison of the chemical shifts and coupling constants for the partially deuterated and undeuterated methyl compounds provides more reliable evidence for or against an agostic  $\text{M}\leftarrow\text{H-C}$  interaction. As shown in Fig. 1, only a small (0.057 ppm) upfield shift is observed on monodeuteration of the scandium methyl group of  $\zeta$ . By comparison the 16-electron derivatives  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3(\text{THF})$  (5) and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{CH}_3)_2$  exhibit 0.047 ppm and 0.094 ppm upfield shifts on monodeuteration, the 18-electron complex  $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2$  exhibits a 0.020 ppm shift, whereas for methane a 0.019 ppm upfield shift is observed. These results suggest that the conventional structure  $\tilde{A}$  is, in fact, correct. On the other hand, structure  $\tilde{B}$  cannot be definitively excluded by these NMR data, since a substantial shift on deuteration will be observed only if the chemical shifts for the terminal and bridging

\*The third possibility discussed by Brookhart and Green, the fluxional methylene hydride ground state structure, appears highly unlikely since the maximum valency of scandium, III, is exceeded for  $\text{Cp}^*_2\text{Sc}\begin{matrix} \text{H} \\ \diagup \\ \text{CH}_2 \end{matrix}$ ; a purely  $\sigma$ -bonded methylene species such as in  $\text{Cp}^*_2\text{Sc}\begin{matrix} \ominus \\ \diagup \\ \text{H} \\ \diagdown \\ \text{CH}_2 \\ \oplus \end{matrix}$  is unprecedented.

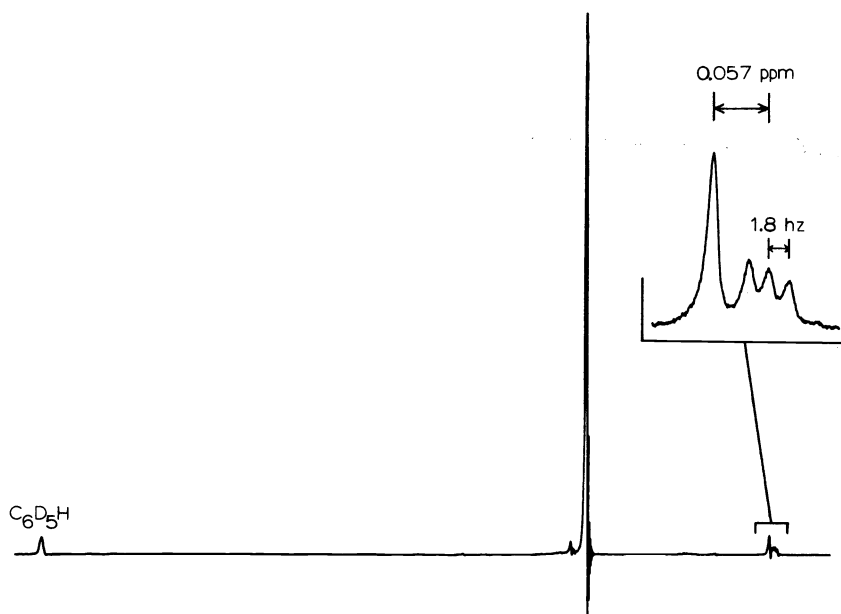


Fig. 1. 90-MHz  $^1\text{H}$  NMR spectrum of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3$  and  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_2\text{D}$  (1:1) in benzene- $\text{d}_6$ .

hydrogens of structure B are very different. Unfortunately, the quadrupolar  $^{45}\text{Sc}$  nucleus has precluded the observation of a Sc-H resonance for 6 or 7. It should be noted, however, that the Sc-CH<sub>3</sub> resonance (Fig. 1) does not appear to be broadened significantly as might be expected if a direct Sc←H-C interaction were present.

Infrared data are also more consistent with structure A. No low energy  $\nu(\text{C-H})$  modes are observed for 2 (Nujol mull). Furthermore, the most prominent C-D vibrations associated with the Sc-CD<sub>3</sub> moiety of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCD}_3$  are at 2195 and 2152  $\text{cm}^{-1}$   $\nu(\text{C-D})$  and 866  $\text{cm}^{-1}$   $\delta_s(\text{CD}_3)$  (cf. 1115  $\text{cm}^{-1}$   $\delta_s(\text{CH}_3)$  for 2-d<sub>0</sub>). By comparison CD<sub>3</sub>I (gas phase) exhibits bands at 2160 and 2140  $\text{cm}^{-1}$   $\nu(\text{C-D})$  and 959  $\text{cm}^{-1}$   $\delta_s(\text{CD}_3)$  (cf. 2980 and 2955  $\text{cm}^{-1}$   $\nu(\text{C-H})$  and 1262  $\text{cm}^{-1}$   $\delta_s(\text{CH}_3)$  for CH<sub>3</sub>I).

The solid state structure of 2 is of interest not only as regards the issue of a possible agostic scandium methyl group, but also for comparison to that recently found by Calabrese and Watson (12) for  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{LuCH}_3]_2$ , where only one CH<sub>3</sub> group bridges the two lutetium atoms in the dimer with a nearly linear Lu-C-Lu configuration. As can be seen in the ORTEP drawing (Fig. 2)  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3$  is monomeric in the crystalline state. Although the data set collected at 25°C indicates considerable static or dynamic disorder in the crystal so that the hydrogens of the Sc-CH<sub>3</sub> could not be located with confidence, the methyl carbon atom lies only 0.01 Å out of the plane of the two C<sub>5</sub>Me<sub>5</sub> ring centroids and scandium atom, that is, in the central equatorial position of the bent sandwich structures as in A. A low temperature data set may allow refinement of the hydrogen atom positions to lay to rest the issue of agosticism for 2.

#### C-H Activation with Alkyl and Hydride Derivatives of Permethylscandocene

The hydride derivatives of permethylscandocene promote H-D exchange for a variety of carbon-hydrogen bonds. For example,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScH}]_x$  (6) catalyzes exchange between H<sub>2</sub> (2 atm) and the C-D bonds of benzene- $\text{d}_6$  (approximately ten turnovers per hr at 80°C). Furthermore, hydrogen and deuterium are scrambled between solvent benzene- $\text{d}_6$  and the C-H positions of the  $(\eta^5\text{-C}_5\text{Me}_5)$  ligands of 6 as well as those of added Si(CH<sub>3</sub>)<sub>4</sub>, and P(CH<sub>3</sub>)<sub>3</sub>\*, although the rates are qualitatively slower than H<sub>2</sub>/C<sub>6</sub>D<sub>6</sub> exchange. The tetrahydrofuran adduct  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScH}(\text{THF})$  (7) exhibits similar catalytic activity. Interestingly, H-D exchange between solvent C<sub>6</sub>D<sub>6</sub> and only the  $\alpha$ -CH positions of THF is observed: whereas essentially statistical  $\alpha$ -CH/

\* A stable adduct between  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScH}]$  and PMe<sub>3</sub> is not obtained, however.

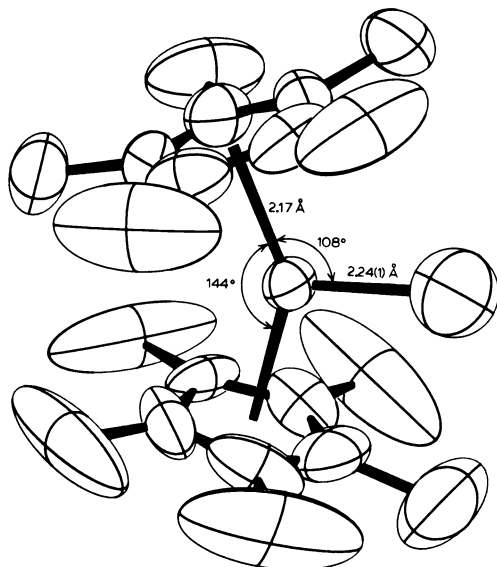


Fig. 2. ORTEP drawing of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3$ .

$\text{C}_6\text{D}_6$  exchange is observed after 24 hrs at  $80^\circ\text{C}$ , there is no significant deuteration of the  $\beta\text{-CH}$  positions.

With pyridine a stoichiometric transformation occurs with  $\underline{5}$  or  $\underline{6}$ , affording the metallated pyridine derivative  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc}(\text{C}, \text{N}-\eta^2\text{-C}_5\text{H}_4\text{N})$  ( $\underline{8}$ ) (see Fig. 3) with release of  $\text{H}_2$  (e.g.

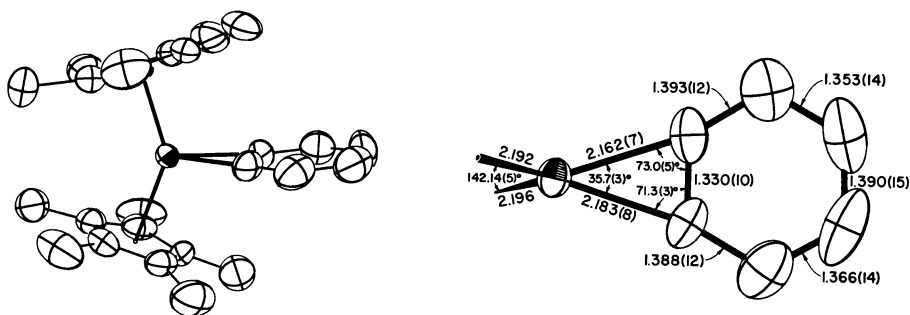
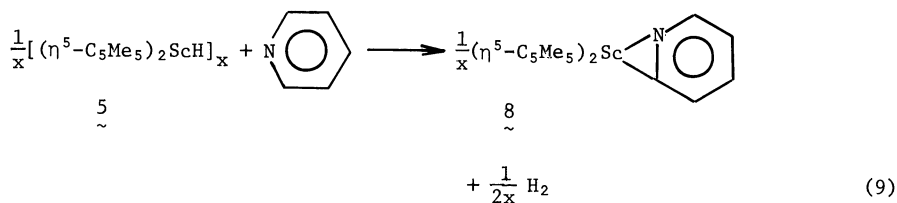


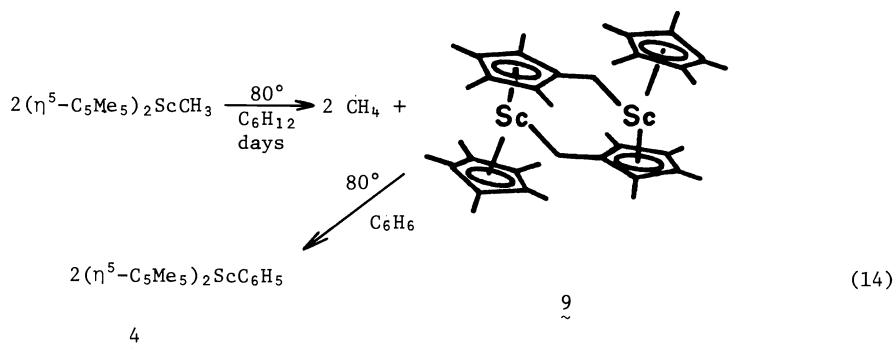
Fig. 3. ORTEP drawing of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc}(\text{C}, \text{N}-\eta^2\text{-C}_5\text{H}_4\text{N})$ . Due to disorder refinement was with 50% N and 50% C in each of the two pyridine positions bound to Sc.

eq 9). The reversibility of reaction (9) as indicated by the specific deuteration as shown

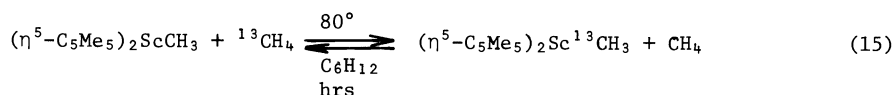


in eq (10) on treatment with  $\text{D}_2$ . Thus these reactions are likely to proceed via a pyri-



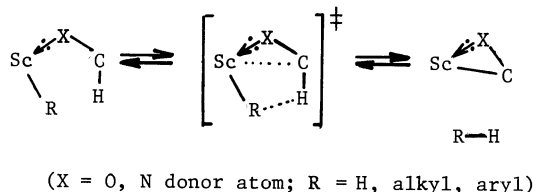


Like the monomeric methyl and benzyl derivatives (2 and 3), 9 reacts smoothly with solvent benzene to afford 4. Furthermore, in cyclohexane solution exchange of methyl groups between added  $^{13}\text{CH}_4$  and 9 (eq 15) is observed, prior to decomposition to 9. This reaction is some-

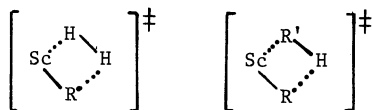


what slower than the corresponding reaction for  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{LuCH}_3$  recently reported by Watson (12).

The mechanisms by which these hydride and alkyl derivatives reversibly react with carbon-hydrogen bonds is currently under investigation. Given the tremendous stability of trivalent scandium vis-à-vis Sc(I) and Sc(V), a conventional sequence involving stepwise oxidative addition and reductive elimination would be prohibitively endoergic. We currently favor  $[2s + 2s]$  mechanisms involving four- or five-center transition states (13) of the types shown below. Thus activation of the  $\alpha$ -C-H bonds of tetrahydrofuran and pyridine (eqs 9, 10, 11, 12) are viewed as proceeding via the general transition state shown below. The Sc-O or Sc-N dative interaction is expected to hold the C-H bond in the



proximity of the Sc-H or Sc-C bond and greatly assist in the formation of the transition state for the  $[2s + 2s]$  reaction with the  $\alpha$  C-H bonds of tetrahydrofuran and pyridine. The facility of the  $[2s + 2s]$  process for  $\text{H}_2$  and simple hydrocarbons (e.g. eq 6, 8, 13, and 15) appears to be governed primarily by steric rather than thermodynamic effects. Thus the higher reactivity of  $\text{H}_2$  and  $\text{CH}_4$  as compared with cyclohexane or  $\beta$  C-H bonds of tetrahydrofuran is probably due to reduced steric crowding for their four-center transition states;

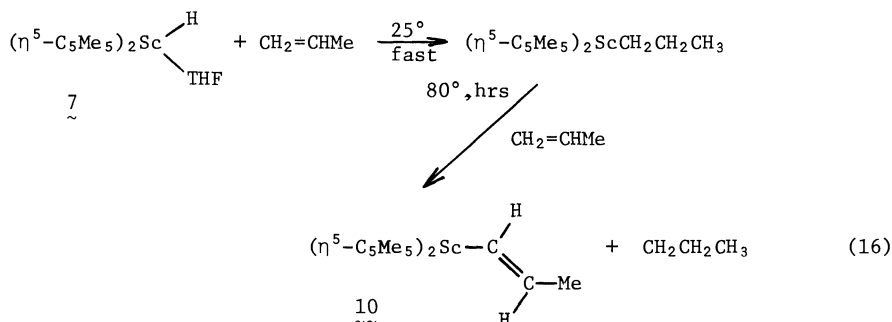


simple bond energy considerations ( $\text{H-H}$ ,  $104\text{ kcal}\cdot\text{mol}^{-1}$ ;  $\text{CH}_4$ ,  $104\text{ kcal}\cdot\text{mol}^{-1}$ ;  $\text{C}_6\text{H}_{12}$ ,  $95\text{ kcal}\cdot\text{mol}^{-1}$ ;  $\beta$  C-H of THF,  $\sim 95\text{ kcal}\cdot\text{mol}^{-1}$ ) lead to a predicted reactivity order opposite to that observed. Moreover, the other H-D exchange reactions which are catalyzed by scandium hydride derivatives 6 and 7 appear to be restricted thus far to primary C-H bonds (e.g.  $\text{Si}(\text{CH}_3)_4$ ,  $\text{P}(\text{CH}_3)_3$ ,  $[\eta^5\text{-C}_5\text{CH}_3]_5$ ), another indication that the transition states are quite crowded. The activation of aryl C-H bonds could conceivably proceed via the same type of transition state; however, the C-C  $\pi$  system may allow for a quite different type of interaction analogous to that proposed in the next section for the activation of the vinylic C-H bonds of olefins.

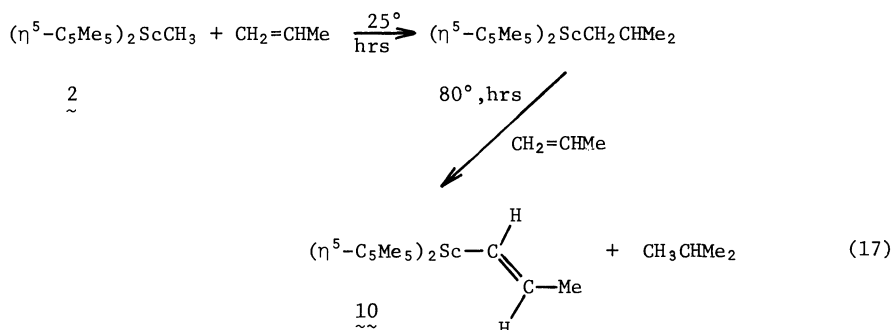


Reactivity of Olefins with Alkyl and Hydride Derivatives of Permethylscandocene

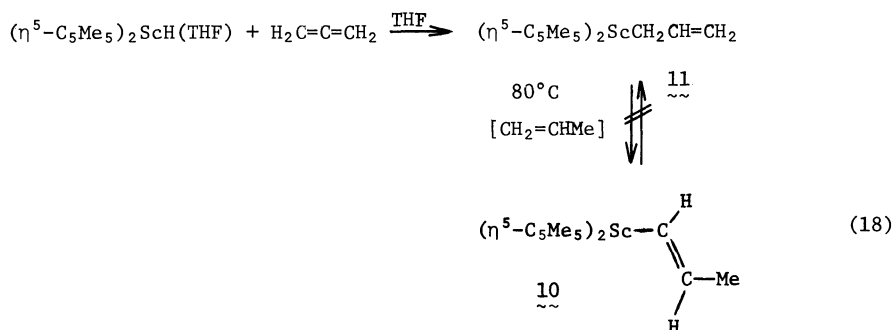
Ethylene is rapidly polymerized by all  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScR}$  ( $\text{R} = \text{H}$ , alkyl) derivatives we have tested. No intermediates or soluble scandium-containing products are observed. By contrast, a clean, stepwise reaction of  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScH}(\text{THF})$  (7) with excess propylene is observed (eq 16). Thus rapid insertion into the scandium hydride bond is followed by a slower elimi-



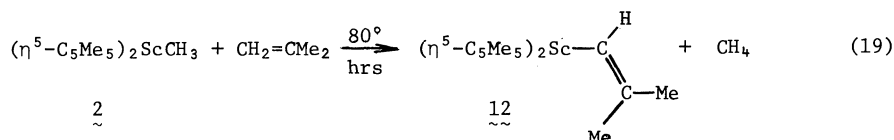
nation of propane and generation of the trans-propenyl derivative,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}=\text{CHMe}$  (10), which is unreactive toward excess propene for prolonged periods at  $80^\circ\text{C}$ .  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_3$  (2) undergoes a similar stepwise reaction with propene (eq 17), although the initial inser-



tion occurs more slowly for 2. The generation of the trans-propenyl derivative by reaction of the n-propyl (eq 16) or isobutyl (eq 17) derivatives with additional propene is an unexpected and significant result, since it represents a rare example of insertion into a vinylic ( $\text{D}(\text{C-H}) = 108 \text{ kcal}\cdot\text{mol}^{-1}$ ) as compared with the weaker allylic ( $\text{D}(\text{C-H}) = 89 \text{ kcal}\cdot\text{mol}^{-1}$ ) C-H bond of propene. Significantly, the allyl derivative  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScCH}_2\text{CH}=\text{CH}$  (11), prepared via treatment of 7 with allene (eq 18), and the propenyl derivative 10 could not be

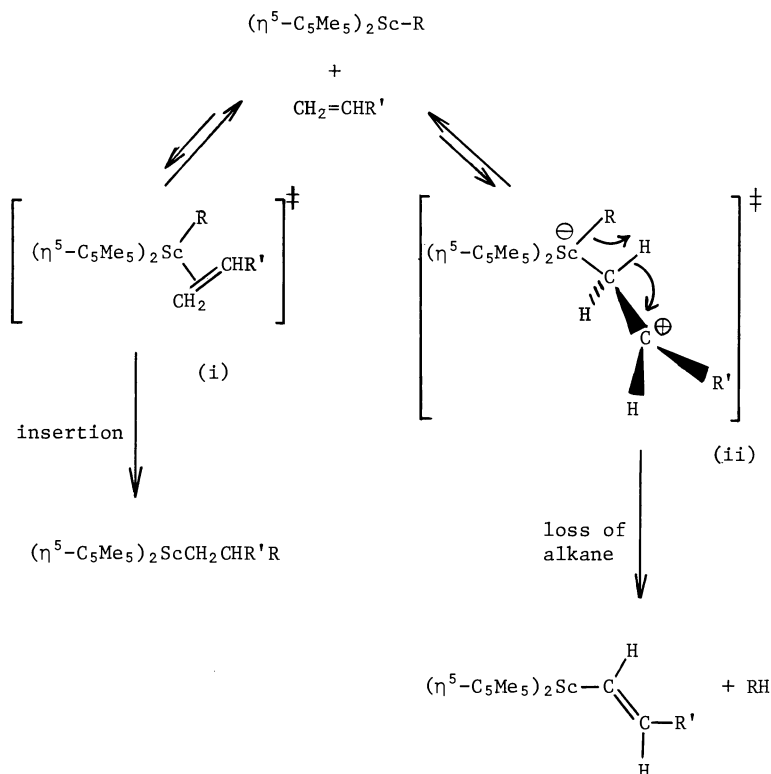


interconverted even on prolonged heating in the presence of propene. The reaction of 2 with excess isobutene affords the isobutenyl derivative 12 and methane directly (eq 19); appar-



rently insertion of  $\text{CH}_2=\text{CMe}_2$  to afford the neopentyl derivative is disfavored (presumably for steric reasons) such that the vinylic C-H insertion pathway dominates.

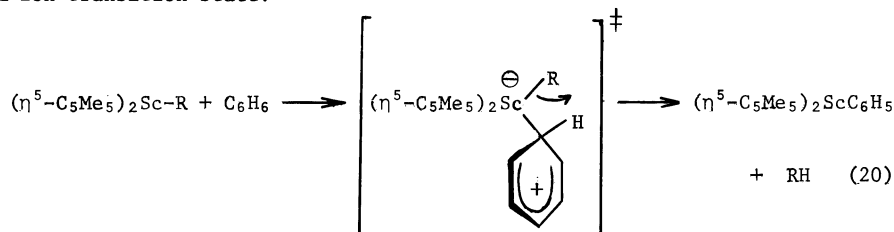
Our studies of the reactivity of olefins hydride and alkyl derivatives of scandium is presently at a very preliminary stage, so that our discussion of the mechanisms of insertion and vinylic C-H activation is quite speculative. Our working hypothesis is that two modes of coordination of olefin to the scandium center are possible (Scheme):



Scheme

The conventional adduct (i) with the alkyl substituent of the olefin in the central equatorial site of the bent sandwich complex leads to insertion, affording the n-alkyl derivative. With increasing steric bulk of R and R', and increasing stability of the (incipient) carbonium ion, the zwitterionic-like transition state (ii) may be favored. The potent Lewis acidity of the scandium center certainly lends some credence to this suggestion. Moreover, a structure determination for  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CH}_2=\text{CHNMe}_2)]^+$  (14) revealed a related structure with the cationic iron center bonded only to the  $[\text{CH}_2]$  end of the olefin (*i.e.*  $\text{Fe}-\text{CH}_2-\text{CH}=\text{NMe}_2 \leftrightarrow \text{Fe}-\text{CH}_2-\text{CH}^+\text{NMe}_2$ ).

The activation of aryl C-H bonds could also be viewed as proceeding via a zwitterionic-like, phenonium ion transition state.



A number of experiments to test these ideas suggest themselves.

#### CONCLUSIONS

The use of two bulky  $(\eta^5\text{-C}_5\text{Me}_5)$  ancillary ligands provides sufficient steric bulk to render these chloro, alkyl and aryl derivatives of scandium monomeric and hence, highly coordinatively unsaturated. The molecularity of the unstable hydride derivative  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{ScH}]_x$  is

uncertain; the tetrahydrofuran adduct ( $\eta^5\text{-C}_5\text{Me}_5$ )<sub>2</sub>ScH(THF) is very likely monomeric. <sup>1</sup>H NMR and infrared spectral data and an X-ray structure determination for the 14-electron methyl derivative indicate that an agostic Sc←H-C interaction is not present in the ground state. Thus a vacant orbital appears to be a necessary but insufficient condition for such an agostic methyl group. All hydride and alkyl derivatives appear to behave as voracious Lewis acids, binding sterically unencumbered bases such as tetrahydrofuran and pyridine, and activating (especially sp<sup>3</sup>) C-H bonds, possibly via four- or five-center [2s + 2s] transition states. Rapid polymerization of ethylene is observed, whereas for propene and isobutene insertion into Sc-H or Sc-C bonds and a competing reaction of scandium alkyls with olefins to afford alkane and scandium alkenyls is noted. A pervasive feature of the chemistry of these new compounds is the potent electrophilicity of the scandium center. Indeed, their reactivity appears to exceed even organoboron and organoaluminum compounds and may be likened to a functionalized proton or carbonium ion.

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