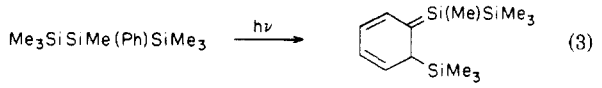
of using oxygen as a scavenger and the possible errors that may be involved, it is more difficult to imagine that the ethanol:triethylsilane experiments are flawed, particularly when they have been confirmed elsewhere.[14]

There are two simple explanations for the discrepancies between the product and flash photolysis studies. First, the transient detected in the flash photolysis work may not have been methylphenylsilylene. In fact, product studies of the photolysis of 2-phenylheptamethyltrisilane[16] show that formation of a silene, IV (reaction 3), is about as efficient as silylene formation (eq 2). It has also been established that silenes of similar structure have absorption spectra in the critical 440-nm region.[17]



(3)

IV

A second explanation can be invoked to rationalize all of the data. This explanation requires that methylphenylsilylene was indeed detected in the flash photolysis experiments but that its rapid reactions with oxygen and ethanol were reversible, so that the rate constants detected in the flash photolysis experiments need not necessarily have matched those of the product studies.

Which of these possibilities is correct remains unanswered. However, a resolution of these problems is only likely to come from more detailed studies of the photochemistry of silylene precursors.

Acknowledgment. We thank Professor P. P. Gaspar for many helpful discussions and for generously sharing unpublished flash photolysis data.

Registry No. I, 69545-85-3; II, 54731-53-2; III, 513-81-5; EtOH, 64-17-5; Et_3SiH, 617-86-7.

(16) Ishikawa, M.; Nakagawa, K.-I.; Enokida, R.; Kumada, M. *J. Organomet. Chem.* **1980**, *201*, 151.
(17) Shizuka, H.; Okazaki, K.; Tanaka, M.; Ishikawa, M.; Sumitani, M.; Yoshihara, K. *Chem. Phys. Lett.* **1985**, *113*, 89.

Carbon–Hydrogen Bond Activation by Rhodium and Iridium Amides: Strategy vs. Serendipity

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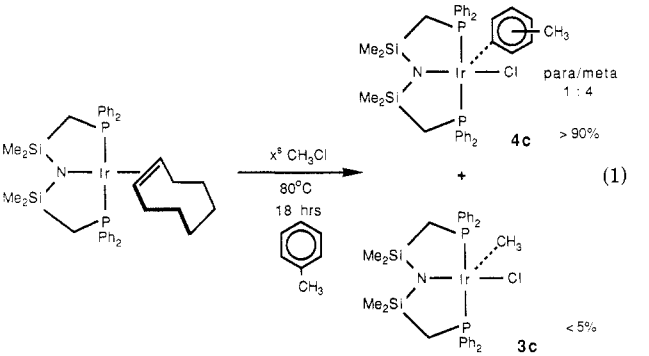
Summary: Iridium amide complexes selectively activate the aromatic C–H bonds of toluene while the analogous rhodium derivatives activate only the benzyl C–H bonds; a radical mechanism appears to be operative in the latter case.

Strategy. Prodded by the success of certain iridium complexes in carbon–hydrogen bond activation,[1] we examined the iridium(III) dihydride $IrH_2[N(SiMe_2CH_2PPh_2)_2]$ (**1**)[2] as a potential source of a reactive, coordinatively unsaturated fragment. Our rationale was straightforward: if the formation of the 16-electron "CpIrL" (L = PMe_3 or CO; Cp = η^5-C_5H_5 or η^5-C_5Me_5) fragments can generate such intruiging results in C–H bond activation, then loss of H_2 from **1**, either photochemically or thermally (by addition of t-BuCH=CH_2), would generate the 14-electron species "$Ir[N(SiMe_2CH_2PPh_2)_2]$", capable of both C–H activation and further elaboration.[3] However, H_2 elimination from **1** proved futile by any technique (photolysis or dehydrogenation by t-BuCH=CH_2) that we tried. We also attempted the preparation of a presumed product of C–H activation, namely, the methyl hydride complex $Ir(CH_3)H[N(SiMe_2CH_2PPh_2)_2]$, in an effort to use this derivative in thermal C–H bond exchange;[4] addition of a variety of hydride reagents to the readily available methyl iodide derivative $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$[5] led to complicated mixtures of products, none of which corresponded to the desired methyl hydride species. Although we still had the option of replacing the phenyl sustituents on phosphorus with the more electron-rich and bulkier isopropyl groups and reexamining the strategy outlined above, we decided to abandon this project. However, in unrelated studies, we happened onto two systems that apparently activate C–H bonds under quite mild but very different conditions.

Serendipity. The oxidative addition of both iodo- and bromomethane to the iridium(I) cyclooctene complex $Ir(\eta^2$-$C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$ (**2**) proceeds smoothly in toluene to generate the corresponding methyl halide complexes $Ir(CH_3)X[N(SiMe_2CH_2PPh_2)_2]$ (X = I, **3a**; X = Br, **3b**).[5] With chloromethane no reaction is observed at room temperature. If, however, a mixture of **2** and CH_3Cl (approximately 100 equiv) in toluene is heated to 80 °C for 12 h, **2** is completely converted to a 4:1 mixture of *m*- and *p*-tolyl chloride complexes $Ir(C_6H_4CH_3)Cl[N(SiMe_2CH_2PPh_2)_2]$ (**4c**);[6] the desired methyl chloride species is formed in only trace quantities (<5%) (eq 1).



(1)

If the temperature is lowered to 60 °C and the reaction time extended to approximately 3 days, then the methyl chloride complex **3c** is formed in a 3:2 ratio (by ^1H NMR)

† Fellow of the Alfred P. Sloan Foundation (1984–1987).

(1) (a) Janowicz, A.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Bergman, R. G.; Janowicz, A. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (c) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723. (d) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (e) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245 and references therein.
(2) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682.
(3) The anticipated products of C–H activation would be the 16-electron species $Ir(R)H[N(SiMe_2CH_2PPh_2)_2]$ capable of undergoing insertion by CO, olefins, or acetylenes. A related 14e fragment can be formed by dehydrohalogenation of $Rh(H)Cl[C_6H_3$-o,o'-$(CH_2P$-t-$Bu_2)_2]$; see: Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.
(4) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 1121.
(5) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1986**, *5*, 2469.
(6) **4c**: ^1H NMR (C_6D_6, ppm): meta isomer, $Si(CH_3)_2$, 0.53, –0.12 (s); PCH_2Si, 1.63 (dt, J_{gem} = 14.0, J_{app} = 6.1 Hz), 1.53 (dt, J_{app} = 5.4 Hz); $C_6H_4CH_3$, 1.81 (s); $C_6H_4CH_3$, 6.76 (d, J = 8.0 Hz, ortho), 6.62 (s, ortho), 6.36 (d, para), 6.31 (t, meta); $P(C_6H_5)_2$, 7.05, 6.94 (m, para/meta), 7.63, 7.98 (m, ortho); para isomer; $Si(CH_3)_2$, 0.54, –0.13 (s); PCH_2Si, same as the meta isomer; $C_6H_4CH_3$, 2.01 (s); $C_6H_4CH_3$, 6.82 (d, J = 8.0 Hz, ortho), 6.21 (d, meta); $P(C_6H_5)_2$, same as the meta isomer. C, H, and N analyses.

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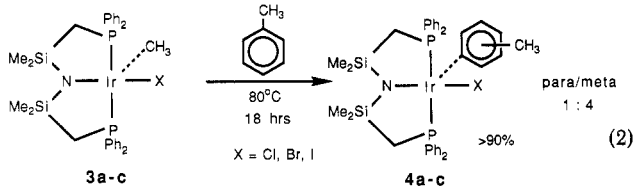
with the tolyl isomers **4c**. Interestingly, heating the crude mixture of **3c** and **4c** in toluene at 80 °C for approximately 12 h results in complete conversion to the tolyl derivatives **4c**. In fact, all of the isolated iridium(III) methyl halide complexes **3a–c** are quantitatively converted to the corresponding tolyl derivatives **4a–c**[7] by simply heating in toluene at 80 °C for approximately 12 h (eq 2). This



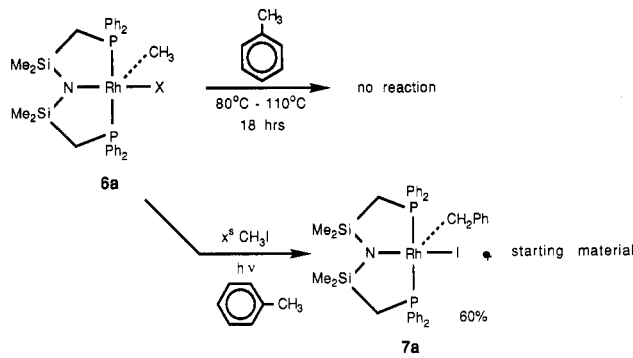
(2)

reaction appears to be general; intermolecular activation of aromatic C–H bonds of a wide variety of arenes is in progress.

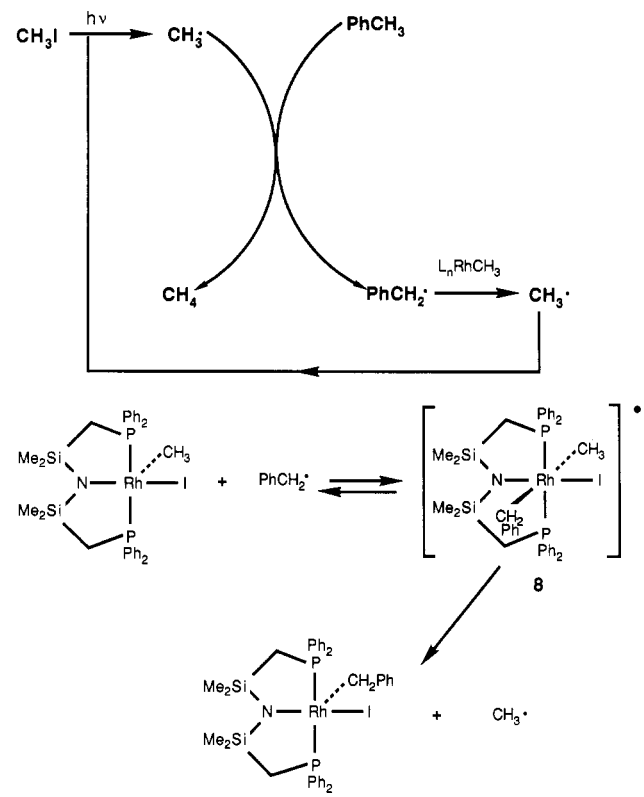
Mechanistically, we can suggest that the five-coordinate square-pyramidal structure is important since this provides an open site, trans to the apical methyl, for η^2-coordination[8] of the arene ring or for direct interaction of the aromatic C–H bond.[9] In any case, either oxidative addition[10] followed by rearrangement or metalation of the aromatic ring by the iridium amide to generate an amine linkage[11] that can subsequently invert and eliminate CH_4 are viable routes to the observed products.

The analogous rhodium system behaves completely differently. Although oxidative addition of iodo- and bromomethane to the rhodium(I) cyclooctene derivative $Rh(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$ (**5**) proceeds smoothly in toluene at room temperature to generate the corresponding methyl halide complexes $Rh(CH_3)X[N(SiMe_2CH_2PPh_2)_2]$ (X = I, **6a**; X = Br, **6b**),[5] we sometimes observed the contamination of these products by the corresponding benzyl halide derivatives $Rh(CH_2Ph)X[N(SiMe_2CH_2PPh_2)_2]$ (X = I, **7a**; X = Br, **7b**). These contaminants can be independently prepared[12] in pure form

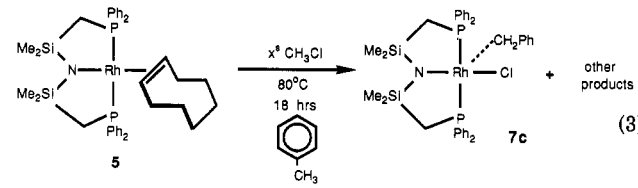
Scheme I



Scheme II



by oxidative addition of $PhCH_2X$ to **5**. Once again, attempts to oxidatively add CH_3Cl to the rhodium(I) complex **5** were unsuccessful at room temperature (i.e. no reaction occurs). However, heating at 80 °C in toluene in the presence of excess CH_3Cl generates reasonable yields (50–60%) of the benzyl chloride complex **7c** (eq 3); although other unidentified products are also produced, no methyl chloride complex could be detected.



(3)

In analogy to the iridium system in eq 2, we heated the pure rhodium methyl iodide derivative **6a** in toluene at 80 °C up to 110 °C for extended periods in an attempt to activate C–H bonds. In all cases, no reaction occurred and starting material was quantitatively recovered. However, addition of excess CH_3I (approximately 50 equiv) to **6a** in neat toluene does result in the formation of the benzyl iodide complex **7a** (Scheme I). We have investigated this

(7) **4a**: ^1H NMR (C_6D_6, ppm): meta isomer; $Si(CH_3)_2$, 0.59, –0.04 (s); PCH_2Si, 1.69 (dt, J_{gem} = 13.5, J_{app} = 6.1 Hz), 1.59 (dt, J_{app} = 6.3); $C_6H_4CH_3$, 1.91 (s); $C_6H_4CH_3$, 6.75 (d, J = 7.9 Hz, ortho), 6.66 (s, ortho), 6.35 (d, para), 6.22 (t, meta); $P(C_6H_5)_2$, 7.08, 6.92 (m, para/meta), 7.57, 7.84 (m, ortho); para isomer; $Si(CH_3)_2$, 0.63, –0.05 (s); PCH_2Si, same as the meta isomer; $C_6H_4CH_3$, 2.14 (s); $C_6H_4CH_3$, 6.81 (d, J = 8.0 Hz, ortho), 6.12 (d, meta); $P(C_6H_5)_2$, same as the meta isomer. C, H, and N analyses. **4b**: ^1H NMR (C_6D_6, ppm): meta isomer; $Si(CH_3)_2$, 0.51, –0.13 (s); PCH_2Si, 1.68 (dt, J_{gem} = 13.8, J_{app} = 5.0 Hz), 1.53 (dt, J_{app} = 5.6 Hz), $C_6H_4CH_3$, 1.79 (s); $C_6H_4CH_3$, 6.75 (d, J = 8.1 Hz, ortho), 6.63 (s, ortho), 6.38 (d, para), 6.30 (t, meta); $P(C_6H_5)_2$, 7.07, 6.94 (m, para/meta), 7.60, 7.93 (m, ortho); para isomer; $Si(CH_3)_2$, 0.50, –0.14 (s); PCH_2Si, same as the meta isomer; $C_6H_4CH_3$, 2.01 (s); $C_6H_4CH_3$, 6.81 (d, J = 8.0 Hz, ortho), 6.20 (d, meta); $P(C_6H_5)_2$, same as the meta isomer. C, H, and N analyses.

(8) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 4814.

(9) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4581.

(10) Gomez, M.; Yarrow, P. I. W.; Robinson, D. J.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *279*, 115.

(11) The amide to amine conversion has precedent, see Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1985**, *4*, 1145.

(12) **7a**: ^1H NMR (C_6D_6, ppm): $Si(CH_3)_2$, 0.62, –0.24 (s); PCH_2Si, 1.81 (dt, J_{gem} = 14.1, J_{app} = 5.9 Hz), 1.55 (dt, J_{app} = 5.4 Hz); $C_6H_5CH_2Rh$, 4.39 (q, $^2J_{Rh}$ = ^3J_P = 3.9 Hz); $C_6H_5CH_2$, 6.61 (t, J = 7.9 Hz, meta), 6.95 (t, para), 7.56 (d, ortho); $P(C_6H_5)_2$, 7.01 (m, para/meta), 7.64, 7.76 (m, ortho). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm relative to external $P(OMe)_3$ set at +141.0 ppm): 21.1 (d, $^1J_{Rh}$ = 114 Hz). C, H, and N analyses. **7b**: ^1H NMR (C_6D_6, ppm): $Si(CH_3)_2$, 0.59, –0.25 (s); PCH_2Si, 1.64 (dt, J_{gem} = 12.8, J_{app} = 4.8 Hz), 1.47 (dt, J_{app} = 5.6 Hz); $C_6H_5CH_2Rh$, 4.52 (q, $^2J_{Rh}$ = ^3J_P = 4.0 Hz); $C_6H_5CH_2$, 6.60 (t, J = 8.0 Hz, meta), 6.89 (t, para), 7.51 (d, ortho); $P(C_6H_5)_2$, 7.02 (m, para/meta), 7.78, 7.85 (m, ortho). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm relative to external $P(OMe)_3$ set at +141.0 ppm): 18.8 (d, $^1J_{Rh}$ = 113 Hz). C, H, and N analyses. **7c**: ^1H NMR (C_6D_6, ppm): $Si(CH_3)_2$, 0.62, –0.17 (s); PCH_2Si, 1.58 (dt, J_{gem} = 13.3, J_{app} = 5.3 Hz), 1.48 (dt, J_{app} = 6.6 Hz); $C_6H_5CH_2Rh$, 4.53 (q, $^2J_{Rh}$ = ^3J_P = 4.7 Hz); $C_6H_5CH_2$, 6.58 (t, J = 7.9 Hz, meta), 6.91 (t, para), 7.53 (d, ortho); $P(C_6H_5)_2$, 7.28 (m, para/meta), 7.64, 7.76 (m, ortho). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm relative to external $P(OMe)_3$ set at +141.0 ppm): 17.1 (d, $^1J_{Rh}$ = 117 Hz). C, H, and N analyses.

peculiar transformation and have found the following reaction parameters to be operative: (i) no reaction occurs in the dark; (ii) no reaction occurs in the presence of radical traps (e.g. TEMPONE[13]); (iii) reaction can be initiated in the dark by radical sources (e.g. AIBN[14]). A proposed mechanism for the rhodium system is outlined in Scheme II. The excess CH_3I serves as the source of the methyl radicals under light-initiated[15] C–I bond cleavage (fluorescent light is sufficient). The $CH_3^\bullet$ abstracts the weakest C–H bond in the system, which is the benzyl C–H bond of the solvent. The benzyl radical is then trapped by the rhodium(III) methyl iodide complex to generate a 17-electron[16] octahedral complex, **8**, which eliminates[17] $CH_3^\bullet$ to propagate the benzyl radical formation. The fact that other as yet unidentified products (10–30%) accompany formation of the benzyl derivatives adds further support to the radical chain mechanism.[18]

Conclusions. The coordination of the tridentate, mixed-donor ligand $^-N(SiMe_2CH_2PPh_2)_2$ to iridium(III) and rhodium(III) generates completely different types of reactivities and structures when compared to cyclopentadienyl-type ligands. Perhaps it is therefore not surprising in retrospect that stategies for C–H activation based on known CpIrL systems fail for these amide derivatives. Mechanistic studies and extensions are currently underway.

Acknowledgment. Financial support was provided by NSERC of Canada and the Alfred P. Sloan Foundation. Johnson-Matthey is gratefully acknowledged for their loan of $RhCl_3$ and $IrCl_3$.

(13) TEMPONE = 4-oxotetramethylpiperidine *N*-oxide.
(14) AIBN = azobis(isobutyronitrile).
(15) Since the process could be a radical chain type, the rate and efficiency of CH_3I homolysis is not critical; however, as suggested by a reviewer, it is possible that the rhodium(III) complexes are also involved in the initiation step by halide abstraction via an excited state.
(16) Substitution at 17-electron metal centers is documented to be fast, see: McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496.
(17) The reaction is driven by the formation of methane.
(18) Samsel, E. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 4790.

Stereochemistry in Electrophilic Substitution (S_E') Reactions of Optically Active Allylfluorosilanes[1]

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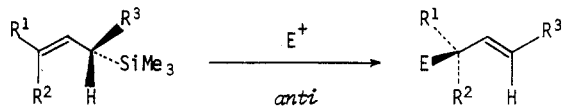
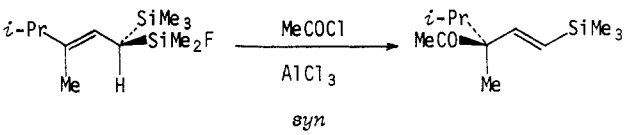
Summary: Electrophilic substitution reactions of optically active allylfluorosilanes, (*S*)-(*Z*)-MeCH=CHCH(SiF_nMe_{3-n})Ph (*n* = 1–3), with MeCOCl/$AlCl_3$ and *t*-BuCl/$TiCl_4$ were carried out. Reaction of the dimethylfluorosilane and methyldifluorosilane compounds proceeded with anti stereochemistry to give the corresponding S_E' products of *S* configuration while the trifluorosilane gave a low yield of racemic product in acetylation and was unreactive toward *tert*-butylation.

(1) Optically active Allylsilanes. 11. For part 10, see: Hayashi, T.; Konishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. Org. Chem.* **1986**, *51*, 3772.

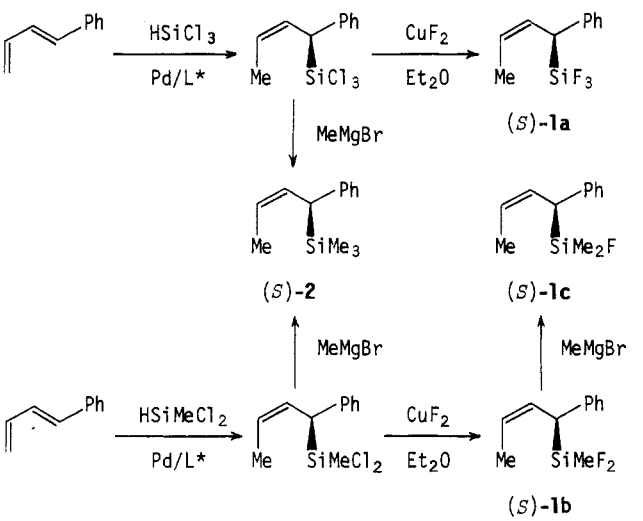
Scheme I



Scheme II



Scheme III



Electrophilic substitution reactions of allylsilanes with a net shift of the double bond (S_E') have been of synthetic and mechanistic interest.[2] We have recently demonstrated that the stereochemistry of the S_E' reaction is anti by using optically active allylsilanes that have a trimethylsilyl group at the chiral α-carbon atom (Scheme I).[3,4] On the other hand, syn stereochemistry has been reported in the reaction of an optically active allyl(dimethylfluoro)silane,[5] though this example seems to be an exceptional case because of the presence of two geminal silyl groups at the chiral carbon in the allylsilane (Scheme II). Use of a simple allylfluorosilane for the S_E' reaction would provide significant information about the general features of the stereochemical course. We have prepared a series of optically active allylsilanes containing trifluorosilyl, methyldifluorosilyl, and dimethylfluorosilyl groups and used them for the S_E' reactions to establish the stereochemistry.

Optically active allylfluorosilanes, (*S*)-(*Z*)-1-phenyl-1-(trifluorosilyl)-2-butene (**1a**)[6] ($[\alpha]_D^{20}$ +72.9° (*c* 2.52,

(2) For review: (a) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (b) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: London, 1981; pp 97–124. (d) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 173–205.
(3) (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4963. (c) Hayashi, T.; Ito, H.; Kumada, M. *Tetrahedron Lett.* **1982**, *23*, 4605. (d) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1983**, 736. (e) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661. (f) Hayashi, T.; Okamoto, Y.; Kabeta, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1984**, *49*, 4224.
(4) (a) Carter, M. J.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1976**, 679. (b) Fleming, I.; Terrett, N. K. *J. Organomet. Chem.* **1984**, *264*, 99. (c) Wickham, G.; Kitching, W. *J. Org. Chem.* **1983**, *48*, 612. (d) Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655.
(5) Wetter, H.; Scherer, P.; Schweizer, W. B. *Helv. Chim. Acta* **1979**, *62*, 1985.

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