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 $IrCl_3$.

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[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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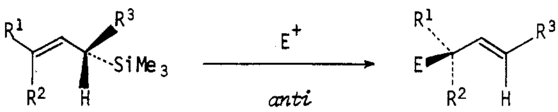
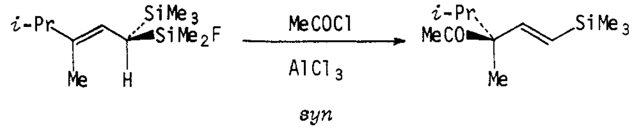
Summary: Electrophilic substitution reactions of optically active allylfluorosilanes, (*S*)-(*Z*)-MeCH=CHCH(SiF_nMe_{3-n})Ph (*n* = 1–3), with MeCOCl/$AlCl_3$ and *t*-BuCl/$TiCl_4$ were carried out. Reaction of the dimethylfluorosilane and methyldifluorosilane compounds proceeded with anti stereochemistry 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.

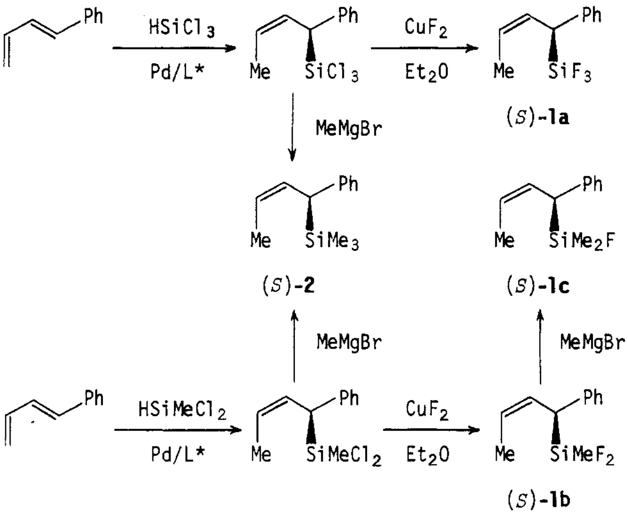
Scheme I



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,

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[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.

[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.

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Scheme IV

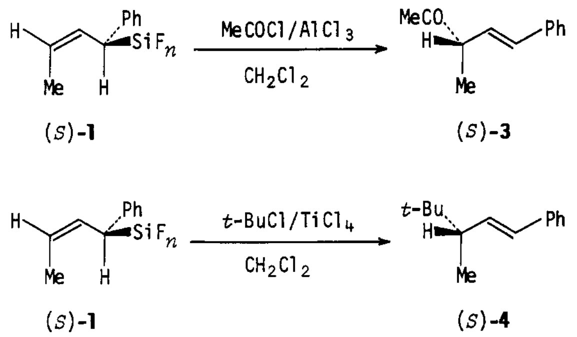

Table I. Electrophilic Reaction of the Allylfluorosilanes

entry	allylsilane (% ee)	electrophile	reaction time, min	yield,[a] %	product, (% ee)[b]
1	(*S*)-**1c** (26)	MeCOCl/AlCl$_3$[c]	20	88	(*S*)-**3** (24)
2		*t*-BuCl/TiCl$_4$[d]	1	73	(*S*)-**4** (29)
3	(*S*)-**1b** (26)	MeCOCl/AlCl$_3$	60	30	(*S*)-**3** (14)
4		*t*-BuCl/TiCl$_4$	3	59	(*S*)-**4** (29)
5	(*S*)-**1a** (37)	MeCOCl/AlCl$_3$	60	10	(*S*)-**3** (<5)
6		*t*-BuCl/TiCl$_4$	5	0	
7[e]	(*R*)-**2** (24)	MeCOCl/AlCl$_3$	5	74	(*R*)-**3** (19)
8[e]		*t*-BuCl/TiCl$_4$	1	75	(*R*)-**4** (27)

[a] Isolated yield by preparative TLC. [b] Determined by optical rotation data for **4** and by ^{1}H NMR analysis in the presence of Eu(dcm)$_3$ for **3**. The maximum rotations of (*S*)-**3** and (*S*)-**4** are $[\alpha]^{20}_D$ +289° (*c* 0.25, CCl$_4$) and −65° (*c* 1.0, CCl$_4$), respectively.[3a] [c] To a mixture of allylsilane and AlCl$_3$ (1.1 equiv) in dichloromethane was added MeCOCl (1.1 equiv) at −78 °C. The mixture was stirred at the same temperature for the given minutes and hydrolyzed with water. [d] To a solution of allylsilane and *tert*-BuCl (1.1 equiv) in dichloromethane was added TiCl$_4$ (1.1 equiv) at −78 °C. [e] These results have been reported previously in ref 3a.

benzene) 37% ee) and its methyldifluorosilyl analogue (*S*)-**1b**[7] ($[\alpha]_D^{20}$ +32.6° (*c* 2.95, benzene), 26% ee), were prepared by palladium- (PdCl$_2$[(*R*)-(*S*)-PPFA[8]]) catalyzed asymmetric hydrosilylation of 1-phenyl-1,3-butadiene[9] with trichlorosilane or methyldichlorosilane followed by fluorination[10] of the resulting allylchlorosilanes with CuF$_2$·2H$_2$O in ether (Scheme III). The enantiomeric purity and configuration of the allylsilanes **1a** and **1b** were determined by methylation of the allylchlorosilanes to give the known allyl(trimethyl)silane (*S*)-**2**.[3a] (*S*)-Allyl(dimethylfluoro)silane **1c**[11] ($[\alpha]_D^{20}$ +25.1° (*c* 2.77, benzene), 26% ee) was obtained by selective monomethylation of difluorosilane **1b**.

The optically active allylfluorosilanes were subjected to electrophilic substitution with MeCOCl/AlCl$_3$ and *t*-BuCl/TiCl$_4$ (Scheme IV). The results are summarized in Table I, which also contains data obtained[3a] in the reaction of allyl(trimethyl)silane **2** for comparison. The acetylation of dimethylfluorosilane (*S*)-**1c** in dichloromethane at −78 °C for 20 min gave (*E*)-3-acetyl-1-phenyl-1-butene (**3**) with *S* configuration of 24% ee in 88% yield (entry 1), and the *tert*-butylation gave a 73% yield of the (*E*)-olefin **4** of *S* configuration (29% ee) (entry 2). These results indicate that the electrophiles attacked the double bond of **1c** anti with respect to the leaving dimethylfluorosilyl group and the stereoselectivity and reactivity of **1c** are quite similar to those of the allyl(trimethyl)silane **2** (entries 7 and 8).[3a] Anti stereochemistry was also observed in the S$_E$′ reactions of methyldifluorosilane (*S*)-**1b**, though the chemical yields are rather low in both acetylation and *tert*-butylation and a significant loss of the enantiomeric purity was observed in the acetylation (entries 3 and 4). The trifluorosilane **1a** underwent electrophilic reactions with difficulty. Thus, the acetylation gave a low yield of the almost racemic product **3** that was contaminated with 15% of the *Z* isomer, and the S$_E$′ product was not formed at all in the *tert*-butylation (entries 5 and 6).

The results obtained above indicate that σ–π conjugative interaction between the carbon–silicon bond and the olefin π system,[12] which increases the electron density on the olefin and is responsible for the anti S$_E$′ reaction, is pronounced in dimethylfluorosilane **1c** as well as in the trimethylsilyl analogue. The σ–π conjugation is less important in the methyldifluorosilane and is not a factor in the trifluorosilane. This order seems to be consistent with the electronic nature of fluorosilyl groups (SiF$_n$R$_{3-n}$).

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(6) **1a**: ^{1}H NMR (CDCl$_3$) δ 1.719 (d, *J* = 5.4 Hz, 3 H), 3.759 (d, *J*. = 8.7 Hz, 1 H), 5.59–5.79 (m, 2 H) 7.15–7.36 (m, 5 H).

(7) Reaction of 1-phenylbutadiene with HSiMeCl$_2$ in the presence of 0.01 mol % of PdCl$_2$[(*R*)-(*S*)-PPFA] at 80 °C for 14 h gave 72% yield of (*S*)-(*Z*)-MeCH═CHCH(SiMeCl$_2$)Ph regio- and stereoselectively. **1b**: ^{1}H NMR (CDCl$_3$) δ 0.279 (t, *J* = 6.1 Hz, 3 H), 1.699 (md, *J* = 6.6 Hz, 3 H), 3.554 (td, *J* = 3.4, 10.4 Hz, 1 H), 5.677 (ddq, *J* = 0.9, 6.6, 10.6 Hz, 1 H), 5.758 (qt, *J* = 1.6, 10.6 Hz, 1 H), 7.17–7.33 (m, 5 H).

(8) (*R*)-(*S*)-PPFA stands for (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine.

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(11) Treatment of **1b** with 1 equiv of MeMgBr/Et$_2$O at 0 °C for 10 min followed by bulb-to-bulb distillation gave 89% yield of the monomethylated product. **1c**: ^{1}H NMR (CDCl$_3$) δ 0.162 and 0.178 (a pair of d, *J* = 7.2 Hz, 6 H), 1.677 (ddd, *J* = 0.4, 1.8, 6.8 Hz, 3 H), 3.443 (dd, *J* = 4.9, 11.1 Hz, 1 H) 5.599 (ddq, *J* = 1.0, 10.7, 6.8 Hz, 1 H) 5.814 (qt, *J* = 1.8, 10.9 Hz, 1 H), 7.11–7.29 (m, 5 H).

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Reaction of $(\eta^5\text{-}C_5Me_5)_2TiOC[{=}Re(CO)_4Re(CO)_5]CH_2CH_2$ with *tert*-Butyl Isocyanide: Molecular Structure of a New Zwitterionic Complex Involving (η^2-Imidoyl)titanium and Acyldirhenium Carbonyl Moieties

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Summary: Reaction of $(\eta^5\text{-}C_5Me_5)_2TiOC[{=}Re(CO)_4Re(CO)_5]CH_2CH_2$ (**1a**) and *tert*-butyl isocyanide results in the

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