

Reactivity of silylene complexes

Masaaki Okazaki,^a Hiromi Tobita^a and Hiroshi Ogino^{*b}

^a Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

^b Miyagi Study Center, The University of the Air, Sendai 980-8577, Japan

Received 28th October 2002, Accepted 27th November 2002

First published as an Advance Article on the web 23rd December 2002

The metal–silicon bond in silylene complexes is highly polarized in a $M^{\delta-}-Si^{\delta+}$ manner. Accordingly, silylene complexes show high reactivities toward nucleophiles, such as water, alcohols, ketones, isocyanates, and phosphorus ylides. The metal–silicon double bond can also activate aromatic carbon–hydrogen bonds. Among the various silylene complexes, silyl(silylene) complexes occupy a

unique position; these complexes undergo intramolecular 1,3-migration, which is postulated as a key step in the metal-mediated redistribution of substituents on organo-silicon compounds. Alkyl(silylene) complexes are not stable and undergo 1,2-alkyl migration to yield alkylsilyl complexes.



Masaaki Okazaki

Masaaki Okazaki was born in 1969 in Hiroshima, Japan. He received his BSc degree in 1992 and his MSc degree in 1994 from Tohoku University under the supervision of Professor Hiroshi Ogino. In 1996, he joined Professor Tatsuo Ido's group at the Cyclotron and Radioisotope Center, Tohoku University as a postdoctoral research associate. He received his PhD degree in 1997 from Tohoku University for his work on the synthesis and properties of electron-rich silyl and silylene iridium complexes under the supervision of Professor Hiroshi Ogino. In the same year, he joined Professor Hiroshi Ogino's group in Tohoku University as a research associate. In 1999, he joined Professor Keiji Morokuma's group at Emory University as a visiting scholar where he worked on theoretical studies of the reactivity of silylene complexes. In 2001, he moved to Professor Hiromi Tobita's group in Tohoku University. His research interest is in the area of synthesis, structure, and reactivity of organotransition metal complexes and clusters.



Hiromi Tobita

Hiromi Tobita was born in 1954 in Ibaraki, Japan. He received his PhD degree in 1982 from Tohoku University for work on tetrasilylethylene under the supervision of Professor Hideki Sakurai. In the same year, he joined Professor Satoru Masamune's group in Massachusetts Institute of Technology as a postdoctoral research associate where he worked on the synthesis of disilenes and silacycles. In 1984, he moved to Professor Masamune's group in Institute for Fundamental Research, Kao Corporation. In 1985, he joined Professor Hiroshi Ogino's group in Tohoku University as a research associate and started his research on transition metal chemistry. He was promoted to Associate Professor in 1992 and full Professor in 2001. He received the Chemical Society of Japan Award for Young Chemists in 1988. His main research interests involve synthesis, structure and reactivity of organo-transition-metal compounds: mono- and di-nuclear silylene, germylene and phosphido complexes, and metal-chalcogen clusters.



Hiroshi Ogino

Hiroshi Ogino was born in Matsue in 1938. He received his MSc and DrSc degrees from Tohoku University. He became an Associate Professor in 1968 and was promoted to Professor in 1983 at Tohoku University. He worked as the Dean of the Graduate School of Science and Faculty of Science from 1996 to 1999. From 1968–1969 he was a postdoctoral fellow at the University of Illinois with Professor John C. Bailar Jr. In 1993, he worked at the Université Louis Pasteur in Strasbourg, France as an invited Professor and in 1990 and 1994, worked at the Consortium of the University of the Philippines, Ateneo de Manila University and De La Salle University as an invited Professor. In 2001, he moved to the University of the Air, where he was appointed Director of the Miyagi Study Center. He is a member of the International Advisory Editorial Board of Dalton Transactions, and has served as a member of the International Advisory Editorial Boards of Organometallics. From 1996 to 2000 he was President of the Society of Coordination Chemistry, Japan, and from 2000 to 2002 he was President of the Society of Silicon Chemistry, Japan. He received the Award of the Chemical Society of Japan for Distinguished Young Chemists in 1970 and the Award of the Chemical Society of Japan in 2001. His main research interests are in the synthesis, structure and reactivity of organometallic and inorganometallic compounds.

1. Introduction

Over the past few decades, considerable attention has been focused on the chemistry of silylene complexes with metal–silicon double bonds,¹ which could participate in various transformation reactions of organosilicon compounds, such as dehydrogenative coupling of hydrosilanes,² redistribution of substituents on silicon atoms,³ Rochow's direct process,⁴ and silylene transfer to unsaturated organic compounds.⁵ Since silylene complexes can provide valuable information for these transformation reactions, preparation of transition-metal silylene complexes have proven to be an important synthetic target. Significant development was attained in 1987, in which two base-stabilized silylene complexes $(\text{CO})_4\text{Fe}=\text{Si}(\text{O}^t\text{Bu})_2 \cdot \text{HMPA}$ (**1**, HMPA = hexamethylphosphoramide)⁶ and $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{SiPh}_2 \cdot \text{NCMe}](\text{BPh}_4)$ (**2**)⁷ were independently synthesized and characterized by X-ray diffraction studies (Scheme 1). In 1988, we reported on the synthesis of a unique type of silylene complex, specifically base-stabilized bis(silylene) complex $\text{Cp}^*(\text{CO})\text{Fe}[\text{SiMe}_2 \cdots \text{OMe} \cdots \text{SiMe}(\text{OMe})]$ (**3**).⁸ Subsequently, not only the related adducts, but also base-free silylene complexes, have been synthesized.⁹ Herein we present a timely review of the reactivities of these silylene complexes.

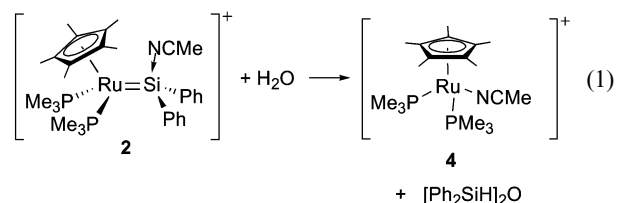
2. Nucleophilic attack on the silylene silicon atom

Reactivity of silylene complexes is intriguing to investigate, not only because of the practical applications toward transformation reactions of organosilicon compounds, but also by providing insight to our understanding of the unique bonding. Theoretical studies on silylene complexes have predicted that silylene complexes, in which the metal–silicon bonds are highly polarized in a $\text{M}^{\delta-}-\text{Si}^{\delta+}$ manner, are more reactive than the comparable Fischer-type carbene complexes.¹⁰ Taking into account this highly polarized nature, the metal–silicon double bond is expected to be highly reactive towards various nucleophiles.

2.1. Reactions with water

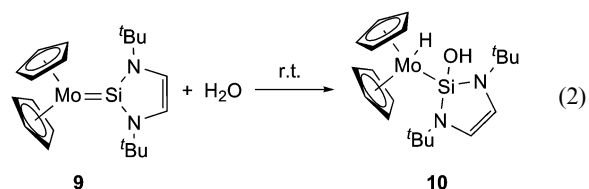
Most silylene complexes show high reactivities toward moisture. Furthermore, reactions with water usually result in a complex mixture of products, which is attributable to additional reactions of the resulting hydroxysilyl complexes with water, as well as condensations, to form siloxane bonds. In some cases, the product(s) have been characterized (Table 1).

Base-stabilized silylen ruthenium complex **2** reacted with water to produce acetonitrileruthenium complex **4** and disiloxane $[\text{Ph}_2\text{SiH}]_2\text{O}$ [eqn. (1)].¹¹



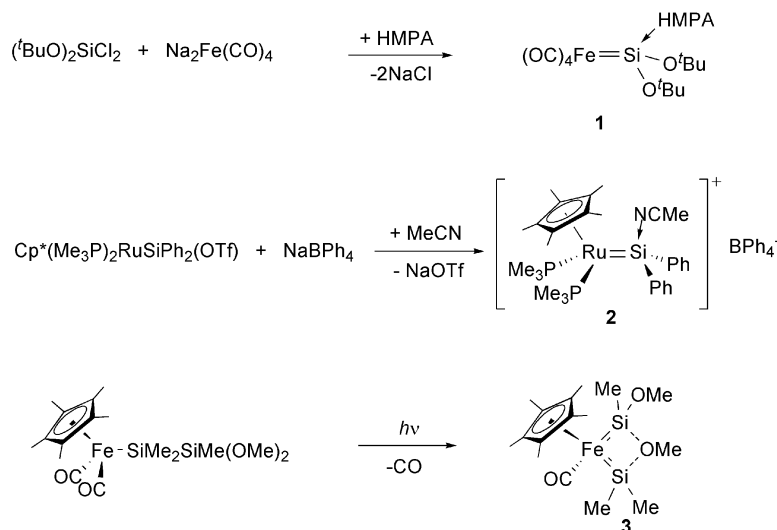
The reaction was initiated by the nucleophilic attack of the water oxygen on the electron-deficient silylene silicon atom, followed by cleavage of the silicon–ruthenium bond. In contrast, treatment of methoxy-bridged bis(silylene)ruthenium complex **5** with water did not result in the cleavage of the ruthenium–silicon bond, but rather rapidly yielded metallacycle **6**, followed by a very slow conversion to tetrasiloxane complex $[\text{Cp}(\text{Ph}_3\text{P})\text{Ru}(\text{H})_2\text{SiMe}_2\text{OSiMe}_2]_2\text{O}$ (**7**) in the presence of excess water (Scheme 2).¹² As illustrated in Scheme 3, a plausible mechanism to explain the formation of **6** and **7** from the reaction between **5** and water involves a nucleophilic attack of the water oxygen at one of the silylene ligands to give water addition product **8**. Subsequently, intramolecular condensation with elimination of MeOH affords metallacycle **6**, which undergoes another nucleophilic attack of water on the silyl silicon atom to give the ring-opened product. Finally, dehydration between two molecules affords condensation product **7**.

Jutzi *et al.* have reported that the hydrolysis of silylene-molybdenum complex **9** afforded hydrido(hydroxysilyl)molybdenum complex **10** via regioselective 1,2-addition of water to the molybdenum–silicon double bond [eqn. (2)].¹⁴ Complex **10** is a water addition product, and is analogous to **8** in Scheme 3.



2.2. Reactions with alcohols

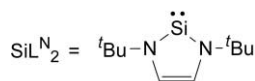
Silylene complexes are also highly reactive towards alcohols (Table 2). Treatment of **2** in dichloromethane with excess ROH (R = Me, Et, ^tBu) led to the rapid and quantitative formation of acetonitrileruthenium complex **4** and alkoxyhydrosilane $\text{HSi-Ph}_2\text{OR}$ [eqn. (3)].¹⁵



Scheme 1

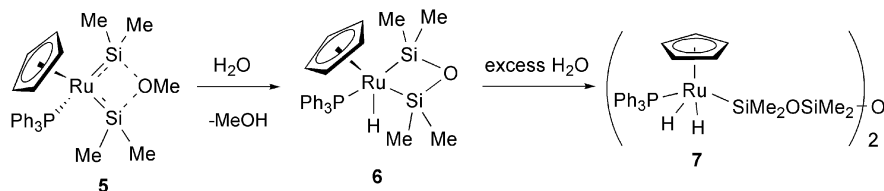
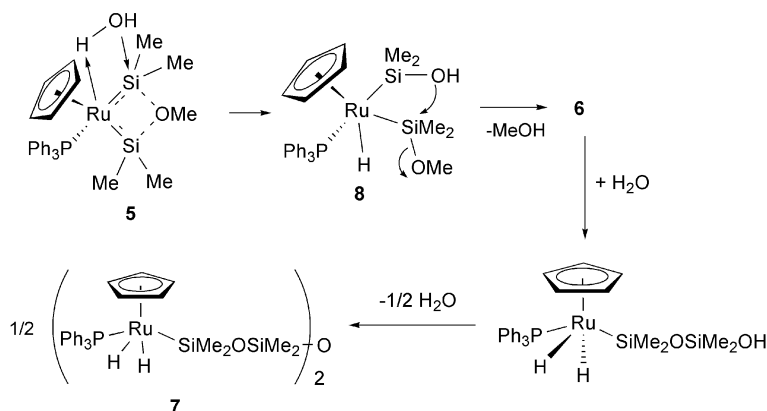
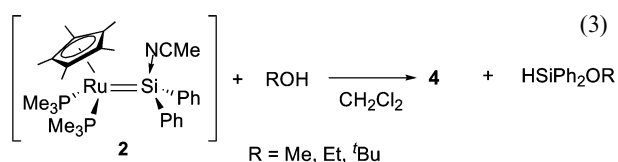
Table 1 Reactivity of silylene complexes towards water

Silylene complexes	Conditions	Products	Ref.
$[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{SiPh}_2\cdot\text{NCMe}]\text{BPh}_4$	rt	$[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}(\text{NCMe})]\text{BPh}_4 + [\text{Ph}_2\text{SiH}]_2\text{O}$	11
$\text{Cp}(\text{PPh}_3)\text{Ru}\{\text{QSiMe}_2 \cdots \text{O}(\text{Me}) \cdots \text{SiMe}_2\}$	rt	$\text{Cp}(\text{PPh}_3)\text{Ru}(\text{H})(\text{SiMe}_2\text{OSiMe}_2) + \text{MeOH}$	12
$(\text{PCy}_3)_2\text{Pt}=\text{SiMe}_2$	rt, excess H_2O	$\{\text{Cp}(\text{PPh}_3)(\text{H})_2\text{RuSiMe}_2\text{OSiMe}_2\}_2\text{O} + \text{MeOH}$	12
$\text{Cp}_2\text{Mo}=\text{SiL}^{\text{N}}_2$	rt	$\text{Pt}(\text{PCy}_3)_2 + \text{Mes}_2\text{SiH}(\text{OH})$	13
		$\text{Cp}_2\text{MoH}(\text{SiL}^{\text{N}}_2\text{OH})$	14

**Table 2** Reactivity of silylene complexes towards alcohol

Silylene complexes	Conditions	Products	Ref.
$[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}=\text{SiPh}_2\cdot\text{NCMe}]\text{BPh}_4$	rt, ROH (R = Me, Et, ^tBu)	$[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}(\text{NCMe})]\text{BPh}_4 + \text{HSiPh}_2\text{OR}$	15
$\text{Cp}^*(\text{CO})\text{Fe}\{\text{SiMe}_2 \cdots \text{O}(\text{Me}) \cdots \text{SiMe}_2\}$	rt, MeOH	$\text{Cp}^*(\text{CO})\text{FeH}(\text{SiMe}_2\text{OMe})_2$	16
$(\text{CO})_4\text{Fe}=\text{SiPh}_2\cdot\text{DMI}$	$h\nu$, excess MeOH	$\text{Ph}_2\text{Si}(\text{OMe})_2$	17
	$h\nu$, excess $^t\text{BuOH}$	$\text{Ph}_2\text{SiH}(\text{O}^t\text{Bu})$	17
$(\text{CO})_4\text{Fe}=\text{SiHAr}\cdot\text{DMI}$ (Ar = Ph, 1-Np)	rt, MeOH	$\text{ArSi}(\text{OMe})_3$	18
	rt, $^t\text{BuOH}$	$\text{ArHSi}(\text{O}^t\text{Bu})_2$	18
$[(\text{CO})_4\text{Fe}=\text{SiPhAr}^{\text{N}}](\text{PF}_6)$	$h\nu$, excess MeOH, dppe	$(\text{CO})_3\text{Fe}(\text{dppe}) + \text{Ar}^{\text{N}}\text{PhSi}(\text{OMe})_2$	17
	$h\nu$, excess $^t\text{BuOH}$, dppe	$(\text{CO})_3\text{Fe}(\text{dppe}) + \text{Ar}^{\text{N}}\text{PhSiH}(\text{O}^t\text{Bu})$	17
$\text{Cp}(\text{CO})_2\text{Fe}=\text{SiMeAr}^{\text{N}}$	rt, MeOH	$[\text{Cp}(\text{CO})_2\text{SiMe}(\text{OMe})\{2-(\text{Me}_2\text{N}(\text{H})\text{CH}_2)\text{C}_6\text{H}_4\}](\text{PF}_6)$	19
$\text{Cp}(\text{PPh}_3)\text{Ru}\{\text{SiMe}_2 \cdots \text{O}(\text{Me}) \cdots \text{SiMe}_2\}$	rt, MeOH	$\text{Cp}(\text{PPh}_3)\text{RuH}(\text{SiMe}_2\text{OMe})_2$	12
	rt, excess MeOH	$\text{Cp}(\text{PPh}_3)\text{RuH}_2(\text{SiMe}_2\text{OMe}) + \text{SiMe}_2(\text{OMe})_2$	12
$(\text{PCy}_3)_2\text{Pt}=\text{SiMe}_2$	rt, ROH (R = Me, Et)	$\text{Pt}(\text{PCy}_3)_2 + \text{Mes}_2\text{SiH}(\text{OR})$	13
$\text{Cp}^*(\text{CO})\text{Fe}\{\text{SiMe}_2 \cdots \{\text{O}(2-\text{C}_5\text{H}_4\text{N})\} \cdots \text{SiMe}_2\}$	rt, 2-hydroxypyridine	$\text{Cp}^*(\text{CO})\text{FeH}\{\text{SiMe}_2\text{O}(2-\text{C}_5\text{H}_4\text{N})_2\}$	20

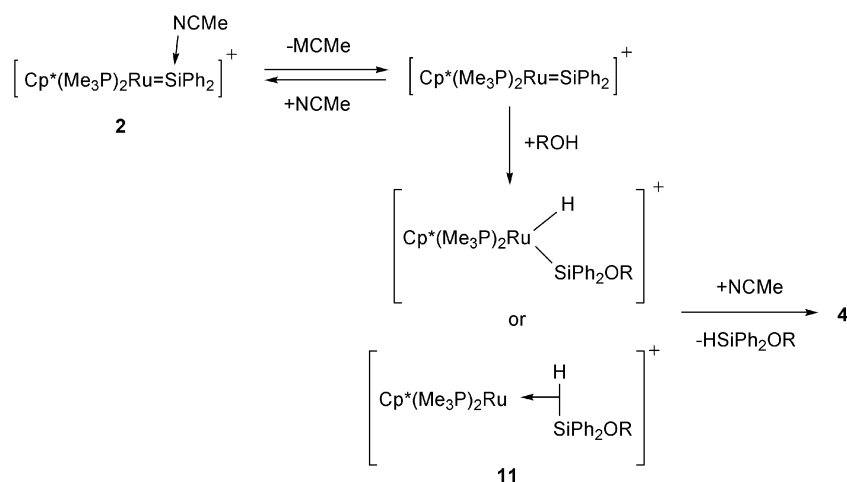
$\text{Ar}^{\text{N}} = 2-(\text{Me}_2\text{NCH}_2\text{C}_6\text{H}_4)$; DMI = 1,3-dimethylimidazolidinone.

**Scheme 2****Scheme 3**

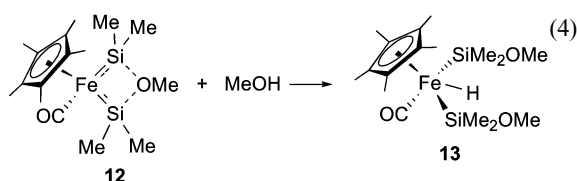
It was shown using variable temperature NMR studies that the reaction proceeded at -60°C , through the formation of intermediate **11**, in which the ruthenium–silicon bond was

maintained (Scheme 4). Intermediate **11** was tentatively assigned to either oxidative addition product, *cis*- $[\text{Cp}^*(\text{PMe}_3)_2\text{Ru}(\text{H})\text{SiPh}_2\text{OR}]\text{BPh}_4$, or a complex containing $\eta^2\text{-HSiPh}_2\text{OR}$ as a ligand. As the temperature was raised above -60°C , intermediate **11** was converted to a mixture of **4** and HSiPh_2OR [$t_{1/2} = 40$ min at -40°C].

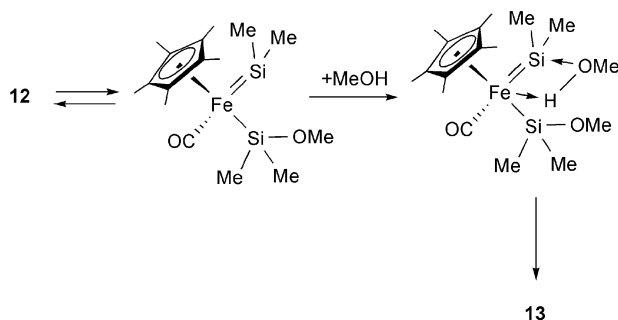
Reaction between methoxy-bridged bis(silylene)iron complex **12** and MeOH afforded a thermally stable product, hydrido-bis(methoxysilyl)iron complex $\text{Cp}^*(\text{CO})\text{FeH}(\text{SiMe}_2\text{OMe})_2$ (**13**) [eqn. (4)],¹⁶



Scheme 4



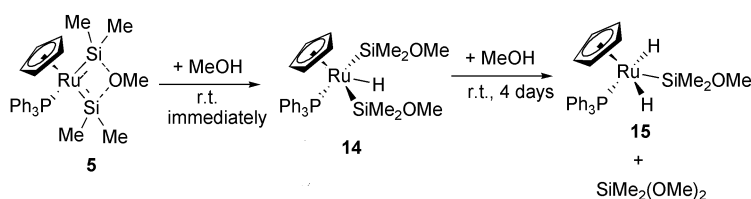
which can be regarded as a 1,2-MeOH addition product across the iron–silicon double bond (Scheme 5).



Scheme 5

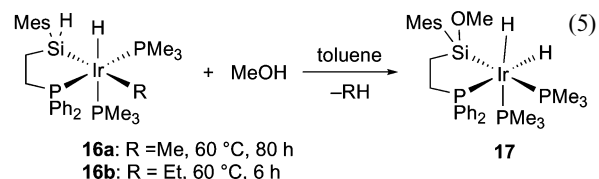
For studies on the reactivity of methoxy-bridged bis(silylene)ruthenium complex **5** toward MeOH, addition of MeOH to a benzene solution of **5** resulted in the immediate formation of hydridobis(methoxysilyl)ruthenium complex **14** in good yield (Scheme 6).¹² When the reaction mixture of **14** in C₆D₆ was allowed to stand in the presence of excess MeOH at room temperature for 4 days, complex **14** was converted to a mixture of dihydrido(methoxysilyl) complex **15** and SiMe₂(OMe)₂. In the secondary reaction, one of the silyl ligands in **14** apparently undergoes nucleophilic attack by MeOH, resulting in the cleavage of the ruthenium–silicon bond.

Based on these experimental results, alcohols have since been recognized as efficient trapping agents of transient transition-

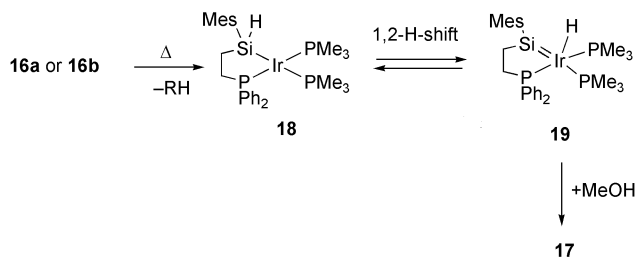


Scheme 6

metal silylene complexes (Table 3). Thermal reaction of **16** in the presence of MeOH to afford dihydrido(methoxysilyl)iridium(III) complex **17**, in quantitative yield [eqn. (5)],



can be explained using the transient formation of hydrido(silylene)iridium(I) complex **19**, as shown in Scheme 7.²² The



Scheme 7

mechanism initially involves the generation of coordinatively unsaturated (hydrosilyl)iridium(I) complex **18** via reductive elimination of the alkane, followed by the subsequent 1,2-hydride-migration from silicon to iridium to produce **19**, which is then trapped by MeOH to give **17**.

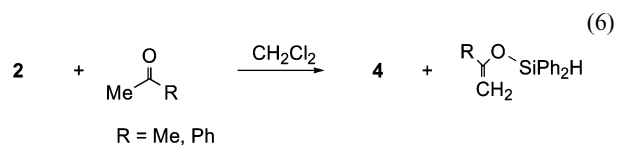
2.3. Reactions with polar unsaturated compounds

Reactivities of silylene complexes toward several polar unsaturated compounds have been examined. Reactions of silylene complex **2** with enolizable ketones provided acetonitrile-coordinated complex **4** and silyl enol ethers in quantitative yields [eqn. (6)],

Table 3 Alcohol trapping of transiently generated silylene complexes

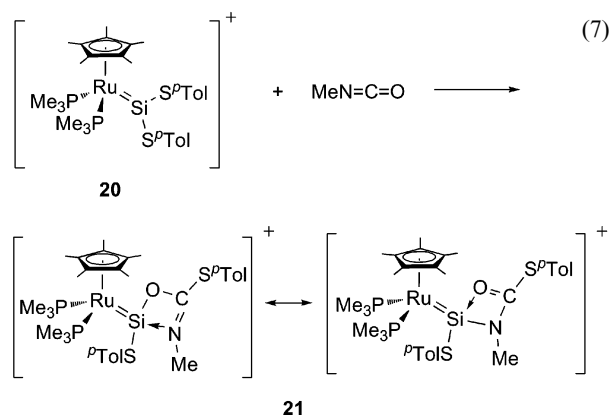
Reactants	Conditions	Proposed silylene intermediate	Products	Ref.
FpSiMe ₂ SiMe ₂ OMe + MeOH	<i>hν</i>	Cp(CO)Fe(SiMe ₂ ... O(Me) ... SiMe ₂)	Cp(CO)FeH(SiMe ₂ OMe) ₂ (55%) + FpSiMe ₂ OMe (13%) + Fp ₂ (12%) + MeOSiMe ₂ H (9%)	21
IrH(R)(η ² -Mes(H)Si(CH ₂) ₂ PPh ₂)(PMe ₃) ₂ + MeOH (R = Me, Et)	60 °C	IrH(η ² -MesSi(CH ₂) ₂ PPh ₂)(PMe ₃)	IrH ₂ (η ² -Mes(MeO)Si(CH ₂) ₂ PPh ₂)(PMe ₃) ₂	22
L _n IrH(SiMe ₂ SiMe ₃)(PMe ₃) + MeOH	45 °C	L _n IrH(SiMe ₃)(=SiMe ₂)	L _n IrH(SiMe ₂ OMe)(PMe ₃)	23
L _n Ir(Me)(H)(PMe ₃) + H ₃ SiR + MeOH (R = <i>n</i> -C ₄ H ₉ , <i>n</i> -C ₃ H ₇ , <i>n</i> -C ₂ H ₅ , <i>n</i> -C ₁ H ₃)	45 °C	L _n IrH ₂ (=SiRH)	L _n Ir(Me)(H)(PMe ₃) + HSiR(OMe) ₂ + H ₂	24

Fp = Cp(CO)₂Fe; L_n = {η²-Me₂Si(CH₂)₂PPh₂}(PMe₃).



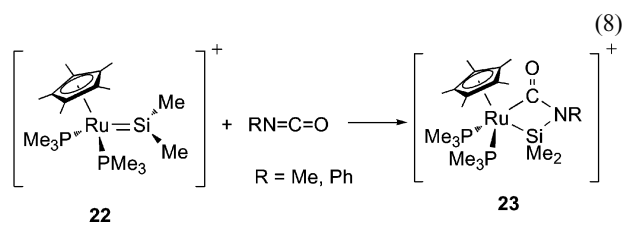
and although intermediates have not been observed, the authors have assumed that coordination of the carbonyl moiety of the ketones to the electron-deficient silylene silicon atom is critical.¹⁵

Methyl isocyanate reacted cleanly with silyleneruthenium complex **20** to form **21** [eqn. (7)].²⁵

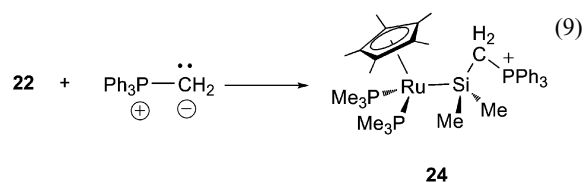


Although the detailed structure of **21** is unclear, it is certain that **21** was formed *via* 1,2-dipolar addition to the silicon–sulfur bond of **20** across the isocyanate moiety. Complex **21** can be regarded as a base-stabilized silylene complex.

In contrast to complex **20**, treatment of dimethylsilylene complex **22** with methyl and phenyl isocyanate led to a rapid and quantitative formation of the 2 + 2 cycloaddition product **23** [eqn. (8)].²⁵



Reaction of **22** with ylide CH₂PPh₃ proceeded spontaneously to afford pure product **24**, in which the ylide was coordinated to the silylene ligand through the carbon atom [eqn. (9)].²⁶



The X-ray crystal structure analysis described complex **24** as a cationic silyl ruthenium complex with the positive charge localized on the phosphorus atom.

3. Reactions with HX (X = Cl, H, SiR₃)

3.1. Reaction with hydrogen chloride

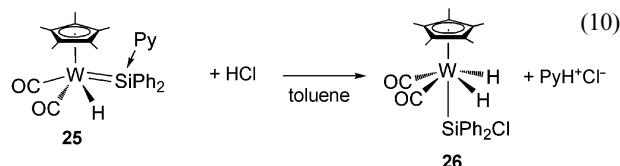
Pyridine-stabilized silylenetungsten complex, Cp*(CO)₂HW=SiPh₂·Py (**25**), reacted rapidly with HCl to give the 1,2-addition product, Cp*(CO)₂H₂W(SiPh₂Cl) (**26**) [eqn. (10)], in which

Table 4 Dissociation of silylene fragments from silylene complexes

Silylene complexes	Conditions	Products	Ref.
(OC) ₄ Fe=SiR ₂ ·HMPA (R = Me, O ^t Bu)	120 °C <i>hν</i> , PPh ₃	Polysilanes (<i>M_n</i> = 550 ± 10) + Fe ₃ (CO) ₁₂	31a
(OC) ₄ Fe=SiR ₂ ·HMPA (R = O ^t Bu, S ^t Bu)	<i>hν</i> , 2,3-dimethylbutadiene	Fe(CO) ₃ (PPh ₃) ₂ + polysilanes	31a
(CO) ₅ Cr=Si(O ^t Bu) ₂ ·HMPA	<i>hν</i> , PPh ₃	silacyclopentene + (2,3-dimethylbutadiene)Fe(CO) ₃	31c
(OC) ₅ Cr=Si ^t Bu ₂ ·HMPA·Na(CF ₃ SO ₃)·2THF	<i>hν</i> , PPh ₃	Cr(CO) ₄ (PPh ₃) ₂ + polysilanes	31a
(OC) ₄ Fe=SiPh ₂ ·DMI	pyr CO	Cr(CO) ₅ (pyr) + (Si ^t Bu ₂) ₃	31d
(OC) ₄ Fe=SiPh ₂ ·DMI	<i>hν</i> , 2,3-dimethylbutadiene <i>hν</i> , Et–C≡C–Et	Cr(CO) ₆ + (Si ^t Bu ₂) ₃	31d
(CO) ₄ Fe=SiPh(Ar ^N)	<i>hν</i> , MeOH (excess), dppe	silacyclopentene	17
(Cy ₃ P) ₂ Pt=SiMes ₂	<i>hν</i> , Et–C≡C–Et	silole [diphenyl-1,2,3,4-tetraethylsilacyclopent-2,4-diene]	17
Pd(SiL ^N) ₂	120 °C, 0.1 mmHg	(SiPh ₂) _{<i>n</i>} (<i>n</i> = 3, 5, 6)	17
(OC) ₄ Fe=SiPh(Ar ^N)	<i>hν</i> , MeOH (excess), dppe	Ph(Ar ^N)Si(OMe) ₂ + Fe(CO) ₃ (dppe)	17
(Cy ₃ P) ₂ Pt=SiMes ₂	<i>hν</i> , ^t BuOH, dppe	Ph(Ar ^N)SiO ^t Bu(H)	17
Pd(SiL ^N) ₂	R ₂ P(CH ₂) ₂ PR ₂ (R = Ph, ^t Pr) or PMe ₃	PtL _{<i>n</i>} + “SiMes ₂ ” (L _{<i>n</i>} = (R ₂ P(CH ₂) ₂ PR ₂) ₂ or (PMe ₃) ₄)	13
Pd(SiL ^N) ₂	rt	SiL ^N ₂ + Pd ₂ (μ-SiL ^N) ₂ (SiL ^N) ₂	32

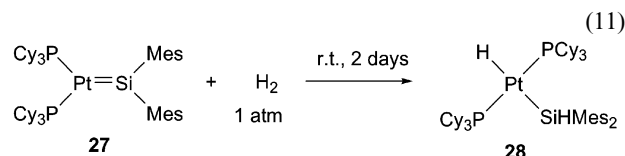
HMPA = Hexamethylphosphoric triamide; Ar^N = 2-(Me₂NCH₂)C₆H₄; pyr = pyridine; dppe = Ph₂P(CH₂)₂PPh₂.

the orientation of the 1,2-addition was consistent with the M^{δ-}=Si^{δ+} polarization.²⁷

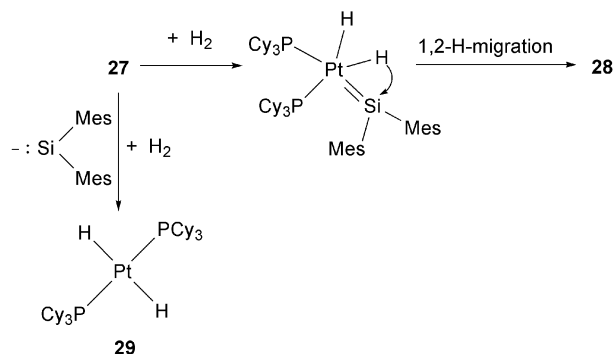


3.2. Reaction with hydrogen

The formation of hydrido(hydrosilyl)platinum(II) complex **28** from platinum(0) silylene complex **27** and H₂ (1 atm) was demonstrated by Tilley *et al.* [eqn. (11)].¹³



As shown in Scheme 8, a mechanism was proposed that involved the oxidative addition of dihydrogen to the metal center, followed by 1,2-hydride migration to the silylene ligand. Competing with this reaction, simultaneous decomposition of **27**



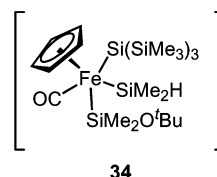
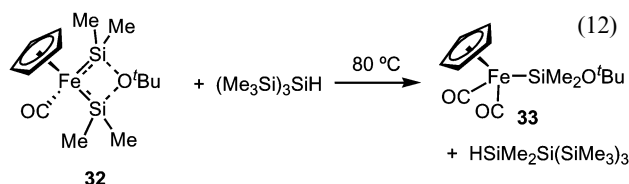
Scheme 8

occurred *via* loss of the :SiMes₂ fragment to form *trans*-(Cy₃P)₂PtH₂ (**29**) in 50% yield.

3.3. Reactions with hydrosilanes

Reaction of pyridine-stabilized silylenetungsten complex Cp*(CO)₂W(H)(=SiEt₂·Py) (**30**) with MePhSiH₂ led to the formation of silylene exchange product Cp*(CO)₂W(H)(=SiMePh·Py) (**31**) and Et₂SiH₂.²⁸ To account for this silylene exchange reaction, a four-center transition state *via* interaction between the Si–H bond of the dihydrosilane and the tungsten–silicon double bond has been proposed (Scheme 9).

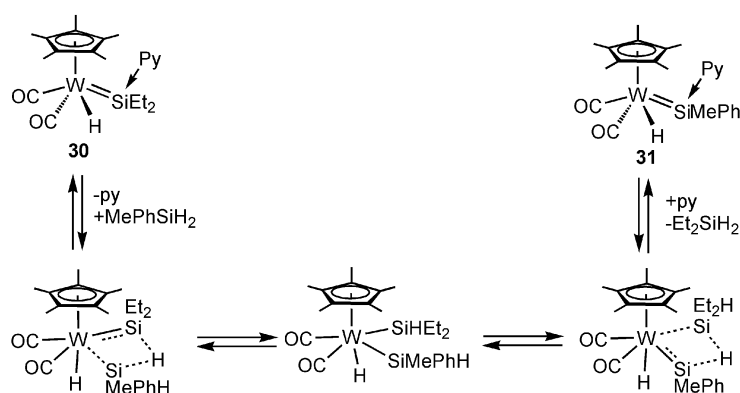
Base-stabilized bis(silylene)iron complex **32** reacted with hydrosilane (Me₃Si)₃SiH at 80 °C to form Cp(CO)₂FeSiMe₂O^tBu (**33**) and HSiMe₂Si(SiMe₃)₃ [eqn. (12)].²⁹ The proposed mechanism for this reaction involves a four-membered ring opening,³⁰ followed by an addition of SiH to the iron–silicon double bond to form intermediate **34** which subsequently results in reductive elimination of disilane and coordination of CO, which is liberated from decomposition pathways of the complexes, to produce **33**.



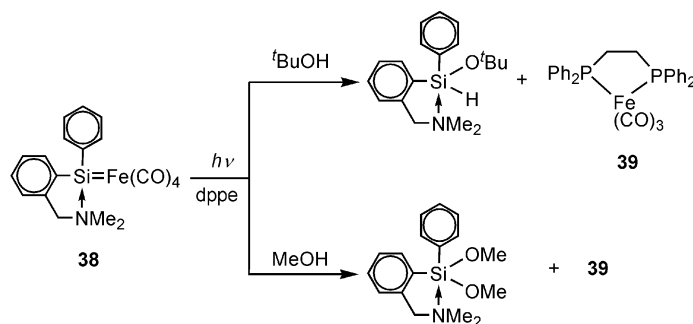
4. Dissociation of silylene fragments from the metal center

For some silylene complexes, the silylene fragment dissociated under thermal or photochemical conditions (Table 4).

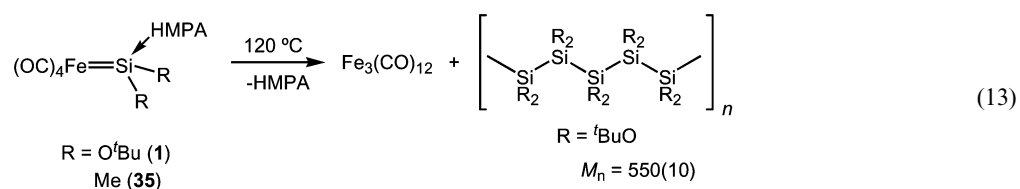
Zybill *et al.* reported that heating (OC)₄Fe=SiR₂·HMPA (**1** or **35**) at 120 °C (10⁻⁴ bar) caused the dissociation of HMPA to give Fe₃(CO)₁₂ and polysilanes [eqn. (13)].^{31a}



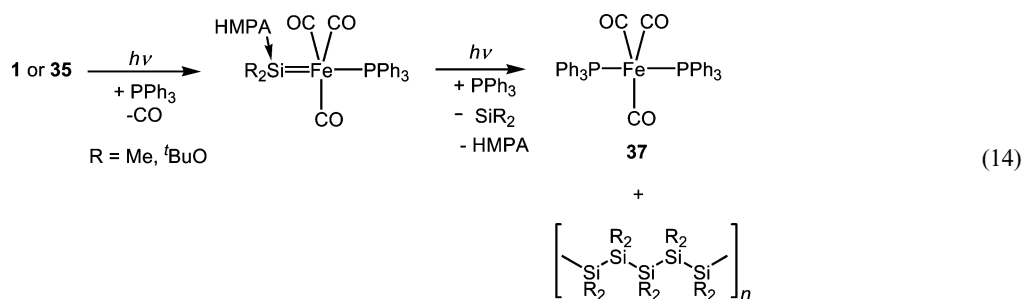
Scheme 9



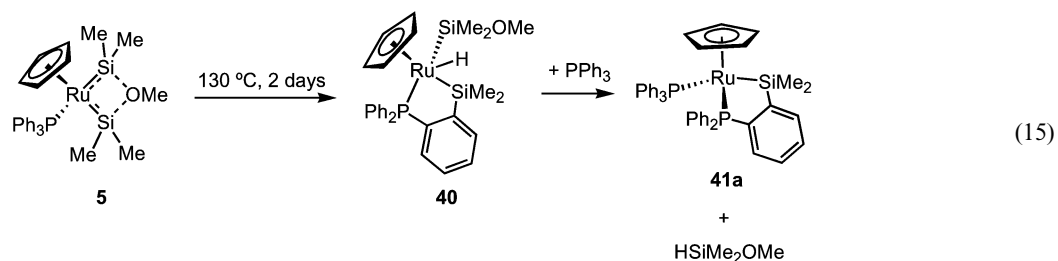
Scheme 10



(13)



(14)

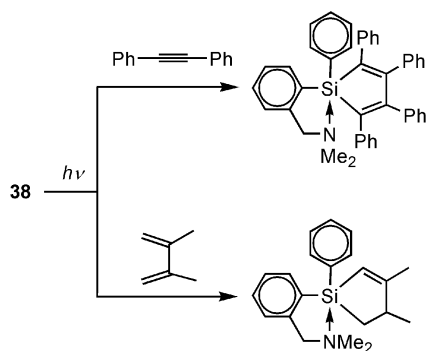


(15)

During the thermal reaction of **35** ($\text{R} = \text{Me}$), transient formation of silylene-bridged diiron complex $[\text{Fe}(\text{CO})_4]_2(\mu\text{-SiMe}_2)_2$ (**36**) was observed.^{31b} Under photochemical conditions, the apical CO and silylene ligands of **1** and **35** were displaced stepwise by triphenylphosphine [eqn. (14)], in which the silylene fragments were converted into polysilanes.^{31a}

In contrast to the examples mentioned above, intramolecularly base-stabilized silylene(carbonyl) complex **38** was less

reactive towards alcohol. However, UV-photolysis in the presence of dppe induces the reaction to give dppe-coordinated iron complex **39** and alkoxy-silanes (Scheme 10).¹⁷ It was likely that free silylene species were generated upon photolysis and trapped with alcohols. Free silylene fragments that were generated from **38** upon photolysis were also trapped using acetylene and 2,3-dimethylbutadiene (Scheme 11).

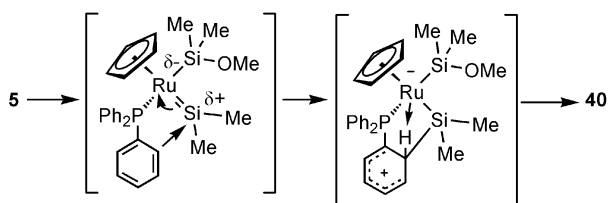


Scheme 11

5. Carbon–hydrogen bond activation by the transition metal–silicon double bond

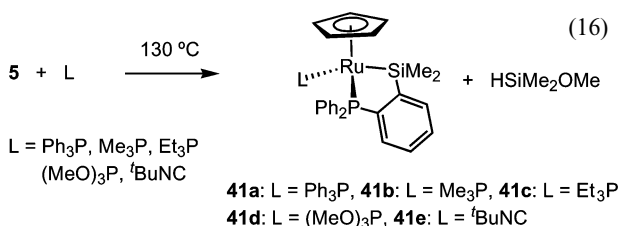
Intramolecular C–H bond can be activated by ruthenium–silicon double bonds.³³ When a solution of methoxy-bridged bis(silylene)ruthenium complex **5** was heated in a sealed tube at 130 °C, a five-membered silametallacycle **40** was formed [eqn. (15)].

The sequence of steps to account for this remarkable carbon–hydrogen bond activation is shown in Scheme 12. The four-

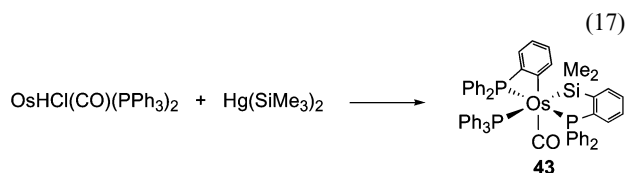


Scheme 12

membered ring opening of bis(silylene) complex **5** at the elevated temperature generates the base-free silyl(silylene) complex.³⁰ As a result, the electron-deficient silylene silicon atom electrophilically attacks the *ortho*-carbon of a phenyl group of the PPh₃ ligand. The proton on the *ortho* position subsequently migrates to the electronegative ruthenium center to give **40**. Heating a solution of **40** and PPh₃ resulted in complex **41a** and HSiMe₂OMe [eqn. (15)]. Thermolysis of **5** in the presence of various two-electron-donor ligands at 130 °C directly gave **41a–e** [eqn. (16)].



For the reaction of OsHCl(CO)(PPh₃)₂ and Hg(SiMe₃)₂, silylene complex OsHCl(=SiMe₂)(CO)(PPh₃) (**42**) is postulated as a key intermediate to give intramolecular C–H bond activation product **43** [eqn. (17)].³⁴



6. Reaction with chloroalkanes

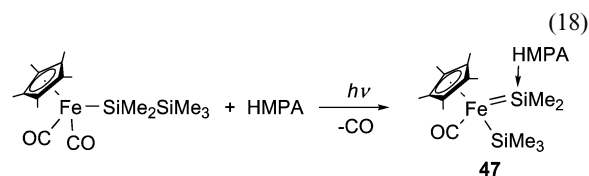
In the direct processes, the silylene fragments are believed to be generated on the surface to react with chloroalkanes to give alkyl(chloro)silanes, and therefore, silylene complexes may serve as a good model for surface-bound silylene fragments.⁴ Dissolving solid silyleneosmium complex [Cp*(Me₃P)₂Os=SiMe₂]B(C₆F₅)₄ (**44**) in CH₂Cl₂ resulted in a complex mixture of compounds, including paramagnetic species.³⁵ Immediate addition of reducing agent Cp₂Co to this mixture afforded Cp*(Me₃P)₂OsSiMe₂Cl (**45**) as a major product. A proposed mechanism involves a radical-based step, in which the silylene silicon atom possessing Lewis acidity abstracts a chloride from CH₂Cl₂, whereas the osmium center is oxidized from the +II to the +III state. The resulting paramagnetic intermediate [Cp*(Me₃P)₂OsSiMe₂Cl]⁺ (**46**) is reduced by Cp₂Co to produce **45**.

7. Rearrangement of substituents on silyl(silylene) complexes

7.1. 1,3-Migration on silyl(silylene) complexes

The photolysis reactions of FpSiMe₂SiR₃ [Fp = Cp(CO)₂Fe, R₃ = Ph₃, MeEt₂] to produce three types of monosilyliron complexes, FpSiPh₃, FpSiMePh₂ and FpSiMe₂Ph for R₃ = Ph₃ and FpSiMe₃, FpSiMe₂Et and FpSiMeEt₂ for R₃ = MeEt₂, have been reported by Pannell *et al.*³⁶ and our laboratories.^{30a,37} As outlined in Scheme 13, a suggested mechanism for the photolysis of FpSiMe₂SiMeEt₂ involves four successive reactions: (i) photochemically induced dissociation of one carbonyl ligand, (ii) 1,2-silyl migration to generate a silyl(silylene) complex, (iii) 1,3-alkyl-migrations from the silyl group to the silylene group and (iv) silylene displacement by CO. It is likely that the proposed silyl(silylene) intermediates are stabilized by the electron-donating group. Observations that the photolysis of FpSiMe₂SiMe(OMe)₂, which contains internal donors, can result in the formation of methoxy-bridged bis(silylene) complex **3** (Scheme 1) support the mechanism in Scheme 13.⁸ Related base-stabilized bis(silylene), (silylene)(germylene) and bis(germylene) complexes have also been isolated for Ta,³⁸ Cr,^{30d} Mo,^{30d} W,^{30c} Mn,³⁹ Fe,^{8,40} Ru,^{30e,41,42} Os⁴² and Ir²³ (Fig. 1).

Silyl(silylene) complexes that are generated upon photolysis can also be stabilized by an external base. Irradiation of a toluene-*d*₈ solution of Cp*(CO)₂FeSiMe₂SiMe₃ and HMPA afforded HMPA-stabilized silyl(silylene) complex Cp*(CO)-Fe(=SiMe₂·HMPA)SiMe₃ (**47**) [eqn. (18)].⁴³



1,3-Methyl migration from the silyl ligand to the silylene ligand in **47** was confirmed by variable temperature ¹H NMR studies. As the temperature was gradually increased from 250 to 280 K, two singlet signals, which are assignable to the two diastereotopic methyl groups on the silylene ligand, broadened then coalesced into a singlet due to exchange of the methyl groups in the SiMe₂ ligand. Another spectral change is observed above 280 K. The two singlets of the SiMe₂ and SiMe₃ ligands gradually broadened, then coalesced at 318 K, and became a sharp singlet at 360 K. This dynamic behavior can be explained as the 1,3-methyl migration from the silyl ligand to the silylene ligand on the base-free silyl(silylene)iron complex (Scheme 14).

We have recently succeeded in the synthesis of base-free silyl(silylene)tungsten complex **48** by photolysis of

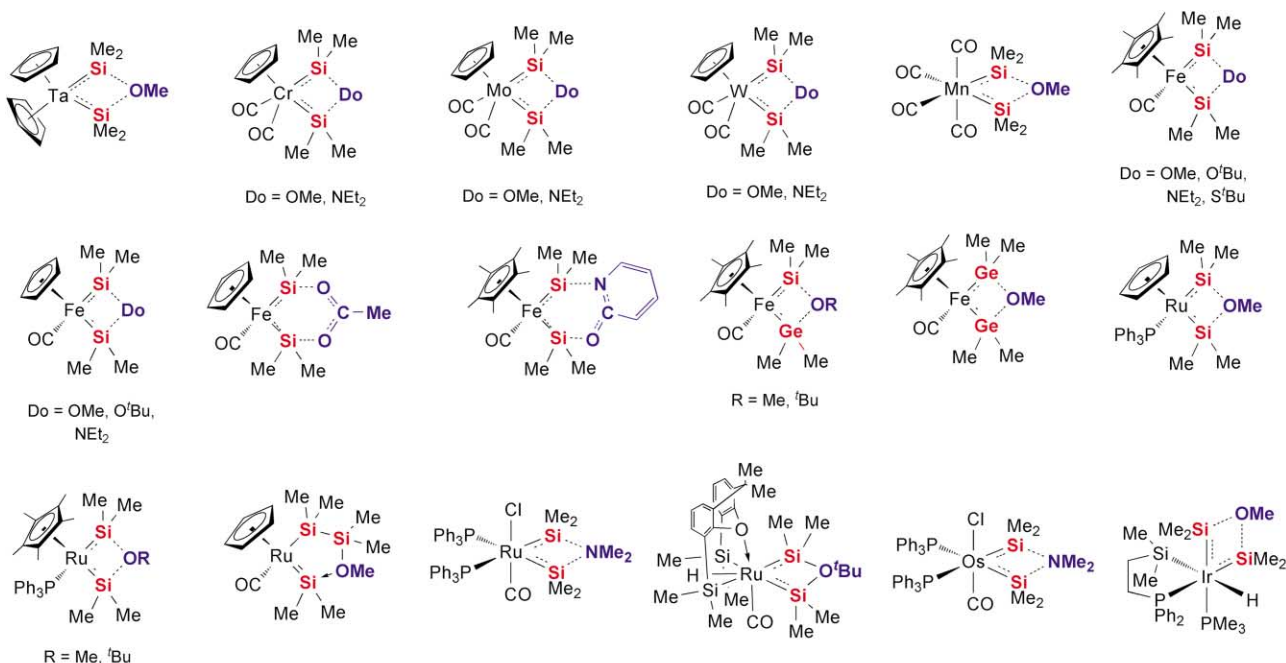
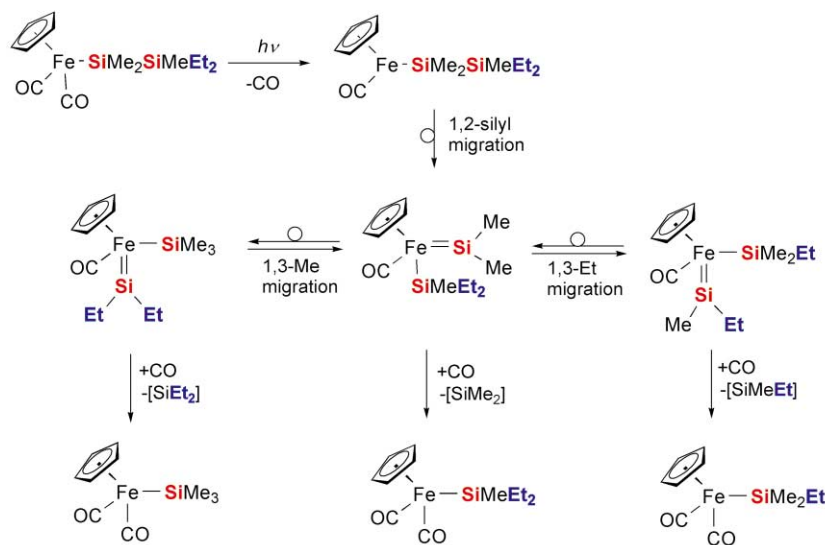
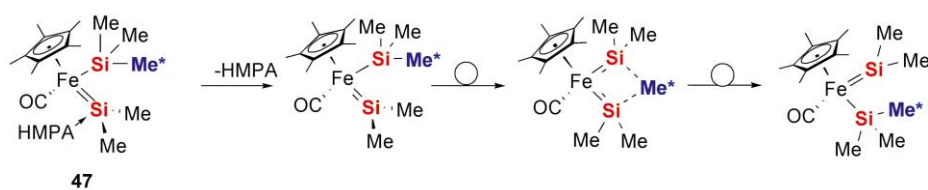


Fig. 1



Scheme 13



Scheme 14

Cp*(OC)₃WMe in the presence of HMe₂SiSiMeMe₂. It is likely that the formation mechanism of **48** involves 1,2-silyl and 1,3-methyl migrations (Scheme 15).⁴⁴

Ojima *et al.* have reported on the observations of transition metal-mediated disproportionation of dihydrosilanes.³ The reaction may be explained as the transient formation of a silyl(silylene) complex, in which the 1,3-migration of the R substituent on the complex, followed by reductive elimination of hydrosilane, results in scrambling of substituents on the silicon atom (Scheme 16). Our experimental results clearly support the 1,3-R-migration step on the transient silyl(silylene) complex.

Several transformation reactions that are mediated by various transition-metals (W, Fe, Co, Rh, Ir, Ni, Pd and Pt) have been reported to proceed through 1,3-migration on the silyl(silylene), silyl(germylene) and germyl(germylene) complexes (Table 5).

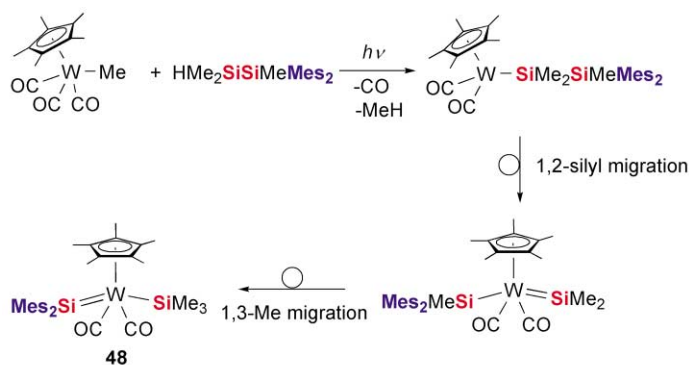
In eqn. (19), the redistribution of the substituents of hydrodisilanes was mediated by an iridium complex in which iridium(I) complex **54** reacted with HPhMeSiSiMe₃ to give **55** via rearrangement of the substituents on a disilanyl ligand.²³ Prolonged heating of the solution at 45 °C for 5 days led to the rearrangement of the hydrodisilane to yield an isomeric 2 : 3 mixture of HPhMeSiSiMe₃ and HMe₂SiSiMe₂Ph.

Table 5 1,3-Migration of substituents on silyl(silylene), silyl(germylene) and germyl(germylene) complexes

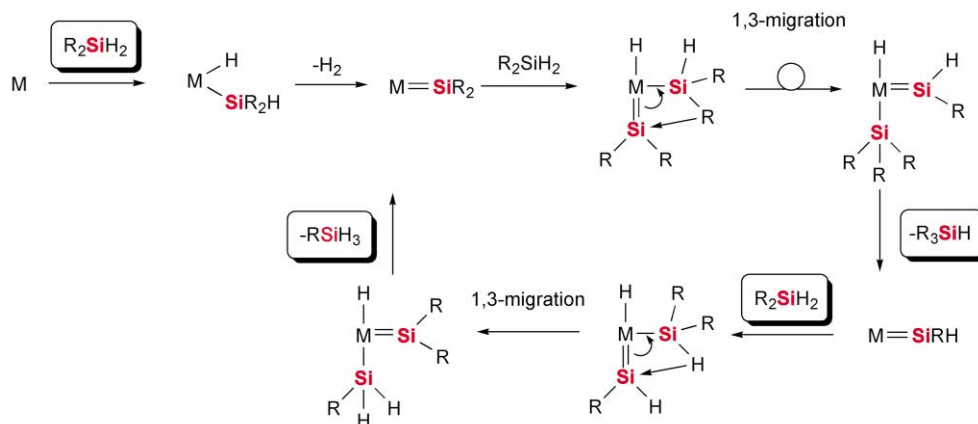


Reactant(s)	Conditions	Product(s)	A proposed intermediate	Ref.
FpSiMe ₂ SiPh ₃	<i>hν</i>	FpSiMe ₂ Ph (7%) + FpSiMePh ₂ (85%) + FpSiPh ₃ (8%)	Cp(CO)Fe(SiPh ₃)(=SiMe ₂)	36a
Fp(SiMe ₂) ₃ SiMe ₃	<i>hν</i>	FpSi(SiMe ₃) ₃	Cp(CO)Fe{(SiMe ₂) ₂ SiMe ₃ }(=SiMe ₂)	36d
PhMe ₂ SiSiMe ₂ H + Cp(CO)(PPh ₃) ₂ FeSiMe ₃ (catalyst)	Δ	a mixture of PhSiMe ₂ SiMe ₂ H and HPhMeSiMe ₃ in the ratio 65 : 35	Cp(CO)Fe(SiMe ₂ Ph)(=SiMe ₂)	36e
FpSiMe ₂ SiMeEt ₂	<i>hν</i>	FpSiMe ₂ Et (33%) + FpSiMeEt ₂ (26%) + FpSiMe ₃ (4%)	Cp(CO)Fe(SiMeEt ₂)(=SiMe ₂)	37
FpGeMe ₂ GeMe ₂ Et	<i>hν</i>	FpGeMe ₂ Et (62%) + FpGeMe ₃ (31%) + Cp ₂ Fe (5%)	Cp(CO)Fe(GeMe ₂ Et)(=GeMe ₂)	30a
Cp ₂ W(SiMe ₃)(Si(<i>i</i> -Pr) ₂ Cl) (49)	160 °C	49 + Cp ₂ W(SiMe ₃ Cl)(Si(<i>i</i> -Pr) ₂ Me)	[Cp ₂ W(SiMe ₃)](=Si(<i>i</i> -Pr) ₂)Cl	45
Cp ₂ W(SiMe ₃)(Si(<i>i</i> -Pr) ₂ OTf)	25 °C, 24 h	Cp ₂ W(SiMe ₂ OTf)(Si(<i>i</i> -Pr) ₂ Me)	[Cp ₂ W(SiMe ₃)](=Si(<i>i</i> -Pr) ₂)]OTf	45
Cp ₂ W(SiMe ₃)(GeMe ₂ Cl) (50)	170 °C, 24 h	50 (60%) + Cp ₂ W(SiMe ₃ Cl)(GeMe ₃) (16%) + Cp ₂ W(SiMe ₂ Cl)(GeMe ₂ Cl) (12%)	[Cp ₂ W(SiMe ₃)](=GeMe ₂)Cl + 51	46
Fp*SiMe(η ⁶ -C ₆ H ₅ Cr(CO) ₃) ₂ SiMe ₃	<i>hν</i>	Cp*(CO)FeSiMe ₂ (η ⁶ -C ₆ H ₅ Cr(CO) ₂)(μ-SiMe ₂)	Cp*(CO)Fe(SiMe ₃)(=SiMe ₂ {η ⁶ -C ₆ H ₅ Cr(CO) ₃ })	47
(Ph ₃ HSi) ₂ + Co ₂ (CO) ₈	rt	(Ph ₃ Si)Co(CO) ₄	(Ph ₃ HSi)Co(=SiPh ₃)(CO) ₃	48
Ph ₃ GeSiEt ₂ H + Co ₂ (CO) ₈	rt	(Ph ₃ Si)Co(CO) ₄ + Ph ₂ Ge[Co(CO) ₄]	(PhEt ₂ Si)Co(=GePh ₂)(CO) ₃	48
(Me ₂ P) ₃ RhCl + (THF) ₃ LiSi(SiMe ₃) ₃ + R-C≡C-R (R = Me, Ph)	rt	(Me ₂ P) ₃ Rh{(Me ₂ Si)Rh{η ² -Me ₂ SiC(R)=C(R)SiMe(SiMe ₃)}}	(Me ₂ P) ₃ Rh(SiMe ₃) ₂ {=Si(SiMe ₃) ₂ }	49
(Me ₂ P) ₃ IrCl + (THF) ₃ LiSi(SiMe ₃) ₃	rt	<i>fac</i> -(Me ₂ P) ₃ Ir{κ ² -Si, C-SiMe ₂ SiMe(SiMe ₃)SiMe ₂ CH ₂ }	(Me ₂ P) ₃ Ir(SiMe ₃) ₂ {=Si(SiMe ₃) ₂ }	50
L ₂ Ir(PMe ₃) + HPhMeSiSiMe ₃	45 °C	L ₂ Ir(H)SiMe ₂ SiMe ₂ Ph + HMe ₂ SiSiMe ₂ Ph	L ₂ IrH(SiMe ₂)(=SiMePh)	23
Cl(SiMe ₂) ₂ Cl + Pt(PMe ₃) ₃	60 °C, 2 h	<i>cis</i> -(ClMe ₂ Si)(Me ₂ SiClMeSi)Pt(PMe ₃) ₂	(Me ₂ ClSi) ₂ Pt(=SiMe ₂)(PEt ₃)	51
(MeO)Me ₂ Si(OMe) ₂ SiMe ₂ (OMe) + Pd(PPh ₃) ₄ (4 mol%)	80 °C, 2 h	(MeO)Me ₂ SiSiMe ₂ Si(OMe) ₃	{(MeO)Me ₂ Si}{(MeO)Si}; Pd{(=SiMe ₂)(PPh ₃) ₃ }	52
Cp ^N NiI + (THF) ₃ LiSi(SiMe ₃) ₃	rt	52	53	53
Wp*Me + HSiMe ₂ SiMeMe ₂	<i>hν</i>	Cp*(CO) ₂ W(SiMe ₃)(=SiMe ₂)	Cp*(CO) ₂ W(SiMeMe ₂)(=SiMe ₂)	44

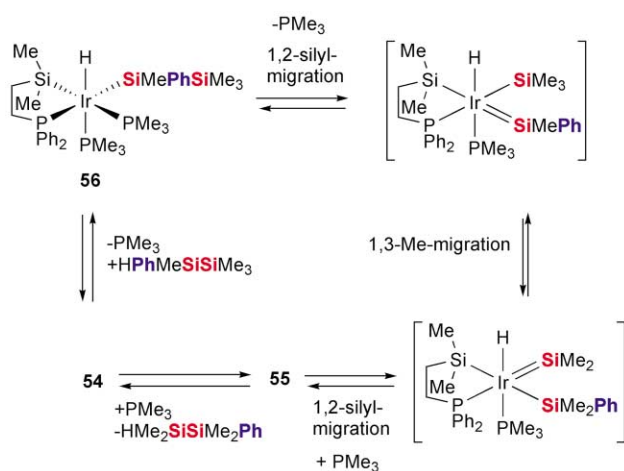
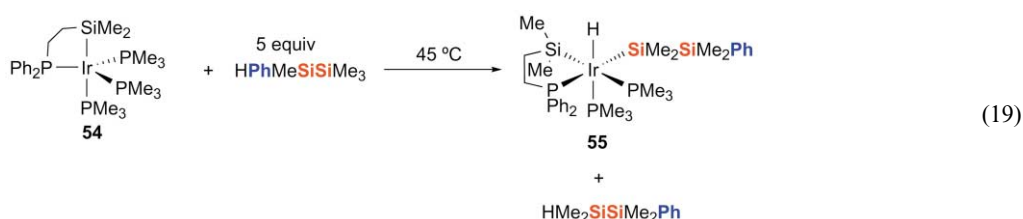
Fp = Cp(CO)₂Fe, Fp* = Cp*(CO)₂Fe, L_{*n*} = {η²-SiMe₂(CH₂)₂PPh₂}, PMe₃, Cp^N = [2-(*N,N*-dimethylamino)ethyl]cyclopentadienyl; Wp* = Cp*(CO)₃W.



Scheme 15



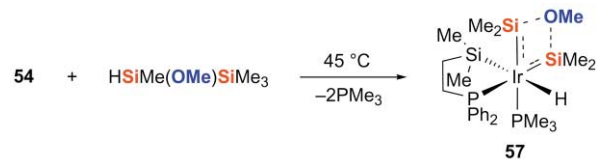
Scheme 16



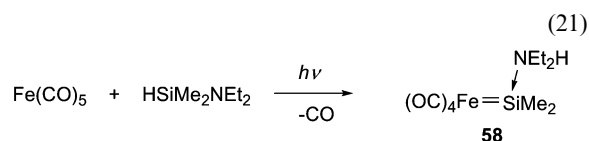
Scheme 17

As outlined in Scheme 17, the isomerization mechanism can be explained involving the oxidative addition of hydrodisilane, followed by 1,2-silyl migration. The resulting silyl(silylene) intermediate causes successive 1,3-Me, 1,2-silyl migrations, followed by the ligation of PMe_3 to afford disilanyl complex **55**, which releases the isomeric hydrodisilane by reductive elimination. To confirm the existence of the silyl(silylene) intermediates, iridium(I) complex **54** was allowed to react with $\text{HSiMe}(\text{OMe})\text{SiMe}_3$ to yield hydridobis(silylene) complex **57**

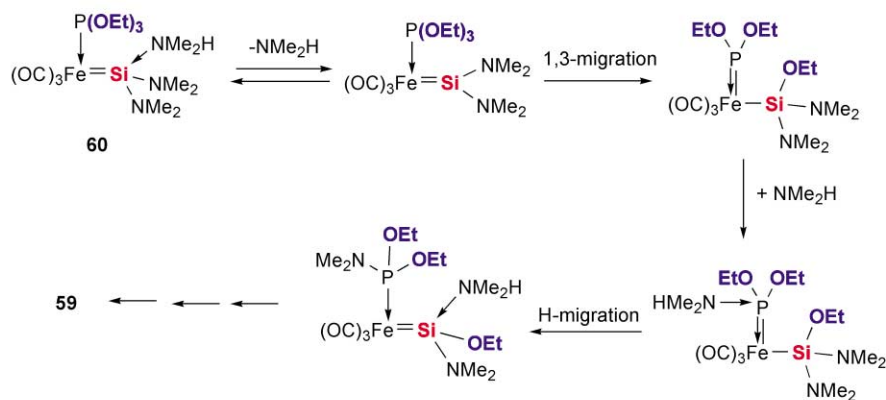
[eqn. (20)]. Formation of **57** strongly supports the proposed mechanism (Scheme 17). Pannell *et al.* reported the $\text{Cp}(\text{CO})(\text{Ph}_3\text{P})\text{FeSiMe}_3$ -catalyzed isomerization of $\text{HMe}_2\text{SiSiMe}_2\text{Ph}$ and HPhMeSiSiMe_3 , in which they have proposed a mechanism involving a silyl(silylene)iron intermediate.^{36e}



Schmid and Welz have reported on the formation of diethylamine-stabilized silylene complex **58** by the irradiation of $\text{Fe}(\text{CO})_5$ and $\text{HSiMe}_2(\text{NET}_2)$ [eqn. (21)].⁵⁴

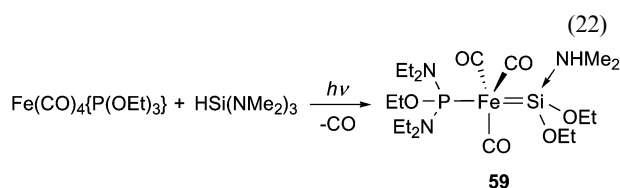


Braunstein *et al.* also examined the related photo-reaction of $\text{Fe}(\text{CO})_4\{\text{P}(\text{OEt})_3\}$ and $\text{HSi}(\text{NMe}_2)_3$ that yielded amine-stabilized silyleneiron complex **59**, in which the two ethoxy



Scheme 18

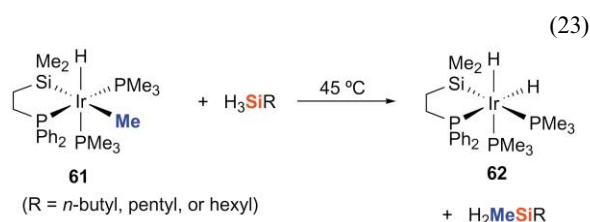
groups of the phosphorus were exchanged with two amino groups of the silicon [eqn. (22)].⁵⁵



The formation mechanism of **59** involves the initial formation of $(\text{CO})_3\{(\text{EtO})_3\text{P}\}\text{Fe}=\text{Si}(\text{NMe}_2)_2\cdot\text{NMe}_2\text{H}$ (**60**), which corresponds to Schmid and Welz's silylene complex **59**. The remarkable redistribution of the substituents on the silicon and phosphorus, the sequence of repeated steps involving dissociation of NMe_2H from the silylene ligand, 1,3-migration on the silylene(phosphine) complex, coordination of NMe_2H to phosphorus and H-migration is postulated as shown in Scheme 18. In summary, it is likely that the 1,3-migration of substituents generally occurs in the compounds with a $\text{R}_n\text{E}=\text{M}=\text{E}'\text{R}_m$ framework, in which the sp^2 E' atoms are electron-deficient.⁴³

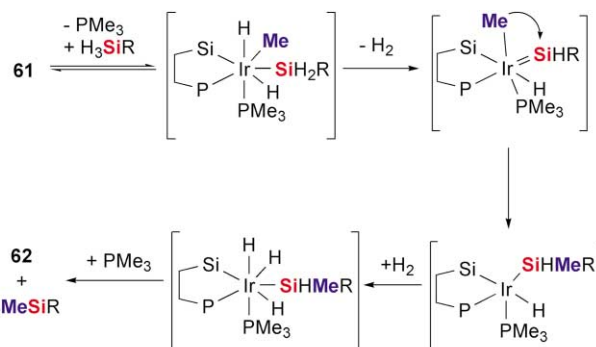
7.2. 1,2-Migration on silylene complexes

Thermal reaction of hydrido(methyl)iridium(III) complex **61** with H_3SiR was monitored spectroscopically to yield **62** and H_2MeSiR , in which the methyl group was transferred from iridium to silicon [eqn. (23)].²⁴



The reaction is very important from the viewpoint of functionalization of alkanes. Complex **61**, which contains hydride and methyl ligands can be regarded as an activation product of methane. Therefore, the occurrence of eqn. (23) indicates that dehydrogenative silylation of alkane is possible. It is interesting to note that the reaction did not afford the expected hydrido(silyl) complex, $\text{IrH}(\text{SiH}_2\text{R})\{\eta^2\text{-Me}_2\text{Si}(\text{CH}_2)_2\text{PPh}_2\}(\text{PMe}_3)_2$, via reductive elimination of methane and oxidative addition of H_3SiR . To illustrate the formation of **62**, a conventional mechanism might explain the unusual silicon-carbon bond formation that involves an Si-H oxidative addition and an Si-C reductive elimination. However, if this mechanism is operating, carbon-silicon reductive elimination has to occur preferentially over carbon- or hydrogen-hydrogen reductive elimination from

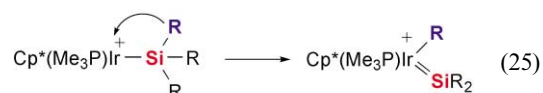
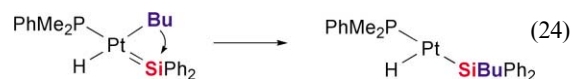
$\text{IrH}_2(\text{Me})(\text{SiH}_2\text{R})\{\eta^2\text{-Me}_2\text{Si}(\text{CH}_2)_2\text{PPh}_2\}(\text{PMe}_3)$. This assumption is in contradiction to the expected tendency of reductive elimination,⁵⁶ and to our DFT calculation results [model system: $\text{Ir}(\text{H})(\text{Me})\{\eta^2\text{-H}_2\text{Si}(\text{CH}_2)_2\text{PPh}_2\}(\text{PH}_3)_2 + \text{H}_3\text{SiMe}$; $\Delta E_{\ddagger\text{C-H}} = +21.0 \text{ kcal mol}^{-1}$, $\Delta E_{\ddagger\text{Si-C}} = +30.2 \text{ kcal mol}^{-1}$].⁵⁷ An alternative mechanism, as shown in Scheme 19, involves the transient



Scheme 19

formation of a methyl(silylene) complex. The carbon-silicon bond forms via 1,2-migration of the methyl group on the methyl(silylene) intermediate. In this case, the proposed mechanism is supported by the DFT calculations on the model system, in which the activation barrier of the 1,2-migration is estimated to be adequately small ($3.8 \text{ kcal mol}^{-1}$).⁵⁷ Experimentally, when the reaction is carried out in the presence of MeOH , which is a trapping agent of silylene complexes, the silicon-carbon bond formation reaction is completely suppressed. This result strongly supports the generation of silylene complexes.

1,2-Alkyl-migration on the transition metal-silylene complex was also recently reported by Ozawa *et al.* [eqn. (24)].⁵⁸ Furthermore, reverse 1,2-alkyl-migration on a silyl complex to generate an alkyl(silylene) complex was reported by Bergman and Tilley [eqn. (25)].^{59,60}



$\text{R}_3 = \text{Me}_3, \text{Ph}_3, \text{PhMe}_2, \text{Ph}_2\text{H}$

8. Summary and outlook

Since 1987, various transition metal-silylene complexes have been synthesized and characterized. However, in order to

obtain the products in their thermally stable form, various chemical modifications have been carried out. As a result, silylene complexes have lost their reactivities, as originally expected in the catalytic transformation of organosilicon compounds. In order to obtain information on how they behave in the catalytic reactions, we should examine the syntheses and reactivities of silylene complexes which are similar to those existing in real catalytic reactions.

Theoretical studies on the properties of early transition metal-silylene complexes have been reported by Nakatsuji *et al.*⁶¹ They concluded that the Schrock-type metal-silylene complex $L_n Nb=SiR_2$ is more stable than the Fischer-type $L_n M=SiR_2$ ($M = Fe, Cr$). The reactive center of the silylene-niobium complex for both nucleophiles and electrophiles is predicted to be at the niobium atom; however, a nucleophilic attack on the silicon atom cannot be ruled out. The fact that all silylene complexes synthesized to date are of the Fischer-type, in which the metal-silicon bond is polarized toward $M^{\delta-}$ and $Si^{\delta+}$, necessitates synthesis and reactivity studies of early transition metal-silylene complexes.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research (Nos. 13440193, 14044010, 14078202 and 14204065) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. One of the authors (M. O.) wishes to thank Tokuyama Science Foundation for financial support. We also acknowledge Shin-Etsu Chemical Co., Ltd. for a gift of silicon compounds.

References

- (a) T. D. Tilley, in *The Chemistry of Organosilicon Compounds*, S. Patai and Z. Rappoport, eds., Wiley, New York, 1989, ch. 24, p. 1415; (b) T. D. Tilley, in *The Silicon-Heteroatom Bond*, S. Patai and Z. Rappoport, eds., Wiley, New York, 1991, ch. 9 and 10, pp. 245 and 309; (c) C. Zybilla, H. Handwerker and H. Friedrich, *Organomet. Chem.*, 1994, **36**, 229; (d) M. S. Eisen, in *The Chemistry of Organosilicon Compounds*, vol. 2, Z. Rappoport and Y. Apeloig, eds., Wiley, New York, 1998, ch. 35, p. 2037.
- (a) J. Y. Corey, in *Advances in Silicon Chemistry*, G. Larson, ed., JAI Press, Greenwich, CT, 1991, vol. 1, p. 327; (b) T. D. Tilley, *Acc. Chem. Res.*, 1993, **26**, 22.
- (a) M. D. Curtis and P. S. Epstein, *Adv. Organomet. Chem.*, 1981, **19**, 213; (b) I. Ojima, S. Inaba and T. Kogure, *J. Organomet. Chem.*, 1973, **55**, C7.
- (a) M. P. Clarke, *J. Organomet. Chem.*, 1989, **376**, 165; (b) M. P. Clarke and I. M. T. Davidson, *J. Organomet. Chem.*, 1991, **408**, 149; (c) M. Okamoto, S. Onodera, T. Okano, E. Suzuki and Y. Ono, *J. Organomet. Chem.*, 1997, **531**, 67.
- (a) H. Yamashita, M. Tanaka and M. Goto, *Organometallics*, 1992, **11**, 3227; (b) Y. Tanaka, H. Yamashita and M. Tanaka, *Organometallics*, 1995, **14**, 530; (c) W. S. Palmer and K. A. Woerpel, *Organometallics*, 1997, **16**, 4824.
- C. Zybilla and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 669.
- D. A. Straus and T. D. Tilley, *J. Am. Chem. Soc.*, 1987, **109**, 5872.
- (a) K. Ueno, H. Tobita, M. Shimoi and H. Ogino, *J. Am. Chem. Soc.*, 1988, **110**, 4092; (b) H. Tobita, K. Ueno, M. Shimoi and H. Ogino, *J. Am. Chem. Soc.*, 1990, **112**, 3415.
- H. Ogino, *The Chemical Record*, 2002, **2**, 291.
- (a) H. Nakatsuji, J. Ushio and T. Yonezawa, *J. Organomet. Chem.*, 1983, **258**, C1; (b) T. R. Cundari and M. S. Gordon, *J. Phys. Chem.*, 1992, **96**, 631; (c) A. Márquez and J. F. Sanz, *J. Am. Chem. Soc.*, 1992, **114**, 2903; (d) H. Jacobsen and T. Ziegler, *Inorg. Chem.*, 1996, **35**, 775; (e) C. Boehme and G. Frenking, *Organometallics*, 1998, **17**, 5801; (f) F. P. Arnold, Jr., *Organometallics*, 1999, **18**, 4800; (g) K. K. Pandey, *Inorg. Chem. Commun.*, 2000, **3**, 39; (h) T. Matsubara, *Organometallics*, 2001, **20**, 1462; (i) T. A. Schmedake, M. Haaf, B. J. Paradise, A. J. Millevolte, D. R. Powell and R. West, *J. Organomet. Chem.*, 2001, **636**, 17; (j) H. P. Hratchian, T. Prendergast and M. C. Milletti, *Polyhedron*, 2001, **20**, 209.
- D. A. Straus, C. Zhang, G. E. Quimbita, S. D. Grumbine, R. H. Heyn, T. D. Tilley, A. L. Rheingold and S. J. Geib, *J. Am. Chem. Soc.*, 1990, **112**, 2673.
- H. Wada, H. Tobita and H. Ogino, *Organometallics*, 1997, **16**, 2200.
- J. D. Feldman, G. P. Mitchell, J.-O. Nolte and T. D. Tilley, *J. Am. Chem. Soc.*, 1998, **120**, 11184.
- S. H. A. Petri, D. Eikenberg, B. Neumann, H.-G. Stammer and P. Jutz, *Organometallics*, 1999, **18**, 2615.
- C. Zhang, S. D. Grumbine and T. D. Tilley, *Polyhedron*, 1991, **10**, 1173.
- K. Ueno, H. Tobita, S. Seki and H. Ogino, *Chem. Lett.*, 1993, 1723.
- B. P. S. Chauhan, R. J. P. Corriu, G. F. Lanneau and C. Priou, *Organometallics*, 1995, **14**, 1657.
- R. J. P. Corriu, B. P. S. Chauhan and G. F. Lanneau, *Organometallics*, 1995, **14**, 1646.
- H. Kobayashi, K. Ueno and H. Ogino, *Organometallics*, 1995, **14**, 5490.
- T. Sato, H. Tobita and H. Ogino, *Chem. Lett.*, 2001, 854.
- K. Ueno, S. Seiji and H. Ogino, *Chem. Lett.*, 1993, 2159.
- (a) M. Okazaki, H. Tobita and H. Ogino, *Chem. Lett.*, 1996, 477; (b) M. Okazaki, H. Tobita, Y. Kawano, S. Inomata and H. Ogino, *J. Organomet. Chem.*, 1998, **553**, 1.
- M. Okazaki, H. Tobita and H. Ogino, *Chem. Lett.*, 1997, 437.
- (a) M. Okazaki, H. Tobita and H. Ogino, *J. Chem. Soc., Dalton Trans.*, 1997, 3531; (b) M. Okazaki, H. Tobita and H. Ogino, *J. Chem. Soc., Dalton Trans.*, 1997, 4829.
- G. P. Mitchell and T. D. Tilley, *J. Am. Chem. Soc.*, 1997, **119**, 11236.
- S. K. Grumbine, G. P. Mitchell, D. A. Straus, T. D. Tilley and A. L. Rheingold, *Organometallics*, 1998, **17**, 5607.
- H. Sakaba, T. Hirata, C. Kabuto and H. Horino, *Chem. Lett.*, 2001, 1078.
- H. Sakaba, M. Tsukamoto, T. Hirata, C. Kabuto and H. Horino, *J. Am. Chem. Soc.*, 2000, **122**, 11511.
- H. K. Sharma and K. H. Pannell, *Organometallics*, 2001, **20**, 7.
- Variable-temperature study of the alkoxy- or amino-bridged bis(silylene) complexes revealed that at elevated temperature, they exist in equilibrium with its open-form, *i.e.* base-free silyl(silylene) complexes. (a) J. R. Koe, H. Tobita, T. Suzuki and H. Ogino, *Organometallics*, 1992, **11**, 150; (b) J. R. Koe, H. Tobita and H. Ogino, *Organometallics*, 1992, **11**, 2479; (c) K. Ueno, A. Masuko and H. Ogino, *Organometallics*, 1997, **16**, 5023; (d) K. Ueno, A. Masuko and H. Ogino, *Organometallics*, 1998, **18**, 2694; (e) H. Wada, H. Tobita and H. Ogino, *Chem. Lett.*, 1999, 993.
- (a) C. Zybilla, D. L. Wilkinson, C. Leis and G. Müller, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 203; (b) C. Leis, D. L. Wilkinson, H. Handwerker and C. Zybilla, *Organometallics*, 1992, **11**, 514; (c) C. Leis and C. Zybilla, *Polyhedron*, 1991, **10**, 1163; (d) H. Handwerker, M. Paul, J. Riede and C. Zybilla, *J. Organomet. Chem.*, 1993, **459**, 151.
- W. A. Herrmann, P. Härter, C. W. K. Gstöttmayr, F. Bielert, N. Seeboth and P. Sirsch, *J. Organomet. Chem.*, 2002, **649**, 141.
- H. Wada, H. Tobita and H. Ogino, *Organometallics*, 1997, **16**, 3870.
- G. R. Clark, C. E. F. Rickard, W. R. Roper, D. M. Salter and L. J. Wright, *Pure Appl. Chem.*, 1990, **62**, 1039.
- P. W. Wanandi, P. B. Glaser and T. D. Tilley, *J. Am. Chem. Soc.*, 2000, **122**, 972.
- (a) K. H. Pannell, J. Cervantes, C. Hernandez, J. Cassias and S. Vincenti, *Organometallics*, 1986, **5**, 1056; (b) K. H. Pannell, J. M. Rozell and C. Hernandez, *J. Am. Chem. Soc.*, 1989, **111**, 4482; (c) H. K. Sharma and K. H. Pannell, *Chem. Rev.*, 1995, **95**, 1351; (d) K. H. Pannell, L.-J. Wang and J. M. Rozell, *Organometallics*, 1989, **8**, 550; (e) K. H. Pannell, M.-C. Brun, H. Sharma, K. Jones and S. Sharma, *Organometallics*, 1994, **13**, 1075.
- (a) H. Tobita, K. Ueno and H. Ogino, *Chem. Lett.*, 1986, 1777; (b) H. Tobita, K. Ueno and H. Ogino, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2797.
- H. Koshikawa, K. Ueno, H. Tobita and H. Ogino, *Eighty-First Annual Meeting of the Chemical Society of Japan*, Tokyo, 2002, 3B4-31.
- T. Takeuchi, H. Tobita and H. Ogino, *Organometallics*, 1991, **10**, 835.
- (a) K. Ueno, S. Ito, K. Endo, H. Tobita, S. Inomata and H. Ogino, *Organometallics*, 1994, **13**, 3309; (b) H. Tobita, T. Sato, M. Okazaki and H. Ogino, *J. Organomet. Chem.*, 2000, **611**, 314.
- (a) H. Tobita, H. Wada, K. Ueno and H. Ogino, *Organometallics*, 1994, **13**, 2545; (b) H. Tobita, H. Kurita and H. Ogino, *Organometallics*, 1998, **17**, 2844; (c) H. Tobita, H. Kurita and H. Ogino, *Organometallics*, 1998, **17**, 2850.
- T. N. Choo, W.-H. Kwok, C. E. F. Rickard, W. R. Roper and L. J. Wright, *J. Organomet. Chem.*, 2002, **645**, 235.
- K. Ueno, K. Nakano and H. Ogino, *Chem. Lett.*, 1996, 459.
- K. Ueno, S. Asami, N. Watanabe and H. Ogino, *Organometallics*, 2002, **21**, 1326.
- D. C. Pestana, T. S. Koloski and D. H. Berry, *Organometallics*, 1994, **13**, 4173.

-
- 46 L. K. Figge, P. J. Carroll and D. H. Berry, *Organometallics*, 1996, **15**, 209.
- 47 K. H. Pannell, H. K. Sharma, R. N. Kapoor and F. Cervantes-Lee, *J. Am. Chem. Soc.*, 1997, **119**, 9315.
- 48 J. S. McIndoe and B. K. Nicholson, *J. Organomet. Chem.*, 1999, **577**, 181.
- 49 G. P. Mitchell and T. D. Tilley, *Organometallics*, 1996, **15**, 3477.
- 50 G. P. Mitchell, T. D. Tilley, G. P. A. Yap and A. L. Rheingold, *Organometallics*, 1995, **14**, 5472.
- 51 Y. Tanaka, H. Yamashita and M. Tanaka, *Organometallics*, 1995, **14**, 530.
- 52 K. Tamao, G.-R. Sun and A. Kawachi, *J. Am. Chem. Soc.*, 1995, **117**, 8043.
- 53 S. Nlate, E. Herdtweck and R. A. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1861.
- 54 G. Schmid and E. Welz, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 785.
- 55 (a) U. Bodensieck, P. Braunstein, W. Deck, T. Faure, M. Knorr and C. Stern, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2440; (b) P. Braunstein, M. Knorr and C. Stern, *Coord. Chem. Rev.*, 1998, **178–180**, 903.
- 56 (a) S. Sakaki and M. Ieki, *J. Am. Chem. Soc.*, 1993, **115**, 2373; (b) M. Aizenberg and D. Milstein, *J. Am. Chem. Soc.*, 1995, **117**, 6456.
- 57 M. Okazaki, D. G. Musaev and K. Morokuma, H. Tobita and H. Ogino, unpublished work.
- 58 F. Ozawa, M. Kitaguchi and H. Katayama, *Chem. Lett.*, 1999, 1289.
- 59 P. Burger and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 10462.
- 60 S. R. Klei, T. D. Tilley and R. G. Bergman, *Organometallics*, 2001, **20**, 3220.
- 61 H. Nakatsuji, M. Hada and K. Kondo, *Chem. Phys. Lett.*, 1992, **196**, 404.