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Synthesis and Properties of (η^4-Silatrimethylenemethane)iron and -ruthenium Complexes

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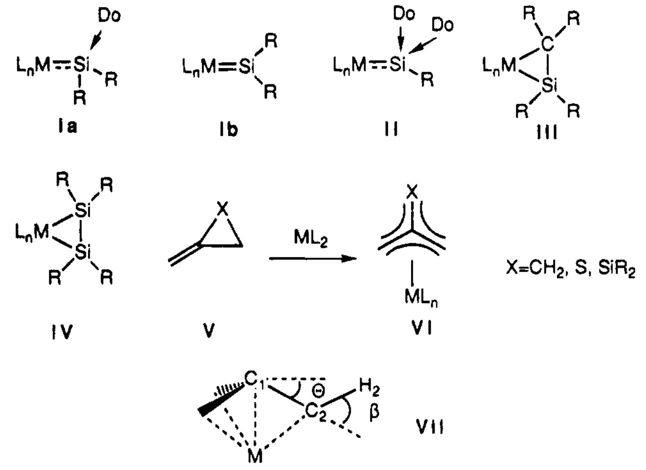
(η^4-Silatrimethylenemethane (STMM))iron and -ruthenium complexes $M(CO)_3[\eta^4\text{-}Mes_2SiC(CH_2)((Z,E)\text{-}CH^tBu)]$ (M = Fe, (*Z*/*E*)-**2**; M = Ru, (*Z*/*E*)-**5**) and $Fe(CO)_3[\eta^4\text{-}Mes_2SiC(CMe_2)_2(C{=}CMe_2)]$ (**4**) were prepared by reactions of alkylidenesiliranes ((*Z*/*E*)-**1** and **3**) with the corresponding metal carbonyls and characterized spectroscopically. The η^4-silatrimethylenemethane structures of (*Z*)-**2** and **4** were furthermore determined by X-ray crystal analysis. Nevertheless, when (*Z*)-**1** was converted with $Ru_3(CO)_{12}$, the trinuclear hydride complex $Ru_3(CO)_9[\mu^3\text{-}Mes_2Si(C{=}CH^tBu)C_2O](\mu\text{-}H)_2$ (**6**) was obtained as the major product. **6** exhibits a 1-oxa-2-silacyclopentene unit as a μ^3-bridging ligand, as has been confirmed by X-ray crystal analysis. The formation of **6** demands a unique metal bond CO insertion into the silirane ring.

Introduction

It is well-known that reactive species such as carbenes, carbynes, cyclobutadiene, and trimethylenemethanes may be stabilized by coordination to transition metals. In a similar manner there has been remarkable progress in the preparation of transition metal complexes of unsaturated silicon compounds over the last few years. For example stable complexes of silylenes (**I**),[1] silylynes (**II**),[2] silenes (**III**),[3] and disilenes (**IV**)[4] have been isolated and characterized. The silylenes[1a−o] and silylynes[2] display coordination of a Lewis base to a silicon atom (**Ia** and **II**) so that the silicon atom has a distorted sp^3 tetrahedral geometry. Recently, base-free silylene complex **Ib**[1p−r] was reported to have sp^2 planar geometry around the silicon atom. Meanwhile, silene[3] and disilene complexes[4] are described as metallacyclopropanes rather than metal−olefin complexes as the predominant resonance form. Therefore silicon atoms in the silene and disilene complexes contain a formal sp^3 rather than sp^2 configuration. These unusual properties exhibited by these classes of compounds have directed our interest toward the fixation of unstable conjugated silenes to metal centers.[5] On the basis of the observation that methylenelecyclopropane (**V**, X = CH_2) reacts with transition metals to yield trimethylenemethane (TMM) metal complexes (**VI**, X = CH_2),[6h] we demonstrated that a η^4-

Scheme 1



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[5] Although few reports containing an η^3-1-silapropenyl transition metal complex appeared, no crystallographic data were accessible; furthermore spectroscopic assignments were controversial. (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7453. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1980**, *184*, 13. (c) Radnia, P.; Mckennis, J. S. *J. Am. Chem. Soc.* **1980**, *102*, 6349.

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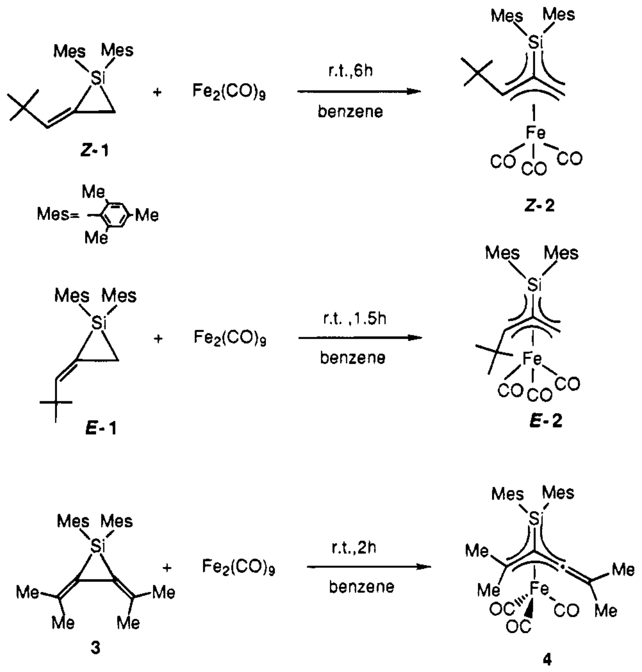
thiatrimethylenemethane iron complex (**VI**, X = S)[8] is formed in the reactions of alkylidenethiirane (**V**, X = S)[7h,i] with $Fe_2(CO)_9$. As no conjugated silene metal complexes besides those mentioned in our preliminary report have been described,[9] we investigated the possibility of preparing η^4-silatrimethylenemethane (STMM) complexes (**VI**, X = SiR_2) by reactions of alkylidenesilirane (**V**, X = SiR_2)[7a–e] with metal carbonyls. Therewith we wish to report the full details on the synthesis of η^4-silatrimethylenemethane metal complexes as well as their spectroscopic and structural features.

Results and Discussion

(η^4-Silatrimethylenemethane)iron Tricarbonyl Complexes ((*Z*/*E*)-2 and 4) by Reaction of Alkylidenesiliranes ((*Z*/*E*)-1 and 3) with $Fe_2(CO)_9$. The reaction of (*Z*)- 1,1-dimesityl-2-neopentylidenesilirane ((*Z*-**1**) or the corresponding *E*-isomer ((*E*)-**1**) with 1 equiv of $Fe_2(CO)_9$ provided stable complexes (*Z*)-**2** and (*E*)-**2**, in 59% and 38% yields, respectively. The IR spectra of (*Z*)-**2** and (*E*)-2 each exhibit two distinct peaks in the region 1950–2050 cm^{-1} for the terminal carbonyl ligand with the characteristic pattern of tricarbonyl metal complexes of *C3v* symmetry. While at room temperature the carbonyl ligands of (*E*)-**2** are fluxional, as indicated by one broad carbonyl carbon signal in the ^{13}C NMR spectrum, this is not the case for (*Z*)-**2**, as three distinct carbonyl signals appear in the ^{13}C NMR spectrum (Table 1). The ^{1}H NMR spectrum of (*Z*)-**2** exhibits five singlets in a 2:1:1:1:1 ratio for the *o*- and *p*-mesityl methyl protons. The same pattern for mesityl methyl protons of (*E*)-**2** is observed at −40 °C. Nevertheless at a higher temperature (20 °C) two of the four *o*-mesityl methyl protons coalesced and, finally, above 30 °C, four *o*-methyl protons coalesced and one broad singlet appeared for the *o*-methyl protons besides one singlet *p*-methyl resonance (Figure 1). Evidently, those different spectral properties of (*Z*)-**2** and (*E*)-**2** were responsible for the *Z*-configuration of the *tert*-butyl groups, which inhibits two *σ*-mesityl rotations. The protons in the monosubstituted TMM–Fe(CO)$_3$ complex do not show any geminal coupling but do exhibit long–range trans coupling (W coupling).[6c] Therefore the lack of observable coupling and methine protons of (*Z*)-**2** supports its being located over an organic ligand having an η^4-TMM type framework, as shown in Scheme 2. The C–H COSY spectrum of (*Z*)-**2** and (*E*)-**2** assigned each methylene proton. A reasonable NOE between one of the methylene protons and methine or *tert*-butyl protons besides two geminal methylene protons unambiguously established configurational assignment of the STMM framework protons. Three sets of ^{13}C NMR chemical shifts ((*Z*)-**2** δ 42.9 (CH$_2$), 73.0 (C), 103.1 ppm (CH); (*E*)-**2** δ 49.5 (CH$_2$), 81.7 (C), 94.0 ppm (CH)) appeared at a reasonably higher field owing to metal coordination. Of a particular interest are the ^{29}Si chemical shift values of 43.6 ppm for (*Z*)-**2** and 23.1 ppm for (*E*)-**2**, which occur at a considerably lower field than the shifts for other silene complexes.[3b–d] Very similar values are observed for isolated silenes $Mes_2Si{=}C(OSiMe_3)R$ (δ 41.4–54.3 ppm).[10] Overall the spectroscopic data are consistent with formulation as η^4-STMM complexes.

Scheme 2



For (*Z*)-**2** the structure was unequivocally assigned by X-ray analysis (Table 2 and Figure 2). The STMM ligand is bound in an η^4 fashion and staggered relative to the three carbonyl ligands. The bond distances C(1)–Si, C(1)–C(2), and C(1)–C(3) are 1.840(8), 1.42(1), and 1.46(1) Å and fall between C–Si or C–C single and double bonds.[10] Especially the C(1)–Si distance of 1.840(8) Å is somewhat longer than the values found in the other silene complexes:[3a–d] Cp*RuHPCy$_3$(η^2-CH$_2$=SiMe$_2$), 1.78–1.79 Å; Cp*IrPMe$_3$(η^2-CH$_2$=SiPh$_2$),

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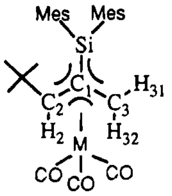
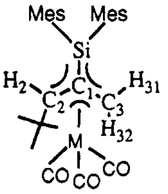
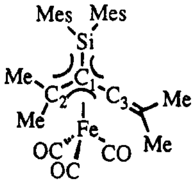
(9) Preliminary results were communicated: Ando, W.; Yamamoto, T.; Saso, H.; Kabe, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2791.

(10) (a) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, G.; Krishuna, R.; Kallury, M. R.; Poon, Y. C.; Chang, Y.-H.; Wang-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (b) Wiberg, N.; Wagner, G.; Riede, J.; Müller, G. *Organometallics* **1987**, *6*, 32.

Table 1. Selected ^{1}H, ^{13}C, and ^{29}Si NMR Data of η^4-Silatrimethylenemethane (STMM) Frameworks

compd		^{1}H NMR δ/ppm			^{13}C NMR δ/ppm			^{29}Si NMR δ/ppm	
		H_2	H_{31}	H_{32}	C_3	C_1	C_2	CO	
	M = Fe ((*Z*)-**2**)	2.78	1.42	0.82	42.9 (t)	73.0 (s)	103.1 (d)	213.6 (s) 213.9 (s) 214.2 (s)	43.6
	M = Ru ((*Z*)-**5**)	2.97	1.44	0.93	36.7 (t)	81.4 (s)	98.6 (d)	198.3 (s) 199.9 (s) 200.7 (s)	40.1
	M = Fe ((*E*)-**2**)	3.35	2.31	2.98	49.5 (t)	81.7 (s)	94.0 (d)	214.4 (br s)	23.1
	M = Ru ((*E*)-**5**)	3.39	2.38	3.07	44.6 (t)	89.5 (s) C_1, C_2, C_3	88.1 (d)	198.9 (s) 200.5 (s) 200.5 (s)	18.9
	**4**				61.1 (s), 100.2 (s), 120.2 (s) [C_1, C_2, C_3]			211.1 (s) 213.2 (s) 214.5 (s)	19.1

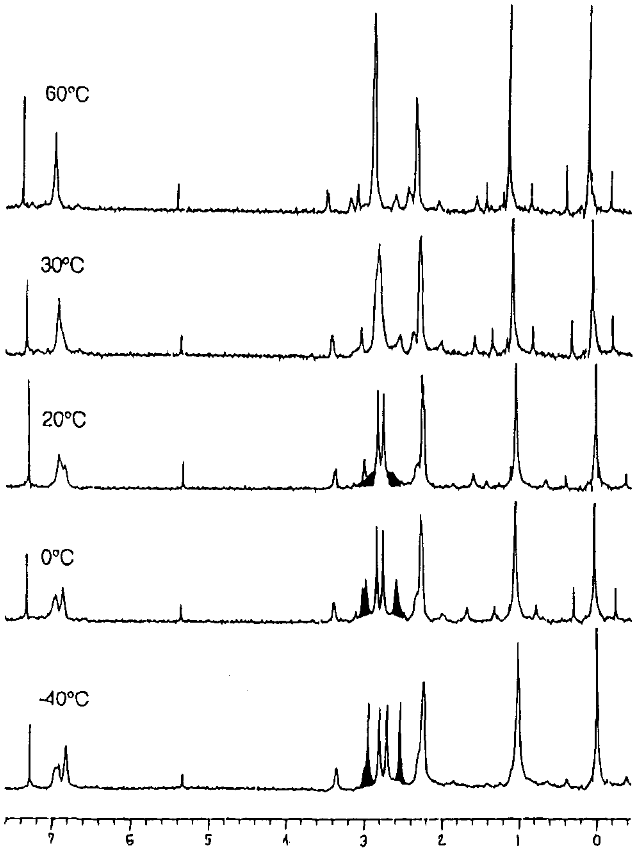


Figure 1. Temperature-dependent ^{1}H NMR (90 MHz) spectra of (*E*)-**2**. Two temperature-dependent resonances of the *o*-methyl protons of the mesityl rings are shown in black.

Table 2. Crystallographic Data for Diffraction Studies

compd	(*Z*)-**2**	**4**	**6**
empirical formula	$C_{28}H_{34}FeSiO_3$	$C_{29}H_{34}FeSiO_3$	$C_{35}H_{34}Ru_3SiO_{10}$
fw	502.51	514.53	945.95
cryst syst	orthorhombic	orthorhombic	triclinic
lattice params			
a, Å	10.254(2)	8.983(1)	10.838(6)
b, Å	14.402(2)	17.201(2)	18.556(9)
c, Å	18.151(3)	18.113(2)	9.848(4)
α, deg			94.22 (4)
β, deg			106.20(4)
γ, deg			87.04(4)
V, Å^3	2680.5	2798.6	1895.8
space group	*Pna*2$_1$ (No. 33)	*P*2$_1$2$_1$2$_1$ (No. 19)	$P\bar{1}$ (No. 2)
Z value	4	4	2
D_{calc}, g/cm^3	1.25	1.22	1.66
F_{000}	1064	1088	940
μ(Mo Kα), cm^{-1}	6.3	6.0	12.4
temp, °C	23	23	23
$2\theta_{max}$, deg	50	50	50
no. of observns ($I > 3\sigma(I)$)	1710	2433	6073
no. of variables	399	409	541
residuals: *R*; R_w	0.044; 0.048	0.029; 0.031	0.024; 0.027
goodness of fit indicator	1.82	0.93	1.20
max shift in final cycle	0.03	0.03	0.03
largest/lowest peak in final diff map, e/Å^3	0.27/−0.73	0.16/−0.21	0.62/−0.43

1.810 Å; $Cp_2W(\eta^2\text{-}CH_2{=}SiMe_2)$, 1.800 Å. Crossconjugative interaction with a C−C double bond may be responsible for this deviation. The methylene and methine protons in (*Z*)-**2** were located and refined to allow a reliable discussion of the pyramidalization of the η^4-STMM ligand. The reasons for pyramidalization have been well documented[6i] and may be quantified by the two angular parameters Θ and *β* shown in **VII**, where *β* is the angle between the line C(1)−C(2) and the plane C(2)H(2).[12] For the complex $Fe(CO)_3[\eta^4\text{-}C(CH_2)_3]$,[6g] Θ = 13.6° and *β* = 14.4°, and in the case of $Fe(CO)_3[\eta^4\text{-}C(CH_2)CHPh]$,[6d,e] Θ values of 13.9, 12.9, and 11.7° and *β* values of 36.6, 37, and 0° were recorded.

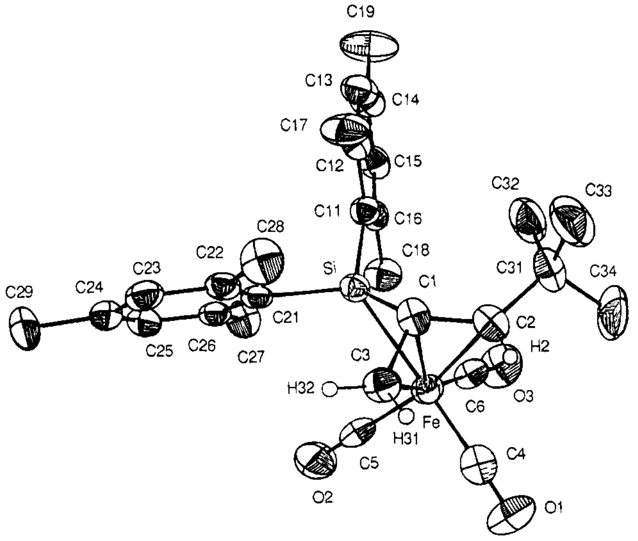


Figure 2. ORTEP drawing of (*Z*)-**2**.

Tricarbonyl[η^4-7-methylenecyclohepta-1,3,5-triene]iron also contains an iron–TMM linkage with Θ values of 11.0, 10.1, and 13.9° and β = 14.8, 15.9, and 23.4°.[6f] In the cation complexes [(η-C_5H_5)(CO)$_2$Mo[η^4-C(CH_2)$_3$]$^+$-BF_4^-],[6m] Θ values of 14.6(5), 12.0(6), and 10.6(6)° with β = 55.1, −15.7, and 6.1° were reported. Whereas TMM complexes have been characterized in the η^4-bonding mode, a variety of hapticities were discussed with heterotrimethylenemethane complexes.[11] Recently, oxa-[11h,i] and thia-TMM complexes[8] have been reported to contain η^4-bound hetero-TMM ligands. For the complex Fe(CO)$_3$[η^4-Ph_2CC(S)CH^{t}Bu],[8] Θ values are 12.8, 10.3, and 6.6° to the sulfur atom and terminal carbons. In (*Z*)-**2**, Θ values are 11.8, 12.5, and 16.6° to Si, C(2), and C(3), respectively. The bend-back angles at Si, C(2), and C(3) are calculated as 33.4, 27.2, and 36.2°, respectively. Thus the crystallographic study confirmed that the structure of STMM ((*Z*)-**2**) closely resembled that of the TMM complex and its hetero-analogues.

The corresponding reactions of 1,1-dimesityl-2,3-isopropylidenesilirane (**3**) with $Fe_2(CO)_9$ provide another STMM complex (**4**) in 17% yield. In the ^{1}H NMR spectrum one of the two σ-mesityl rotations is temperature-dependent, as shown in Figure 3. Three sets of ^{13}C NMR resonances (δ 61.1, 100.2, 120.2 ppm) as well as carbonyl absorptions (see Table 1) easily suggested the η^4-bound structure of **4**. The X-ray diffraction study of **4** was conducted. An ORTEP drawing of the molecular structure of **4** is shown in Figure 4, and the crystal data are listed in Table 2. Apart from the three carbonyl groups, the iron is only coordinated by the STMM fragment. The terminal alkylidene residue is incapable of such coordination. The η^4-bound mode of **4** is very

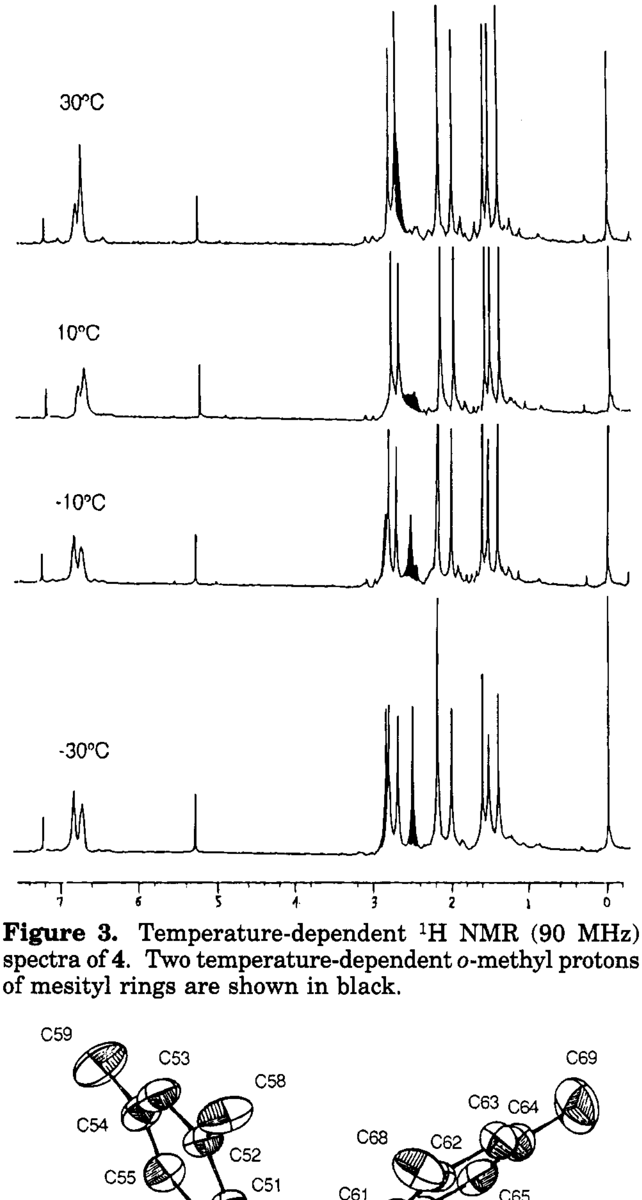


Figure 3. Temperature-dependent ^{1}H NMR (90 MHz) spectra of **4**. Two temperature-dependent *o*-methyl protons of mesityl rings are shown in black.

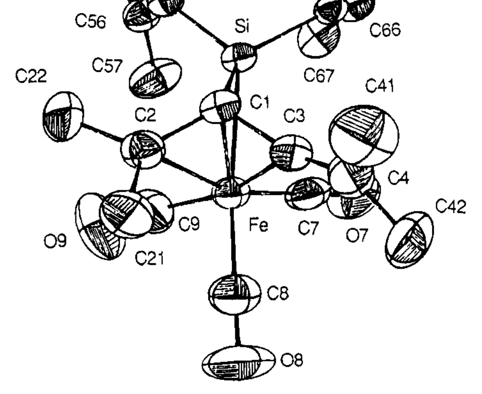


Figure 4. ORTEP drawing of **4**.

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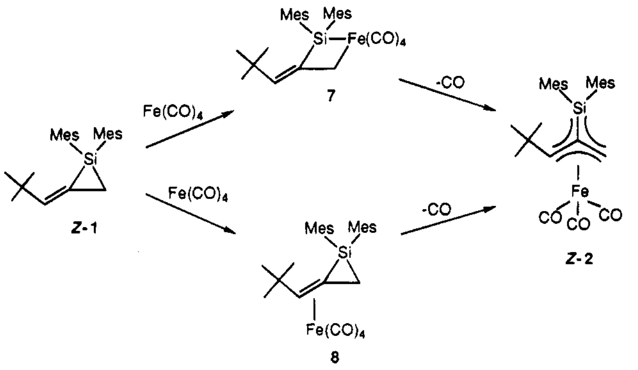
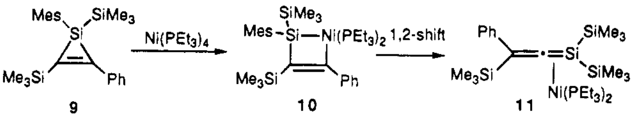
(11) For heterotrimethylenemethane (TMM) complexes: (a) $\eta^1(\sigma)$- and $\eta^4(\pi)$-thia-TMM, see ref 8. (b) $\eta^1(\sigma)$-oxo-TMM: Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61. (c) $\eta^2(\sigma)$-oxa-TMM: Kemmitt, R. D.; Mckenna, P.; Russell, D. R.; Prouse, L. J. S. *J. Chem. Soc., Dalton Trans.* **1989**, 345. (d) $\eta^3(\pi)$-oxa-TMM: Fawcett J.; Henderson, W.; Jones, M. D.; Kemmitt, R. D. W.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, *8*, 1991. (e) $\eta^3(\pi)$-oxa-TMM: Trost, B. M.; Schnider, S. *J. Am. Chem. Soc.* **1989**, *111*, 4430. (f) μ-$\eta^1(\sigma)$,$\eta^3(\pi)$-oxa-TMM dimers: Frey, M.; Jenny, T. A.; Stoeckli-Evans, H. *Organometallics* **1990**, *9*, 1806. (g) μ-$\eta^1(\sigma)$,$\eta^3(\pi)$-oxa-TMM: Holmgren, J. S.; Shaply, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508. (h) $\eta^2(\sigma)$- and $\eta^4(\pi)$-oxa-TMM: Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 5670. (i) $\eta^2(\sigma)$- and $\eta^4(\pi)$-oxa-TMM: Hartwig, J. F.; Bergmann, R. G.; Anderson, R. A. *Organometallics* **1991**, *10*, 3326. (j) $\eta^3(\pi)$-aza-TMM: Ohe, K.; Ishihara, T.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **1990**, *112*, 9646. (k) $\eta^3(\pi)$-aza-TMM: Chen, J.-T.; Huang, T.-M.; Cheng, M.-C.; Lin, Y.-C.; Wang, Y. *Organometallics* **1992**, *11*, 1761. (l) $\eta^2(\sigma)$-oxa-TMM: Ohsuka, A.; Fujimori, T.; Hirao, T.; Kurosawa, H.; Ikeda, I. *J. Chem. Soc., Chem. Commun.* **1993**, 1039.

(12) Angular parameters (Θ and β) of trimethylenemethane (TMM) complex **VII** are calculated according to the following equations; $\Theta = 90° - \angle MC_1C_2$, $\beta = \sin^{-1}[d(C_1{\sim}\Delta C_2H_2)/d(C_1-C_2)]$, with $\angle MC_1C_2$ = bond angles among M, C_1, and C_2 atoms, $d(C_1{\sim}\Delta C_2H_2)$ = shortest distance between the C_1 atom and the plane involving C_2 and two hydrogen atoms, and $d(C_1-C_2)$ = bond distance between C_1 and C_2 atoms.

Scheme 3



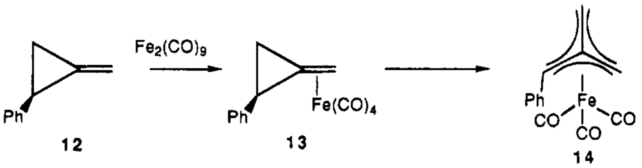
Scheme 4



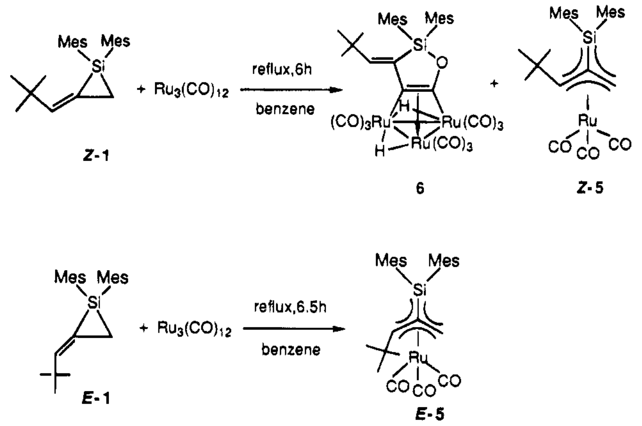
similar to (*Z*)-**2** such that the STMM ligand and $Fe(CO)_3$ moiety adopt a mutually staggered conformation. The bond distances within the STMM moiety are also similar to those in (*Z*)-**2**; C(1)—Si, C(1)—C(2), and C(1)—C(3) are 1.868(8), 1.422(5), and 1.439(5) Å. However, it is noteworthy that the pyramidalization at C(3) exceeded the usual ranges: Θ values of 14.5, 9.4, and 20.5° to Si, C(2), and C(3). The bent-back angles (β) at Si, C(2), and C(3) are 21.2, 35.2, and 32.2°. Compound **4** is a complex that incorporates not only the STMM ligand but also the allene ligand. It has been known that allene binds to metal in an η^2 fashion and does not maintain the orthogonality of the C=C bonds.[13] The typical allene complexes have been predicted to have C—C—C angles ranging from 147 to 150°.[13] These values are comparable with the bent-back angles at C(3) in **4**.

With formation of STMM complexes such as (*Z*)-**2**, (*E*)-**2**, and **4**, it is possible that two different mechanism operate, as shown in Scheme 3. One plausible mechanism is that insertion of iron tetracarbonyl into an Si—C bond of alkylidenesilirane would occur first to give ferracyclobutane complex **7**. Complex **7** undergoes CO loss and then rearranges to the observed STMM complex. The nickelacyclobutene (**10**)[14] was reported to be obtained by the insertion of tetrakis(triethylphosphine)-nickel(0) to silirene **9**, which isomerizes to the (silapropadiene)nickel complex **11** shown in Scheme 4. Another mechanism is that coordination of iron tetracarbonyl to the olefin moiety of alkylidenesilirane causes formation of complex **8** illustrated in Scheme 3. Complex **8** undergoes CO loss and subsequent ring opening of silirane ring to afford the STMM complex. These mechanisms have been established in the reactions of phenyl-substituted methylenecyclopropanes **12** with iron carbonyl.[6j–l] Especially the stereochemistry of phenyl-substituted TMM complex **14** is determined by the frontier orbital symmetry of complex **13**. Up to now we have no evidence to distinguish both mechanisms.

Scheme 5



Scheme 6



Trinuclear Ruthenium Carbonyl Cluster 6 and (η^4-Silatrimethylenemethane)ruthenium Tricarbonyls (*Z*/*E*)-5 by reaction of Alkylidenesiliranes (*Z*/*E*)-1 with $Ru_3(CO)_{12}$. We have also tried the reaction of alkylidenesilirane ((*Z*/*E*)-**1**) with trinuclear carbonyls $Ru_3(CO)_{12}$. We obtained the ruthenium analogue of the η^4-silatrimethylenemethane complex ((*Z*)-**5** and (*E*)-**5**) in 9% and 22% yields, respectively. Selected spectroscopic data for (*Z*)-**5** and (*E*)-**5** are listed in Table 1. The configuration of the STMM ligand was established by C–H COSY and NOESY spectra mentioned above. The low yield realized for (*Z*)-**5** is due to another competing reaction taking place, which proceeds through CO insertion into silirane ((*Z*)-**1**) to produce trinuclear hydride complex **6** (62% yield) containing μ^3-binding (1-oxa-2-silacyclopentene), as shown in Scheme 6. The complex was air-stable orange and pale brown crystals. In the ^1H NMR spectra of **6**, the methylene protons of (*Z*)-**1** gave way to a new upper-field resonance at −17.99 ppm, which is characteristic of the μ-bridging hydride between the metal–metal bond. Although, at room temperature and above, the μ-hydride ligands are coalesced with one broad signal, the spectrum showed two resonances at −55 °C (at −15.79 and −20.31 ppm), illustrated in Figure 5. The signal assigned to mesityl protons was also fluxional, but it is somewhat slower than the hydride exchange process. The energy barrier for this hydride exchange process can be estimated to be 11.3 kcal mol^{-1}.[15b] The IR absorptions and ^{13}C resonances for terminal carbonyl ligands as well as mass fragmentation ($M^+ - n(CO)$, n = 3–9) suggest the carbonyl stoichiometry of **6** as $Ru_3(CO)_9$. Thus these spectroscopic data have identified **6** as having a group formula $Ru_3(CO)_9(\mu\text{-}H)_2$ related to that established for the $M_3(CO)_9(\mu_3\text{-alkyne or -benzyne})(\mu\text{-}H)_2$ (M = Ru, Os) complexes.[15] In the $M_3(CO)_9(\mu^3$-alkylidene or -benzyne)-

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(13) For allene complexes: (a) Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231. (b) Kashiwagi, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *J. Chem. Soc., Chem. Commun.* **1969**, 317. (c) Hewitt, T. G. J.; Anzenhofer, K.; Deboer, J., Jr. *J. Chem. Soc., Chem. Commun.* **1969**, 312. (d) Racanelli, P.; Pantini, G.; Immirzi, A.; Allegra, G.; Porri, L. *J. Chem. Soc., Chem. Commun.* **1969**, 361.

(14) (a) Ishikawa, M.; Ohshita, J.; Ito, Y.; Iyoda, J. *J. Am. Chem. Soc.* **1986**, *108*, 7417. (b) Ohshita, J.; Isomura, Y.; Ishikawa, M. *Organometallics* **1989**, *8*, 2050.

(15) For μ^3-alkyne and benzyne trinuclear complexes: (a) Evans, J.; Johnson, B. F. G.; Lewis, J.; Matheson, T. W. *J. Organomet. Chem.* **1975**, *97*, C16. (b) Deeming, A. J. *J. Organomet. Chem.* **1978**, *150*, 123. (c) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. J. *J. Chem. Soc. Dalton Trans. 2* **1983**, 2257.

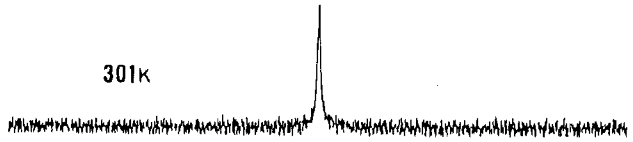
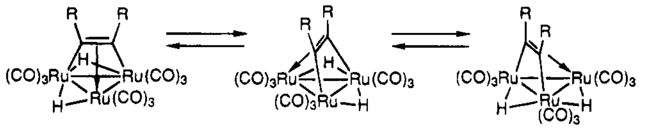


Figure 5. Temperature-dependent ^{1}H NMR (90 MHz) spectra of **6** in the μ-hydride region.

Scheme 7



(μ-H)$_2$ complexes, the fast fluxional process reported to occur is shown in Scheme 7. If the remaining ligand of **6** donates four electrons to the Ru$_3$ triangle, such as the μ^3-alkyne or -benzyne ligand,[15] **6** would have a closed shell configuration of 48 electrons. In order to establish the ligand structure of **6**, an X-ray diffraction study was undertaken.

An ORTEP drawing of the molecular structure of **6** is shown in Figure 6. The crystal data are listed in Table 2. The 1-oxa-2-silacyclopentene ligand lies over one face of the Ru$_3$ triangles such that the dihedral angle between the plane of the ring and that of the Ru$_3$ triangle is 71°. The organic ring forms σ bonds through C(1) and C(310) to two Ru atoms, bridging, the Ru(1)–Ru(3) edge, while the C(1)–C(310) bond interacts with the third Ru atom, Ru(2), in a π fashion. The metal framework is best described as an irregular triangle of Ru atoms. The two edge-bridging hydrides are located in structural analysis and cause the lengthening of the bond distances of Ru(1)–Ru(3) (2.986 Å) and Ru(1)–Ru(2) (2.822 Å), respectively.

It is well-known that siliranes (**VIII**, L$_n$M = SiR$_2$) readily react with carbonyl compounds to afford 1-oxa-2-silacyclopentanes (**IX**, L$_n$M = SiR$_2$) due to the "oxophilic" nature of silicon (Scheme 8).[16] Resemblances to

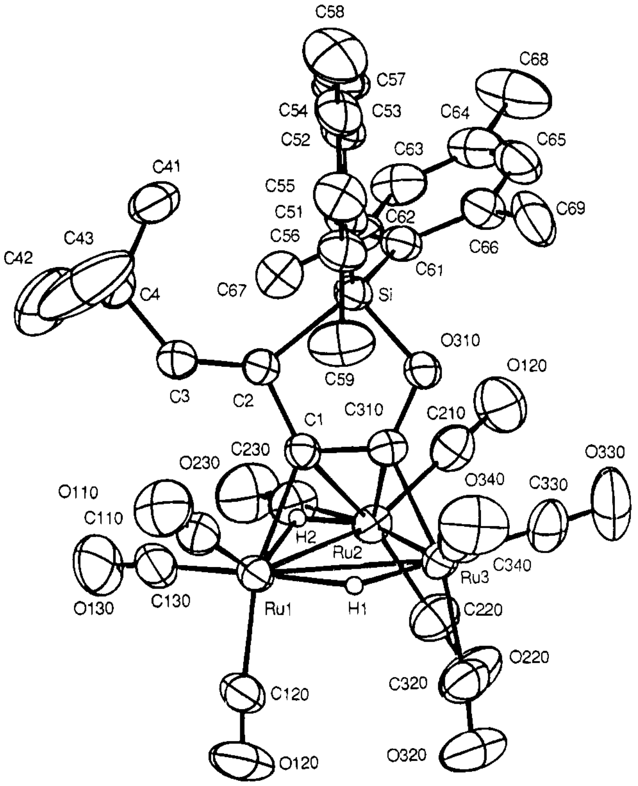
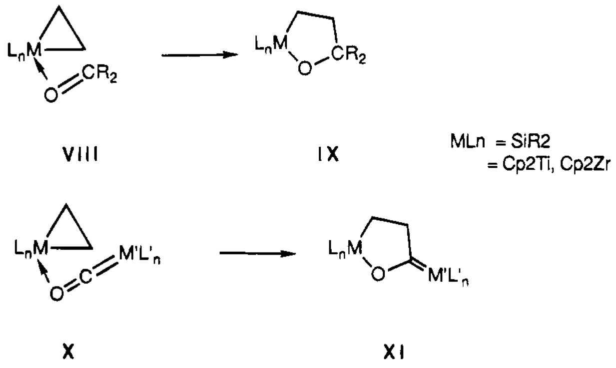


Figure 6. ORTEP drawing of **6**.

Scheme 8



these reaction squences are found in the oxophilic early transition metal chemistry. That is, the oxametallacyclopentanes (**IX**, L$_n$M = Cp$_2$Ti, Cp$_2$Zr) are formed analogously from the reaction of the η^2-olefin complex (**VIII**, L$_n$M = Cp$_2$Ti, Cp$_2$Zr), described as a metallacyclopentane in Scheme 8, with organic carbonyl compounds.[17a] Recently, the organic carbonyl compounds being replaced by metal carbonyls (**X**, L$_n$M = Cp$_2$Ti, Cp$_2$Zr), remarkable progress has been made in the synthesis of a new type of the Fischer-type carbene complex (**XI**, L$_n$M = Cp$_2$Ti, Cp$_2$Zr, M'L'$_n$ = Cr(CO)$_5$, Mo(CO)$_5$, W(CO)$_5$, Mn$_2$(CO)$_9$, etc).[18] However, to our knowledge, there is no counterpart for main group chemistry, i.e. metal-bound carbon monoxide inserting into siliranes. The formation of **6** requires an intermediate CO insertion into the silirane ring of (*Z*)-**1**. We believe this to occur according to Scheme 9. As mentioned above, the

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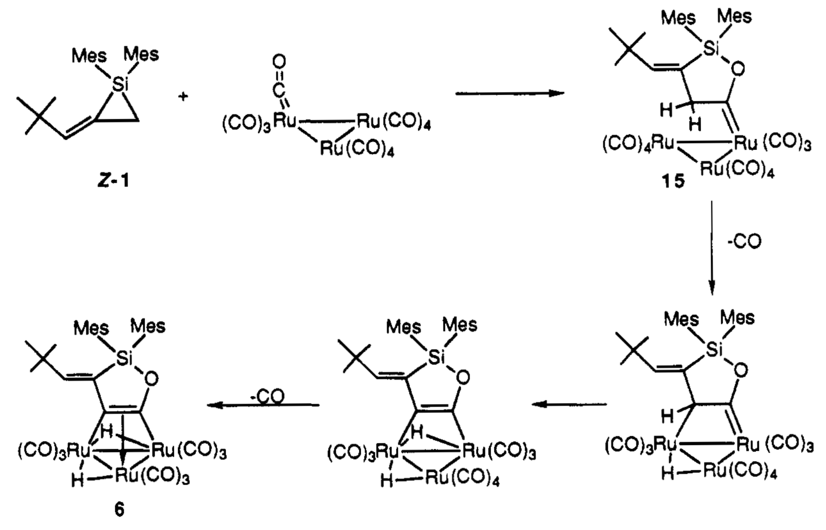
[16] (a) Seyferth, D.; Duncan, D. P.; Shannon, M. L. *Organometallics* **1984**, *3*, 579. (b) Seyferth, D.; Vick, S. C.; Shannon, M. L. *Organometallics* **1984**, *3*, 1897 and ref 7a,d.

[17] For the reaction of the η^2-Cp$_2$Zr-alkene complex with carbonyl compounds: (a) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. For the reaction of the η^2-Cp*$_2$Ti-alkene complex with carbonyl compounds: (b) Cohen, S. A.; Bercaw, J. E.; *Organometallics* **1985**, *4*, 1006. (c) Mashima, K.; Haraguchi, H.; Ohyoshi, A.; Sakai, N.; Takaya, H. *Organometallics* **1991**, *10*, 2731.

Scheme 9



primary product is presumably carbene complex **15**, which then repeats decarbonylation and oxidative addition to form product **6**. The CH bond cleavage in the oxidative addition is a facile and well-studied process,[19] but the metal-bound CO insertion into silirane rings has not been noted before.

In conclusion, the successful construction of η^4-STMM complexes suggests the ring opening of alkylidenesiliranes and η^4-complexation by transition metals to be a versatile synthetic route. The structures of η^4-STMM complexes resemble the corresponding carbon analogue unlie other transition metal complexes of unsaturated silicon compounds.

Experimental Section

All solvents and starting materials were performed according to a standard procedure. (*Z*)- and (*E*)-1,1-dimesityl-2-(*Z*)-neopentylidenesilirane ((*E*)-**1**), 1,1-dimesityl-2-(*E*)-neopentylidenesilirane ((*Z*/*E*)-**1**),[7a–d] and 1,1-dimesityl-2,3-isopropylidenesilirane (**3**)[7e] were prepared by published procedures. All reactions were performed under an argon atmosphere unless specified otherwise. Infrared spectra were recorded on a Hitachi 265-50 IR spectrometer. NMR spectra were run either on a Bruker AM500 or a JEOL EX-90 spectrometer. Elemental analyses were carried out by the Chemical Analytical Center of the University of Tsukuba. Mass spectra and high-resolution mass spectra were obtained on a JEOL SX102A mass spectrometer.

Reaction of (*Z*)-1,1-Dimesityl-2-(*Z*)-neopentylidenesilirane ((*Z*)-1) with Fe$_2$(CO)$_9$. A mixture of (*Z*)-**1** (56 mg, 0.15 mmol) and Fe$_2$(CO)$_9$ (61 mg, 0.16 mmol) in benzene (2.5 mL) was stirred for 6 h at room temperature. After complete consumption of (*Z*)-**1**, as indicated by TLC, the solvent was removed in vacuo and the residue was purified by preparative silica gel TLC using hexane as eluent to give Fe(CO)$_3$[η^4-Mes$_2$SiCCH$_2$((*Z*)-CH^{t}Bu)] ((*Z*)-**2**) (44 mg, 59%). For (*Z*)-**2**: pale brown crystals; mp 174–176 °C; ^{1}H-NMR (500 MHz, CDCl$_3$) δ 0.82 (s, 10H), 1.42 (s, 1H), 2.19 (s, 6H), 2.48 (s, 3H), 2.67 (s, 3H), 2.78 (s, 1H), 2.85 (s, 3H), 2.89 (s, 3H), 6.72 (s, 2H), 6.81 (s, 1H), 6.89 (s, 1H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 20.9 (q), 21.0 (q), 25.4 (q), 25.7 (q), 26.0 (q), 28.1 (q), 31.7 (q), 35.1 (s), 42.9 (t), 73.0 (s), 103.1 (d), 128.4 (d), 128.8 (d), 129.1 (d), 129.3 (d), 130.6 (s), 132.3 (s), 138.9 (s), 139.6 (s), 143.0 (s), 143.2 (s), 143.8 (s), 145.8 (s), 213.6 (s), 213.9 (s), 214.2 (s); ^{29}Si-NMR (18 MHz, CDCl$_3$) δ 43.6; IR (KBr) ν 2028 (s, sh), 1959 (s, br) cm^{-1}; mass *m/e* 502 (M$^+$, 9), 474 (M$^+$ − CO, 8), 446 (M$^+$ − 2CO, 10), 418 (M$^+$ − 3CO, 100), 326 (M$^+$ − Fe(CO)$_3$, 2). Exact Mass: calcd for C$_{28}$H$_{34}$O$_3$SiFe *m/e* 502.1627; found *m/e* 502.1596. Anal. Calcd: C, 66.93; H, 6.82. Found: C, 66.90; H, 6.70.

Reaction of (*E*)-1,1-Dimesityl-2-neopentylidenesilirane ((*E*)-1) with Fe$_2$(CO)$_9$. A mixture of (*E*)-**1** (59 mg, 0.16 mmol) and Fe$_2$(CO)$_9$ (65 mg, 0.17 mmol) in benzene (3.5 mL) was stirred for 1.5 h at room temperature. After complete consumption of (*E*)-**1** by TLC, the solvent was removed in vacuo and the residue was purified by preparative silica gel TLC using hexane as eluent to give Fe(CO)$_3$[η^4-Mes$_2$SiCCH$_2$((*E*)-CH^{t}Bu)] ((*E*)-**2**) (31 mg, 38%). For (*E*)-**2**: pale yellow oil; ^{1}H-NMR (90 MHz, CDCl$_3$, −40 °C) δ 1.03 (s, 9H), 2.21 (s, 3H), 2.23 (s, 3H), 2.31 (s, 1H), 2.61 (br s, 3H), 2.74 (s, 3H), 2.81 (s, 3H), 2.89 (br s, 3H), 2.98 (s, 1H), 3.35 (s, 1H), 6.79 (s, 1H), 6.82 (br s, 2H), 6.88 (s, 1H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 20.96 (q), 21.03 (q), 26.2 (q), 26.4 (br q), 26.5 (q), 27.3 (br q), 31.8 (q), 36.6 (s), 49.5 (t), 81.7 (s), 94.0 (d), 127.1 (s), 127.2 (s), 128.0 (d), 129.1 (br d), 129.34 (d), 139.6 (s), 139.9 (s), 143.5 (br s), 144.2 (s), 145.7 (s), 146.9 (br s), 214.4 (br s); ^{29}Si-NMR (18 MHz, CDCl$_3$) δ 23.1; IR (NaCl) ν 2028 (s, sh), 1957 (s, br) cm^{-1}; mass *m/e* 502 (M$^+$, 16.6), 474 (M$^+$ − CO, 5.2), 446 (M$^+$ − 2CO, 25.3), 418 (M$^+$ − 3CO, 100). Exact Mass: calcd for C$_{28}$H$_{34}$O$_3$SiFe *m/e* 502.1627; found *m/e* 502.1624.

Reaction of 1,1-Dimesityl-2,3-diisopropylidenesilirane (3) with Fe$_2$(CO)$_9$. A mixture of **3** (56 mg, 0.14 mmol) and Fe$_2$(CO)$_9$ (54 mg, 0.14 mmol) in benzene (3 mL) was stirred for 2 h at room temperature. After complete consumption of **3** by TLC, the solvent was removed in vacuo and the residue was purified by preparative silica gel TLC using hexane as eluent to give Fe(CO)$_3$[η^4-Mes$_2$SiC(CMe$_2$)(C=CMe$_2$)] (**4**) (12 mg,

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[18] For metallocene carbene complexes of Ti and Zr: (a) Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397. (b) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R. D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. (c) Erker, G.; Dorf, U.; Mynott, R.; Tsay, Y.-H.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 584–585. (d) Mashima, K.; Jyodoi, K.; Ohyoshi, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1145. (e) Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem.* **1989**, *368*, 315. (f) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712. (g) Anslyn, E. V.; Santarsiero, B. D.; Grubbs, R. H. *Organometallics* **1988**, *7*, 2137.

[19] For the reactions of trinuclear clusters of Ru and Os: (a) Lewis, J.; Johnson, B. F. G. *Pure Appl. Chem.* **1982**, *54*, 97. (b) Burgess, K. *Polyhedron* **1984**, *3*, 1175. (c) Deeming, A. *J. Adv. Organomet. Chem.* **1986**, *26*, 1. (d) Bennet, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. From recent literature: (e) Bohle, D. S.; Heineke, D.; Tiripicchio, A.; Camellini, M. T.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 896. (f) Deeming, A. J.; Nuel, D.; Powell, N. I.; Whittaker, C. *J. Chem. Soc., Chem. Commun.* **1990**, 68. (g) Rosenberg, E.; Kabir, S. E.; Hardcastle, K. I.; Day, M.; Wolf, E. *Organometallics* **1990**, *9*, 2214. (h) Jenke, T.; Stoecki-Evans, H.; Bodensieck U. Suss-Fink, G. *J. Organomet. Chem.* **1991**, *401*, 347.

[20] (a) *International Tables for X-ray Crystallography*; The Knoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *International Tables for X-ray Crystallography*; The Knoch Press: Birmingham, England, 1975; Vol. IV, Table 2.3.1, pp 149–150.

Table 3. Intramolecular Distances (Å) for (Z)-2

Fe−Si	2.422(2)	C(11)−C(16)	1.37(1)
Fe−C(1)	1.993(8)	C(12)−C(13)	1.39(1)
Fe−C(2)	2.182(9)	C(12)−C(17)	1.51(1)
Fe−C(3)	2.107(8)	C(13)−C(14)	1.36(1)
Fe−C(4)	1.81(1)	C(14)−C(15)	1.39(1)
Fe−C(5)	1.81(1)	C(14)−C(19)	1.50(1)
Fe−C(6)	1.756(9)	C(15)−C(16)	1.40(1)
Si−C(1)	1.840(8)	C(16)−C(18)	1.51(1)
Si−C(11)	1.899(8)	C(21)−C(22)	1.41(1)
Si−C(21)	1.921(7)	C(21)−C(26)	1.42(1)
O(1)−C(4)	1.15(1)	C(22)−C(23)	1.40(1)
O(2)−C(5)	1.15(1)	C(22)−C(28)	1.51(1)
O(3)−C(6)	1.15(1)	C(23)−C(24)	1.37(1)
C(1)−C(2)	1.42(1)	C(24)−C(25)	1.39(1)
C(1)−C(3)	1.46(1)	C(24)−C(29)	1.49(1)
C(2)−C(31)	1.51(1)	C(25)−C(26)	1.39(1)
C(2)−H(2)	1.0(1)	C(26)−C(27)	1.48(1)
C(3)−H(31)	1.07(9)	C(31)−C(32)	1.54(1)
C(3)−H(32)	1.0(1)	C(31)−C(33)	1.58(2)
C(11)−C(12)	1.43(1)	C(31)−C(34)	1.52(1)

Table 4. Intramolecular Bond Angles (deg) for (Z)-2

Si−Fe−C(1)	48.1(2)	Fe−C(3)−H(32)	130.(6)
Si−Fe−C(2)	79.0(2)	C(1)−C(3)−H(31)	122.(5)
Si−Fe−C(3)	71.4(2)	C(1)−C(3)−H(32)	122.(6)
Si−Fe−C(4)	160.4(3)	H(31)−C(3)−H(32)	97.(8)
Si−Fe−C(5)	83.8(3)	Fe−C(4)−O(1)	179.2(9)
Si−Fe−C(6)	102.1(3)	Fe−C(5)−O(2)	178.6(9)
C(1)−Fe−C(2)	39.4(4)	Fe−C(6)−O(3)	175.9(9)
C(1)−Fe−C(3)	41.6(3)	Si−C(11)−C(12)	116.4(6)
C(1)−Fe−C(4)	114.2(4)	Si−C(11)−C(16)	124.8(6)
C(1)−Fe−C(5)	121.6(4)	C(12)−C(11)−C(16)	118.6(7)
C(1)−Fe−C(6)	123.9(4)	C(11)−C(12)−C(13)	119.3(8)
C(2)−Fe−C(3)	66.5(3)	C(11)−C(12)−C(17)	121.9(7)
C(2)−Fe−C(4)	90.0(4)	C(13)−C(12)−C(17)	118.8(8)
C(2)−Fe−C(5)	160.3(4)	C(12)−C(13)−C(14)	122.5(9)
C(2)−Fe−C(6)	98.9(4)	C(13)−C(14)−C(15)	117.6(9)
C(3)−Fe−C(4)	89.4(4)	C(13)−C(14)−C(19)	121.6(9)
C(3)−Fe−C(5)	95.0(4)	C(15)−C(14)−C(19)	121(1)
C(3)−Fe−C(6)	164.7(4)	C(14)−C(15)−C(16)	121.8(9)
C(4)−Fe−C(5)	96.9(5)	C(11)−C(16)−C(15)	120.1(7)
C(4)−Fe−C(6)	95.6(4)	C(11)−C(16)−C(18)	125.2(8)
C(5)−Fe−C(6)	98.8(5)	C(15)−C(16)−C(18)	114.7(7)
Fe−Si−C(1)	53.7(3)	Si−C(21)−C(22)	124.0(6)
Fe−Si−C(11)	127.4(3)	Si−C(21)−C(26)	118.1(6)
Fe−Si−C(21)	118.7(2)	C(22)−C(21)−C(26)	117.9(7)
C(1)−Si−C(11)	126.6(4)	C(21)−C(22)−C(23)	119.7(8)
C(1)−Si−C(21)	110.9(3)	C(21)−C(22)−C(28)	126.0(7)
C(11)−Si−C(21)	109.1(3)	C(23)−C(22)−C(28)	114.3(7)
Fe−C(1)−Si	78.2(3)	C(22)−C(23)−C(24)	122.5(8)
Fe−C(1)−C(2)	77.5(5)	C(23)−C(24)−C(25)	117.8(8)
Fe−C(1)−C(3)	73.4(5)	C(23)−C(24)−C(29)	120.8(9)
Si−C(1)−C(2)	127.8(6)	C(25)−C(24)−C(29)	121.5(8)
Si−C(1)−C(3)	106.5(6)	C(24)−C(25)−C(26)	122.4(8)
C(2)−C(1)−C(3)	109.6(7)	C(21)−C(26)−C(25)	119.8(7)
Fe−C(2)−C(1)	63.1(5)	C(21)−C(26)−C(27)	121.4(7)
Fe−C(2)−C(31)	128.0(6)	C(25)−C(26)−C(27)	118.8(7)
Fe−C(2)−H(2)	106.5(5)	C(2)−C(31)−C(32)	117.0(8)
C(1)−C(2)−C(31)	133.0(8)	C(2)−C(31)−C(33)	103.3(8)
C(1)−C(2)−H(2)	107.(6)	C(2)−C(31)−C(34)	108.7(9)
C(31)−C(2)−H(2)	110.(5)	C(32)−C(31)−C(33)	109.8(8)
Fe−C(3)−C(1)	65.0(4)	C(32)−C(31)−C(34)	108.9(9)
Fe−C(3)−H(31)	121.(6)	C(33)−C(31)−C(34)	108.9(9)

Table 5. Intramolecular Distances (Å) for 4

Fe−Si	2.395(1)	C(4)−C(42)	1.479(7)
Fe−C(1)	2.039(8)	C(51)−C(52)	1.415(5)
Fe−C(2)	2.288(9)	C(51)−C(56)	1.407(5)
Fe−C(3)	2.044(8)	C(52)−C(53)	1.391(5)
Fe−C(7)	1.773(9)	C(52)−C(58)	1.503(6)
Fe−C(8)	1.800(1)	C(53)−C(54)	1.385(6)
Fe−C(9)	1.804(1)	C(54)−C(55)	1.364(5)
Si−C(1)	1.868(8)	C(54)−C(59)	1.513(6)
Si−C(51)	1.906(8)	C(55)−C(56)	1.410(6)
Si−C(61)	1.903(8)	C(56)−C(57)	1.506(6)
O(7)−C(7)	1.134(5)	C(61)−C(62)	1.412(6)
O(8)−C(8)	1.137(6)	C(61)−C(66)	1.416(5)
O(9)−C(9)	1.132(6)	C(62)−C(63)	1.397(6)
C(1)−C(2)	1.422(5)	C(62)−C(68)	1.485(6)
C(1)−C(3)	1.439(5)	C(63)−C(64)	1.372(6)
C(2)−C(21)	1.521(6)	C(64)−C(65)	1.369(8)
C(2)−C(22)	1.500(6)	C(64)−C(69)	1.502(7)
C(3)−C(4)	1.302(6)	C(65)−C(66)	1.390(6)
C(4)−C(41)	1.520(8)	C(66)−C(67)	1.498(6)

Table 6. Intramolecular Bond Angles (deg) for 4

Si−Fe−C(1)	49.0(2)	C(1)−C(2)−C(22)	122.5(4)
Si−Fe−C(2)	75.4(2)	C(21)−C(2)−C(22)	112.0(5)
Si−Fe−C(3)	73.3(3)	Fe−C(3)−C(1)	69.2(4)
Si−Fe−C(7)	88.3(3)	Fe−C(3)−C(4)	140.9(4)
Si−Fe−C(8)	161.4(3)	C(1)−C(3)−C(4)	147.8(4)
Si−Fe−C(9)	100.2(3)	C(3)−C(4)−C(41)	121.2(4)
C(1)−Fe−C(2)	37.8(4)	C(3)−C(4)−C(42)	122.9(6)
C(1)−Fe−C(3)	41.3(3)	C(41)−C(4)−C(42)	115.8(4)
C(1)−Fe−C(7)	122.2(4)	Si−C(51)−C(52)	117.6(3)
C(1)−Fe−C(8)	113.9(4)	Si−C(51)−C(56)	124.3(3)
C(1)−Fe−C(9)	117.9(4)	C(52)−C(51)−C(56)	117.9(3)
C(2)−Fe−C(3)	67.2(3)	C(51)−C(52)−C(53)	119.8(3)
C(2)−Fe−C(7)	160.6(4)	C(51)−C(52)−C(58)	122.8(3)
C(2)−Fe−C(9)	89.7(4)	C(53)−C(52)−C(58)	117.4(3)
C(3)−Fe−C(7)	97.4(4)	C(52)−C(53)−C(54)	122.4(4)
C(3)−Fe−C(8)	88.6(4)	C(53)−C(54)−C(55)	118.0(4)
C(3)−Fe−C(9)	156.9(4)	C(53)−C(54)−C(59)	121.3(5)
C(7)−Fe−C(8)	98.4(5)	C(55)−C(54)−C(59)	120.7(5)
C(7)−Fe−C(9)	104.6(5)	C(54)−C(55)−C(56)	122.2(4)
C(8)−Fe−C(9)	94.9(5)	C(51)−C(56)−C(55)	119.7(4)
Fe−Si−C(1)	55.5(5)	C(51)−C(56)−C(57)	125.(5)
Fe−Si−C(51)	125.2(4)	C(55)−C(56)−C(57)	115.3(4)
Fe−Si−C(61)	121.1(4)	Si−C(61)−C(62)	123.9(3)
C(1)−Si−C(51)	120.8(4)	Si−C(61)−C(66)	118.6(3)
C(1)−Si−C(61)	116.(3)	C(62)−C(61)−C(66)	117.3(3)
C(51)−Si−C(61)	108.6(3)	C(61)−C(62)−C(63)	119.2(3)
Fe−C(1)−Si	75.5(3)	C(61)−C(62)−C(68)	125.7(3)
Fe−C(1)−C(2)	80.6(5)	C(63)−C(62)−C(68)	115.1(3)
Fe−C(1)−C(3)	69.5(5)	C(62)−C(63)−C(64)	123.5(5)
Si−C(1)−C(2)	120.4(6)	C(63)−C(64)−C(65)	117.(4)
Si−C(1)−C(3)	106.7(6)	C(63)−C(64)−C(69)	122.6(5)
C(2)−C(1)−C(3)	114.5(3)	C(65)−C(64)−C(69)	120.3(5)
Fe−C(2)−C(1)	61.6(5)	C(64)−C(65)−C(66)	122.8(4)
Fe−C(2)−C(21)	112.8(5)	C(61)−C(66)−C(66)	120.2(4)
Fe−C(2)−C(22)	117.7(5)	C(61)−C(66)−C(67)	122.7(5)
C(1)−C(2)−C(21)	120.3(4)	C(65)−C(66)−C(67)	117.2(4)

17%). For **4**: yellow crystals; mp 155−156 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 3H), 1.54 (s, 3H), 1.61 (s, 3H), 2.01 (s, 3H), 2.18 (s, 6H), 2.54 (br s, 3H), 2.72 (s, 3H), 2.82 (s, 3H), 2.84 (br s, 3H), 6.71 (br s, 1 H), 6.74 (s, 1H), 6.80 (br s, 1H), 6.83 (s, 1H); ^{13}-NMR (125 MHz, $CDCl_3$) δ 20.9 (q), 24.3 (q), 24.8 (q), 25.7 (br q), 25.9 (q), 26.0 (q), 26.3 (q), 27.6 (q), 27.9 (br q), 61.1 (s), 100.2 (s), 120.2 (s), 128.2 (d), 128.3 (br d), 129.4 (d), 129.9 (s), 132.3 (s), 138.6 (s), 139.4 (s), 143.3 (br s), 143.4 (s), 143.5 (s), 145.7 (br s), 154.4 (s), 211.1 (s), 213.2 (s), 214.5 (s); ^{29}Si-NMR (18 MHz, $CDCl_3$) δ 19.1; IR (KBr) ν 2028 (s, sh), 1966 (s, br), 1951 (s, br) cm^{-1}; mass *m/e* 514 (M^+, 4.7), 486 (M^+ − CO, 9.5), 458 (M^+ − 2CO, 95.5), 430 (M^+ − 3CO, 100), 374 (M^+ − $Fe(CO)_3$, 3.7). Anal. Calcd for $C_{29}H_{34}O_3SiFe$: C, 67.67; H, 6.66. Found: C, 66.80; H, 6.66.

Reaction of (*Z*)-1,1-Dimesityl-2-neopentylidenesilirane ((*Z*)-1) with $Ru_3(CO)_{12}$. A mixture of (*Z*)-**1** (36 mg, 0.10 mmol) and $Ru_3(CO)_{12}$ (78 mg, 0.12 mmol) in benzene (3 mL) was refluxed for 6 h. After complete consumption of (*Z*)-**1**, the solvent was removed in vacuo. The residue was purified by preparative silica gel TLC using hexane as eluent to give $Ru(CO)_3[\eta^4\text{-}Mes_2SiCCH_2((Z)\text{-}CH^tBu)]$ ((*Z*)-**5**) (5 mg, 9%) and $Ru_3(CO)_9[\mu^3\text{-}Mes_2SiC(C{=}CH^tBu)C_2O](\mu\text{-}H)_2$ (**6**) (58 mg, 62%). For (*Z*)-**5**: pale brown crystal; mp 139−141 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.81 (s, 9H), 0.93 (s, 1H), 1.44 (s, 1H), 2.18 (s, 3H), 2.19 (s, 3H), 2.51 (s, 3H), 2.67 (s, 3H), 2.90 (s, 3H), 2.91 (s, 3H), 2.97 (s, 1H), 6.71 (s, 1H), 6.72 (s, 1H), 6.78 (s, 1H), 6.89 (s, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 20.9 (q), 21.0 (q), 25.3 (q), 26.3 (q), 28.6 (q), 32.8 (q), 34.1 (s), 36.7 (t), 81.4 (s), 98.6 (d), 128.4 (d), 128.6 (d), 129.0 (d), 129.1 (d), 131.7 (s), 132.4 (s), 138.3 (s), 139.2 (s), 142.7 (s), 143.1 (s), 143.7 (s), 145.3 (s), 198.3 (s), 199.9 (s), 200.7 (s); ^{29}Si-NMR (18 MHz, $CDCl_3$) δ 40.1;

Table 7. Intramolecular Distances (Å) for 6

Ru(1)−Ru(2)	2.8222(4)	O(230)−C(230)	1.121(5)
Ru(1)−Ru(3)	2.9861(4)	O(310)−C(310)	1.359(4)
Ru(1)−C(1)	2.126(3)	O(320)−C(320)	1.117(6)
Ru(1)−C(110)	1.921(4)	O(330)−C(330)	1.138(6)
Ru(1)−C(120)	1.952(4)	O(340)−C(340)	1.122(5)
Ru(1)−C(130)	1.923(4)	C(1)−C(2)	1.496(5)
Ru(1)−H(1)	1.910	C(1)−C(310)	1.407(5)
Ru(2)−Ru(3)	2.7478(3)	C(2)−C(3)	1.334(5)
Ru(1)−H(2)	1.691	C(3)−C(4)	1.512(6)
Ru(2)−C(1)	2.260(3)	C(4)−C(41)	1.486(6)
Ru(2)−C(210)	1.900(4)	C(4)−C(42)	1.558(7)
Ru(2)−C(220)	1.913(4)	C(4)−C(43)	1.501(7)
Ru(2)−C(230)	1.942(4)	C(51)−C(52)	1.414(5)
Ru(2)−C(310)	2.356(3)	C(52)−C(53)	1.386(5)
Ru(2)−H(2)	1.691	C(52)−C(57)	1.516(5)
Ru(3)−C(310)	2.031(3)	C(53)−C(54)	1.379(5)
Ru(3)−C(320)	1.976(4)	C(54)−C(55)	1.373(6)
Ru(3)−C(330)	1.008(5)	C(54)−C(58)	1.518(6)
Ru(3)−C(340)	1.914(4)	C(55)−C(56)	1.395(5)
Ru(3)−H(1)	1.55(5)	C(56)−C(59)	1.507(6)
Si−O(310)	1.706(3)	C(61)−C(62)	1.406(4)
Si−C(2)	1.901(3)	C(61)−C(66)	1.418(6)
Si−C(51)	1.892(3)	C(62)−C(63)	1.394(5)
Si−C(61)	1.883(4)	C(62)−C(67)	1.502(6)
O(110)−C(110)	1.120(5)	C(63)−C(64)	1.382(7)
O(120)−C(120)	1.125(5)	C(64)−C(63)	1.513(6)
O(130)−C(130)	1.116(5)	C(65)−C(66)	1.387(6)
O(220)−C(220)	1.132(5)	C(66)−C(69)	1.498(6)

Table 8. Intramolecular Bond Angles (deg) for 6

Ru(3)−Ru(1)−Ru(3)	56.385(9)	Ru(1)−Ru(3)−Ru(2)	58.80(1)
Ru(2)−Ru(1)−C(1)	52.07(8)	Ru(1)−Ru(3)−C(310)	67.8(1)
Ru(2)−Ru(1)−C(110)	142.0(1)	Ru(1)−Ru(3)−C(320)	96.7(1)
Ru(2)−Ru(1)−C(120)	118.1(1)	Ru(1)−Ru(3)−C(330)	148.8(1)
Ru(2)−Ru(1)−C(130)	96.9(2)	Ru(1)−Ru(3)−C(340)	110.1(1)
Ru(3)−Ru(1)−C(1)	67.25(9)	Ru(1)−Ru(3)−H(1)	34.(1)
Ru(3)−Ru(1)−C(110)	107.7(2)	Ru(2)−Ru(3)−C(310)	56.71(8)
Ru(3)−Ru(1)−C(120)	98.7(2)	Ru(2)−Ru(3)−C(320)	105.9(1)
Ru(3)−Ru(1)−C(130)	153.3(1)	Ru(2)−Ru(3)−C(330)	90.4(1)
C(1)−Ru(1)−C(110)	90.4(1)	Ru(2)−Ru(3)−C(340)	154.7(1)
C(1)−Ru(1)−C(120)	165.6(2)	Ru(2)−Ru(3)−H(1)	93.(1)
C(1)−Ru(1)−C(130)	97.3(1)	C(310)−Ru(3)−C(320)	160.7(1)
C(110)−Ru(1)−C(120)	97.4(2)	C(310)−Ru(3)−C(330)	92.6(2)
C(110)−Ru(1)−C(130)	93.5(2)	C(310)−Ru(3)−C(340)	98.5(1)
C(120)−Ru(1)−C(130)	94.3(2)	C(310)−Ru(3)−H(1)	87.(2)
Ru(1)−Ru(2)−Ru(3)	64.82(1)	C(320)−Ru(3)−C(330)	96.1(2)
Ru(1)−Ru(2)−C(1)	47.89(8)	C(320)−Ru(3)−C(340)	97.7(2)
Ru(1)−Ru(2)−C(210)	152.1(1)	C(320)−Ru(3)−H(1)	86.(2)
Ru(1)−Ru(2)−C(220)	111.6(1)	C(330)−Ru(3)−C(340)	96.2(2)
Ru(1)−Ru(2)−C(230)	98.3(1)	C(330)−Ru(3)−H(1)	176.(1)
Ru(1)−Ru(2)−C(310)	67.62(8)	C(340)−Ru(3)−H(1)	80.(1)
Ru(3)−Ru(2)−C(1)	70.56(7)	O(310)−Si−C(2)	93.4(1)
Ru(3)−Ru(2)−C(210)	101.9(1)	O(310)−Si−C(51)	108.8(1)
Ru(3)−Ru(2)−C(220)	87.5(1)	O(310)−Si−C(61)	103.4(2)
Ru(3)−Ru(2)−C(230)	163.0(1)	C(2)−Si−C(51)	114.8(2)
Ru(3)−Ru(2)−C(310)	46.12(8)	C(2)−Si−C(61)	120.5(1)
C(1)−Ru(2)−C(210)	105.4(1)	C(51)−Si−C(61)	112.6(2)
C(1)−Ru(2)−C(220)	154.6(1)	Si−O(310)−C(310)	112.1(2)
C(1)−Ru(2)−C(230)	96.9(1)	Ru(1)−C(1)−Ru(2)	80.0(1)
C(1)−Ru(2)−C(310)	35.4(1)	Ru(1)−C(1)−C(2)	132.6(2)
C(210)−Ru(2)−C(220)	91.2(2)	Ru(1)−C(1)−C(310)	109.0(2)
C(210)−Ru(2)−C(230)	92.4(2)	Ru(2)−C(1)−C(2)	130.6(2)
C(210)−Ru(2)−C(310)	85.4(1)	Ru(2)−C(1)−C(310)	76.0(2)
C(220)−Ru(2)−C(230)	101.5(2)	C(2)−C(1)−C(310)	113.0(3)
C(220)−Ru(2)−C(310)	131.0(1)	Si−C(2)−C(1)	102.9(2)
C(230)−Ru(2)−C(310)	127.5(1)	Si−C(2)−C(3)	135.2(3)
C(1)−C(2)−C(3)	120.8(3)	C(63)−C(62)−C(67)	116.7(3)
C(2)−C(3)−C(4)	133.7(3)	C(62)−C(63)−C(64)	121.8(4)
C(3)−C(4)−C(41)	116.0(3)	C(63)−C(64)−C(65)	117.7(3)
C(3)−C(4)−C(42)	105.2(4)	C(63)−C(64)−C(68)	120.6(5)
C(3)−C(4)−C(43)	107.1(3)	C(65)−C(64)−C(68)	121.8(5)
C(41)−C(4)−C(42)	107.8(5)	C(64)−C(65)−C(66)	122.9(5)
C(41)−C(4)−C(43)	106.1(4)	C(61)−C(66)−C(65)	119.5(3)
C(42)−C(4)−C(43)	115.1(6)	C(61)−C(66)−C(69)	122.6(4)
Si−C(51)−C(52)	123.7(3)	C(65)−C(66)−C(69)	117.8(4)
Si−C(51)−C(56)	119.1(3)	Ru(1)−C(110)−O(110)	177.8(3)
C(52)−C(51)−C(56)	117.2(3)	Ru(1)−C(120)−O(120)	174.2(3)
C(51)−C(52)−C(53)	120.1(3)	Ru(1)−C(130)−O(130)	176.4(4)
C(51)−C(52)−C(57)	124.7(3)	Ru(2)−C(210)−O(210)	177.3(4)
C(53)−C(52)−C(57)	115.1(3)	Ru(2)−C(220)−O(220)	178.5(4)
C(52)−C(53)−C(54)	122.7(4)	Ru(2)−C(230)−O(230)	177.8(4)
C(53)−C(54)−C(55)	117.6(4)	Ru(2)−C(310)−Ru(3)	77.2(1)
C(53)−C(54)−C(58)	121.2(3)	Ru(2)−C(310)−O(310)	125.2(3)
C(55)−C(54)−C(58)	121.2(3)	Ru(2)−C(310)−C(1)	68.6(1)
C(54)−C(55)−C(56)	122.1(3)	Ru(3)−C(310)−O(310)	127.6(2)
C(51)−C(56)−C(55)	120.3(4)	Ru(3)−C(310)−C(1)	115.0(2)
C(51)−C(56)−C(59)	122.6(3)	O(310)−C(310)−C(1)	117.3(2)
C(55)−C(56)−C(59)	117.1(3)	Ru(3)−C(320)−O(320)	175.2(4)
Si−C(61)−C(62)	125.6(3)	Ru(3)−C(330)−O(330)	178.6(4)
Si−C(61)−C(66)	116.7(2)	Ru(3)−C(340)−O(340)	176.8(4)
C(62)−C(61)−C(66)	117.6(3)	Ru(1)−H(1)−Ru(3)	118.7
C(61)−C(62)−C(63)	120.2(4)	Ru(1)−H(2)−Ru(2)	108.1
C(61)−C(62)−C(67)	123.1(3)		

IR (NaCl) ν 2054 (s, sh), 1992 (s, br), 1970 (s, br) cm^{-1}; mass *m/e* 548 (M$^+$, 54), 520 (M$^+$ − CO, 9), 492 (M$^+$ − 2CO, 34), 464 (M$^+$ − 3CO, 62), 362 (M$^+$ − Ru (CO)$_3$, 50). Exact Mass: calcd for $C_{28}H_{34}O_3SiRu$ *m/e* 548.1321; found *m/e* 548.1345. For **6**: orange crystals; mp 182−183 °C; ^{1}H-NMR (500 MHz, CDCl$_3$) δ −17.99 (s, 2H), 0.97 (s, 9H), 1.91 (br s, 3H), 2.24 (br s, 6H), 2.34 (br s, 3H), 2.39 (br s, 3H), 2.61 (br s, 3H), 6.27 (s, 1H), 6.75 (br s, 3H), 6.84 (br s, 1H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 21.1 (q), 23.1 (br q), 23.7 (br q), 24.3 (br q), 24.7 (br q), 29.1 (q), 35.4 (s), 120.0 (d), 128.6 (br d), 129.7 (br d), 129.8 (br d), 130.3 (br s), 140.0 (s), 140.7 (s), 143.0 (br s), 144.9 (br s), 145.8 (br s), 146.3 (br s), 153.0 (d), 188.9 (br s), 204.6 (s); ^{29}Si-NMR (18 MHz, CDCl$_3$) δ −1.10; IR (KBr) ν 2108 (m, sh), 2080 (s, sh), 2058 (s, sh), 2042 (s, sh), 2014 (s, sh), 1995 (s), 1976 (m) cm^{-1}; mass *m/e* 862 (M$^+$ − 3CO), 834 (M$^+$ − 4CO), 804 (M$^+$ − 5CO), 778 (M$^+$ − 6CO), 750 (M$^+$ − 7CO), 772 (M$^+$ − 8CO), 694 (M$^+$ − 9CO). Anal. Calcd for $C_{35}H_{34}O_{10}SiRu_3$: C, 44.44; H, 3.62. Found: C, 44.39; H, 3.62.

Reaction of (*E*)-1,1-Dimesityl-2-neopentylidenesilirane ((*E*)-1) with $Ru_3(CO)_{12}$. A mixture of (*E*)-**1** (28 mg, 0.07 mmol) and $Ru_3(CO)_{12}$ (50 mg, 0.08 mmol) in benzene (3 mL) was refluxed for 6.5 h. After complete consumption of (*E*)-**1**, the solvent was removed in vacuo and the residue was purified by preparative silica gel TLC using hexane as eluent to give Ru(CO)$_3$[η^4-Mes$_2$SiCCH$_2$((*Z*)-CH^{t}Bu)] (**5E**) (9 mg, 22%). For (*E*)-**5**: pale yellow oil; ^{1}H-NMR (500 MHz, CDCl$_3$) δ 1.03 (s, 9H), 2.20 (s, 3H), 2.22 (s, 3H), 2.38 (br s, 1H), 2.76 (br s, 3H), 2.79 (br s, 6H), 2.84 (br s, 3H), 3.07 (s, 1H), 3.39 (d, 1H, J = 1.7 Hz), 6.77 (s, 1H), 6.79 (br s, 2H), 6.84 (s, 1H); ^{13}C-NMR (125 MHz, CDCl$_3$) δ 20.9 (q), 21.0 (q), 26.0 (br q), 27.1 (br q), 29.1 (q), 32.1 (q), 32.6 (q), 35.7 (s), 44.6 (t), 88.0 (d), 89.5 (s), 127.7 (s), 128.0 (br d), 128.4 (s), 128.8 (br d), 129.2 (br d), 139.1 (s), 139.5 (s), 142.8 (br s), 143.6 (br s), 144.3 (br s), 145.4 (br s), 198.9 (s), 200.47 (s), 200.52 (s); ^{29}Si-NMR (18 MHz, CDCl$_3$) δ 18.9; IR (NaCl) ν 2056 (s, sh), 1984 (s, br) cm^{-1}; mass *m/e* 548 (M$^+$, 0.5), 520 (M$^+$ − CO, 0.5), 492 (M$^+$ − 2CO, 2.4), 464 (M$^+$ − 3CO, 3), 362 (M$^+$ − Ru(CO)$_3$, 13.3). Exact Mass: calcd for $C_{28}H_{34}O_3SiRu$ *m/e* 548.1321; found *m/e* 548.1345.

Crystallographic Analysis. For X-ray analyses crystals of the following dimensions were prepared by slowly cooling hexane solutions: 0.2 × 0.3 × 0.2 mm for (*Z*)-**2**, 0.3 × 0.2 × 0.2 mm for **4**, and 0.3 × 0.2 × 0.3 mm for **6**. Diffraction measurements were made on an Enraf-Nonius CAD4 computer-controlled Kappa axis diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and results of the analyses are listed in Table 2. All data processing was performed on a VAX 4000 computer by using the SDP and MOLEN structure solving programs obtained from Enraf-Nonius Corp., Delft Netherlands. The $\omega-2\theta$ scan technique was adopted by varying the ω scan width as function of θ (ω scan width = (0.8−0.9) + 0.350 tan θ). All intensities were corrected for Lorentz and polarization corrections. Neutral atom scattering factors were calculated by the standard procedures.[16a] An anomalous dispersion correction was applied to all non-hydrogen atoms.[16b] Full-matrix least-squares refinements minimized the function $\Sigma w(|F_o| - |F_c|)^2$, $w = 1$.

Compound (*Z*)-2 crystallized in the orthorhombic crystal system. Inspection of systematic absences observed during the collection of data ($h0l$, $h = 2n$; $0kl$, $k + l = 2n$) indicated space group $Pna2_1$. Removal of systematically absent and redundant data left 2694 unique data in the final data set. The structure was solved by direct methods (MULTAN) and refined via standard least-squares and difference Fourier techniques. Hydrogen atoms were located and their positions were refined by least squares with fixed thermal parameters (4.0 Å^3).

Compound 4 crystallized in the orthorhombic crystal system. Inspection of the systematic absences observed during the collection of data ($h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$) indicated space group $P2_12_12_1$. Removal of systematically absent and redundant data left 2567 unique data in the final data set. The structure was solved by direct methods (MULTAN) and refined via standard least-squares and difference Fourier techniques. Hydrogen atoms were located and their positions were refined by least squares with fixed thermal parameters (4.0 Å^3).

Compound 6 crystallized in the triclinic crystal system. There were no systematic absences, and the space group was determined to be $P\bar{1}$. Removal of redundant data left 6666 unique data in the final data set. The structure was solved by direct methods (MULTAN) and refined via standard least-squares and difference Fourier techniques. Hydrogen atoms were located and their positions were refined by least squares with fixed thermal parameters (4.0 Å^3).

The molecular structures with atomic labeling schemes and the bond lengths and angles are given in Figure 3 and Tables 3 and 4 for (*Z*)-**2**, Figure 5 and Tables 5 and 6 for **4**, and Figure 7 and Tables 7 and 8 for **6**. The positional and thermal parameters as well as a listing of values of F_o and F_c were provided as supplementary materials with the preliminary report of compound (*Z*)-**2**. The data for compounds **4** and **6** are provided as supplementary material for this report.

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Supplementary Material Available: Detailed information of the X-ray crystal analysis of **4** and **6** including a textual presentation of experimental procedures and tables of experimental data, positional and thermal parameters, temperature factors, root-mean-square amplitudes, bond distances and angles, and torsion angles and 2D NMR spectra of (*Z*)-**2** and (*E*)-**2** (48 pages). Ordering information is given on any current masthead page.

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