

Cycloaddition reactions between tetrafluorodisilicyclobutene and cyclic dienes mediated by transition metal carbonyls

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(Received January 5th, 1988; in revised form April 12th, 1988)

Abstract

Under the mediation of transition metal carbonyls, cycloaddition of 3-t-butyl-1,1,2,2-tetrafluoro,2-disilacyclobutane (**1**) to various cyclic dienes have been studied under photochemical conditions. For conjugate dienes, Ni and Co mediated reactions give 1,4-addition products, whereas Fe, Mo and W mediated reactions result in 1,2-addition products. The hard metal Cr mediates the reactions to give products due to F migration. The reaction of non-conjugate norbornadiene with **1** gives 1,2- and 1,4-addition products under Cr mediation but gives only 1,2-addition products in the case of Mo mediation. Correlations between the structures of the intermediates and reaction pathways are discussed.

Introduction

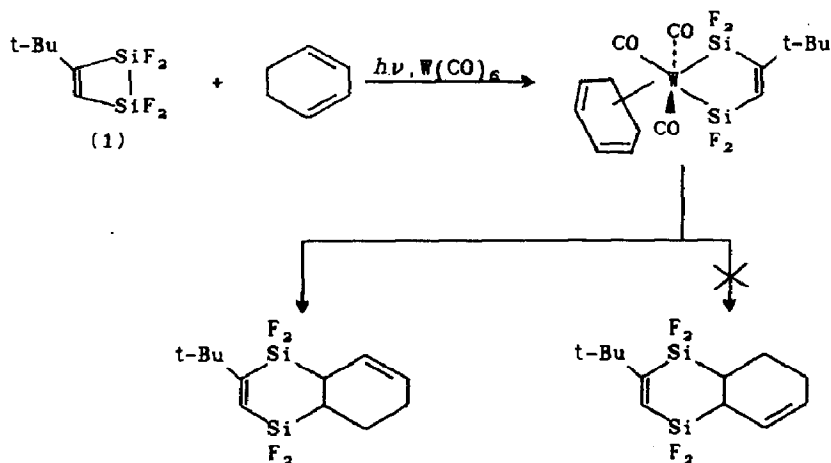
In a series of papers published recently we reported on the metal-mediated cycloaddition reactions between the 1,2-disilacyclobutene (**1**) and conjugate dienes [1–7], in which correlations between the various reaction pathways and the detailed structures (the geometry and the steric and electronic structures) of the intermediates were established. In other words, a “fine-tuning” model seems to be working in such reaction systems.

Of the conjugate dienes studied, cyclic dienes are in a special class because, firstly the orientation of the coordinated cyclic diene relative to that of the disilametallacycle in the intermediate species, (η^4 -diene)metallacycle, provides the regio-selectivity in some of the reactions. A example is shown in eq. 1 [1].

The structure of the intermediate $(F_2\bar{Si}(t-Bu)C=CHSiF_2)-\bar{W}(\eta^4-C_6H_8)(CO)_3$ has been determined by an X-ray diffraction study [1,8].

Secondly, the configuration of the coordinated diene also plays an important role in determining the reaction pathway shown in Scheme 1 [7].

Since cyclic dienes are intrinsically in the *cis* configuration, the pathway of 1,1-addition via 1,2 H-shift would not be expected.



Here we report the results of a systematic study of the reactions, mediated by metal carbonyls ($M = \text{Fe}, \text{Cr}, \text{Mo}, \text{W}, \text{Co}$ and Ni) of **1** with various cyclic dienes. For comparison, we also include norbornadiene, a non-conjugate cyclic diene with good ability to form η^4 -diene complexes with transition metal carbonyls.

Results and discussion

The results of the reactions between 3-t-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene (**1**) and cyclohexa-1,3-diene, cyclohepta-1,3-diene and cycloheptatriene are summarized in Tables 1 and 2.

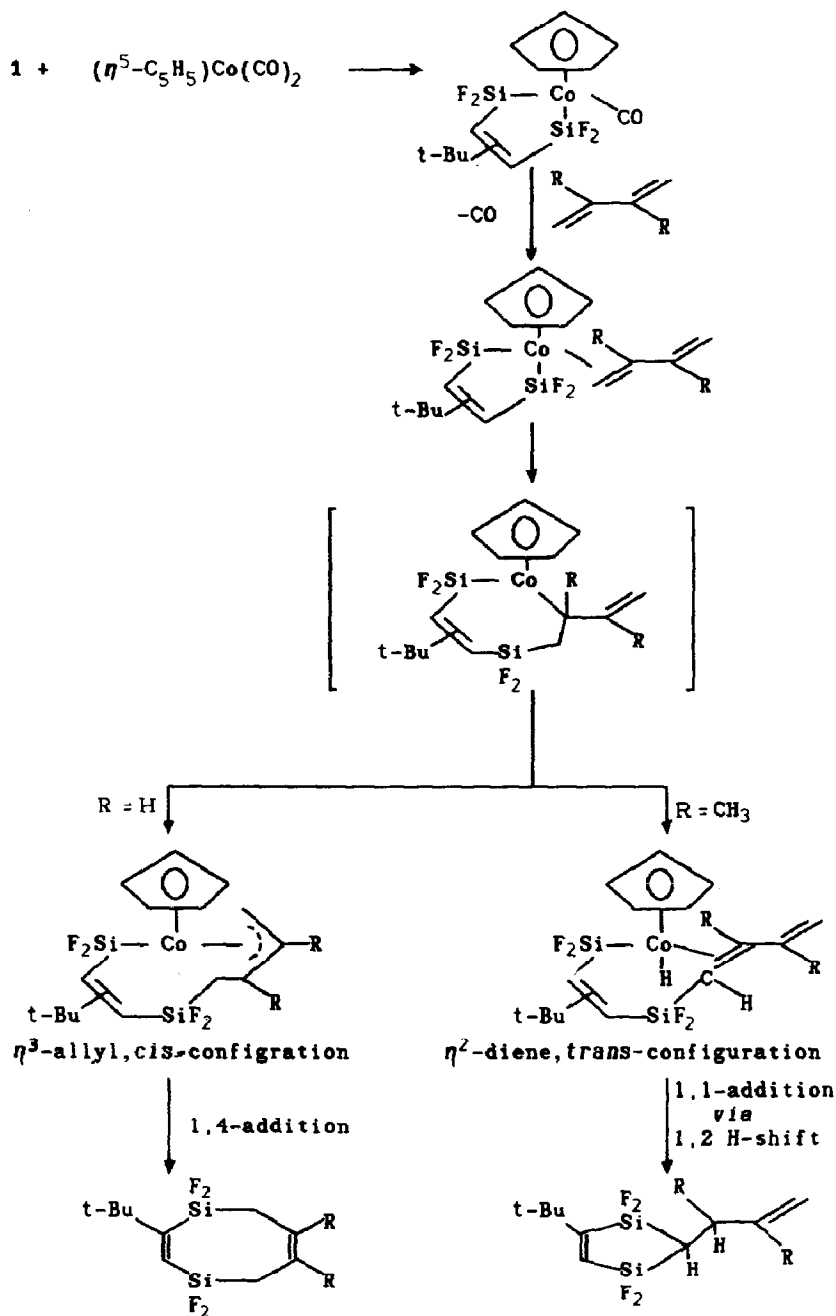
There are usually three types of products: products of the 1,4-addition (family **2**), products of the 1,2-addition (family **3**) and products resulting from the process involving F migration (family **4**). These compounds were characterized by a previously reported method [1-4].

In general no product resulting from H migration is obtained. This is as expected because the intrinsic *cis,cis* configuration of the cyclic conjugate dienes for steric reasons would hinder H migration from C_1 to the central metal after initial silyl attack has taken place [3]. In such a case, the reaction would choose other more facile pathways such as 1,2- or 1,4-additions. The reaction with cyclohexa-1,3-diene is shown in eq. 2.

However, the product from H migration can be obtained by photo-initiated isomerization of **3a/3b** in the presence of $\text{Fe}(\text{CO})_5$ (eq. 3) [3].

From our previous reports on the effects of the geometry of the intermediate [6,7], it is expected that the sterically more-crowded intermediates (with $M = \text{Fe}, \text{Cr}, \text{Mo}, \text{W}$) would prefer 1,2-addition to 1,4-addition reactions. Indeed, no products **2** were detected after reactions mediated by $\text{Fe}(\text{CO})_5$ or $M(\text{CO})_6$ where $M = \text{Cr}, \text{Mo}, \text{W}$. Only the reactions mediated by $\text{Ni}(\text{CO})_4$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ which involve less-crowded intermediates give 1,4-addition products, namely, **2a** and **2b**, after reaction with C_6H_8 and C_7H_{10} , respectively.

It is interesting to note that in spite of more steric hindrance of the cyclic dienes, products due to F migration are obtained when hard metal Cr is used as the



Scheme 1

mediator [4]. In the reactions of $(\text{F}_2\text{Si}(t\text{-Bu})\text{C}=\text{CHSiF}_2)\text{Cr}(\text{CO})_5$ with both cyclohexadiene and cycloheptadiene, products **4a** (run 3, Table 3) and **4b** (run 3, Table 2), respectively, from 1,1-addition involving F migration are detected. However, from the reaction with cycloheptatriene, a different F migration product, **4c** is obtained (run 14 and 15, Table 2). The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum of **4c** shows the typical doublet and quartet for SiF_3 and SiF which confirms that migration of a fluorine

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Table 1

Cycloaddition reactions of 1 and cyclohexa-1,3-diene mediated by various metal carbonyls ^a

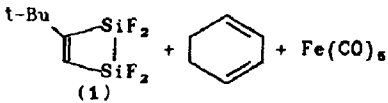
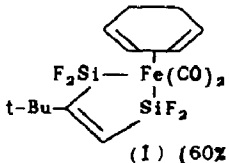
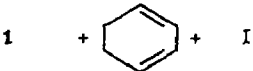
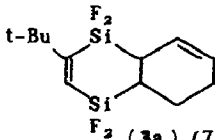
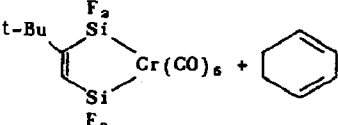
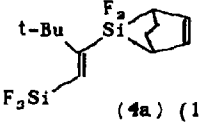
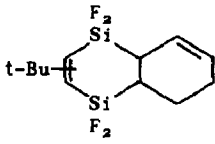
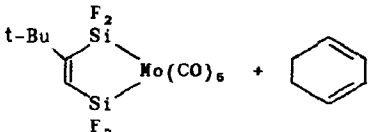
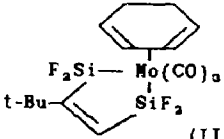
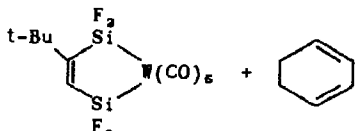
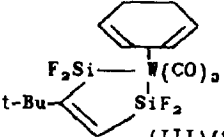
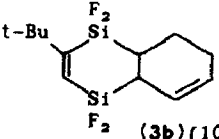
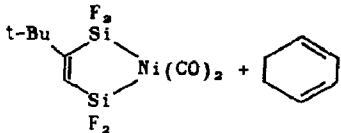
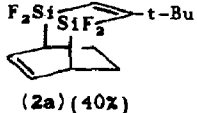
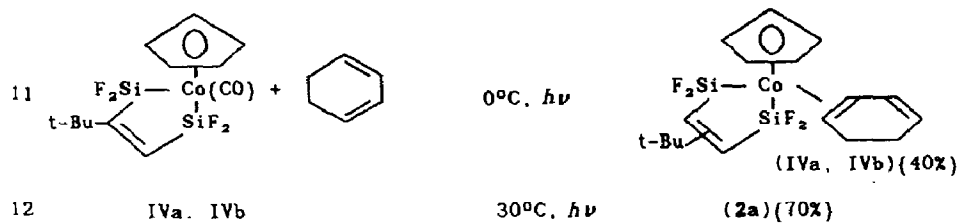
Run	Reactions	Conditions	Products (% yield)
1	 $\text{t-Bu-C}(\text{SiF}_2)=\text{CH}_2 + \text{Cyclohexa-1,3-diene} + \text{Fe}(\text{CO})_5$	0°C, <i>hν</i>	 (I) (60%)
2		120°C	 (3a) (70%)
3		70°C	 (4a) (10%) polymers
4		-30°C, <i>hν</i>	 (3a, 3b) (55%) 4a (15%)
5		90°C	(3a) (20%), polymers
6		-30°C, <i>hν</i>	 (II) (70%)
7	II	50°C	(3a) (100%)
8		0°C, <i>hν</i>	 (III) (85%)
9	III	100°C	 (3b) (100%)
10		-30°C	3a (15%), 3b (5%),  (2a) (40%)

Table 1 (continued)



^a Numbering systems of compounds: "Arabic numerals indicate final products and "Roman" numerals indicate intermediate compounds involving metals.

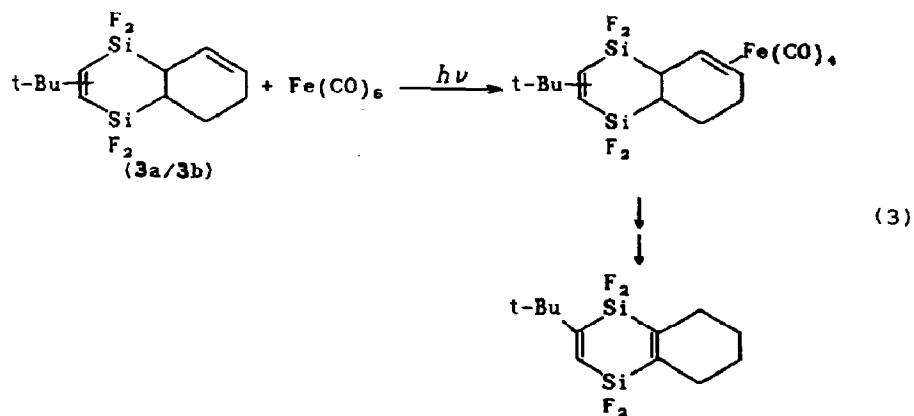
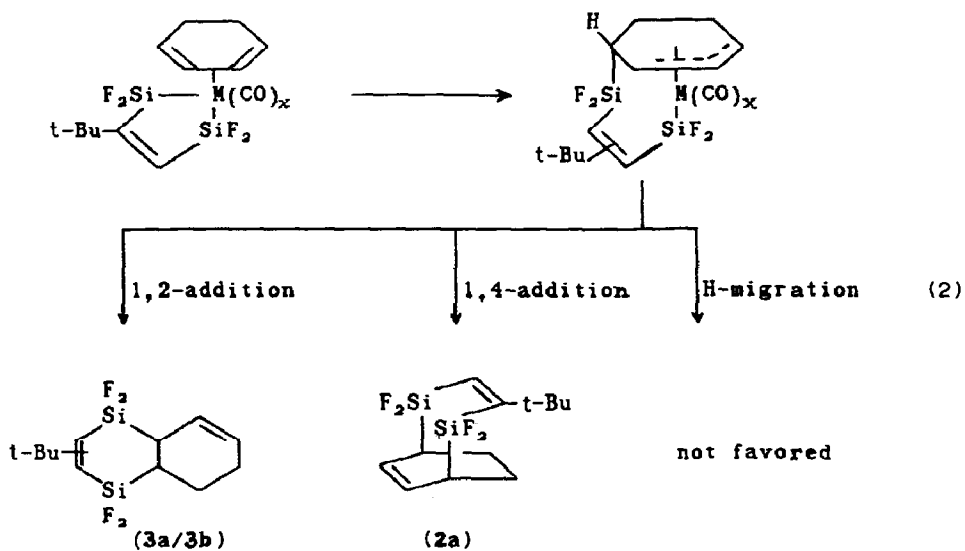


Table 2

Cycloaddition reactions of 1 with cyclohepta-1,3-diene cycloheptatriene mediated by various metal carbonyls^a

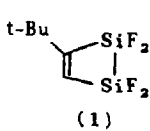
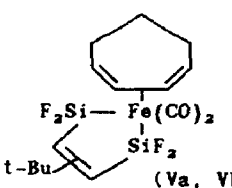
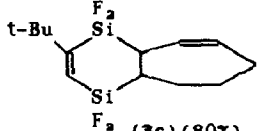
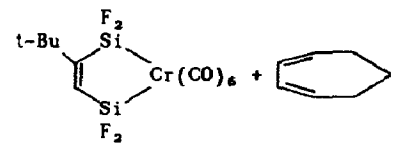
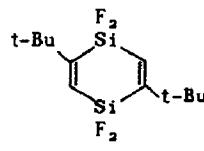
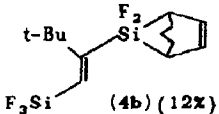
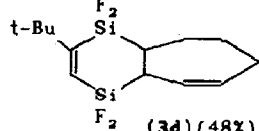
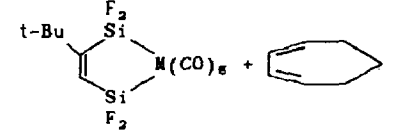
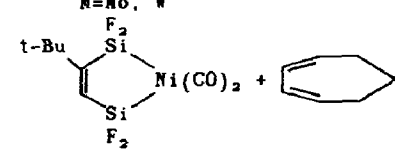
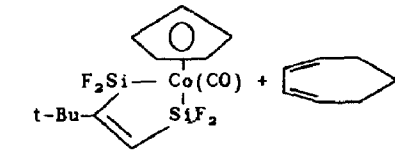
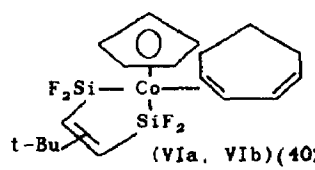
Run	Reactants	Conditions	Products (% yield)
1	 (1)	+ cyclohepta-1,3-diene + Fe(CO) ₅ -30°C, hν	 (Va, Vb) (55%)
2	1 + cyclohepta-1,3-diene + V (cat.)	140°C	 (3c) (80%)
3	 (5a)	+ cyclohepta-1,3-diene 70°C	 (5b) (14%) (5a) (14%)
4	 (4b)	-50°C, hν	 (3c) (15%) (3d) (48%)
5	 (5a)	+ cyclohepta-1,3-diene 90°C	(3c) (60%), (3d) (5%)
6	M=Mo, W	-30°C, hν	(3c) (60%), (3d) (3%)
7	 (5a)	+ cyclohepta-1,3-diene -30°C, hν	(3c) (30%), (3d) (5%) (2b) (25%)
8	 (VIa, IVb)	+ cyclohepta-1,3-diene, hν	 (VIa, VIb) (40%)
9	(VIa, IVb)	30°C, hν	(2b) (70%)

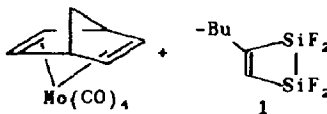
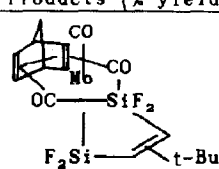
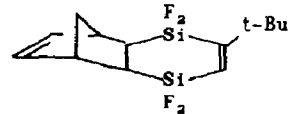
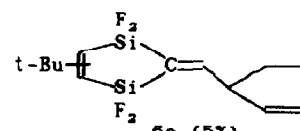
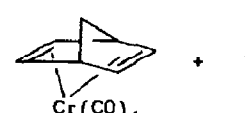
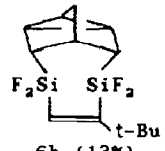
Table 2 (continued)

10		0°C, <i>hν</i> , dist. 90°C	 (3g)
11		dist. 130°C	 (3e', 3f') (40%)
12		150°C	 (3g') (80%)
13		PPh ₃ , 150°C	 (3g) (80%)
			 (3h, 3i) (20%)
14		90°C (5a, 5b) (30%),	 (4c) (15%)
15		-50°C, <i>hν</i>	(3e, 3f) (50%), (4c) (25%)
16		90°C	(3e, 3f) (45%), (4c) (10%)
17	M=Mo, W	-50°C, <i>hν</i>	(3e, 3f) (65%)
18		-30°C, <i>hν</i>	(3g) (20%), (3h, 3i) (40%)
19		0°C, <i>hν</i>	 (VIIa, VIIb) (40%)
20	(VIIa, VIIb)	30°C, <i>hν</i>	no reaction

^a Arabic numerals indicate final products and "Roman" numerals indicate intermediate compounds involving metals.

Table 3

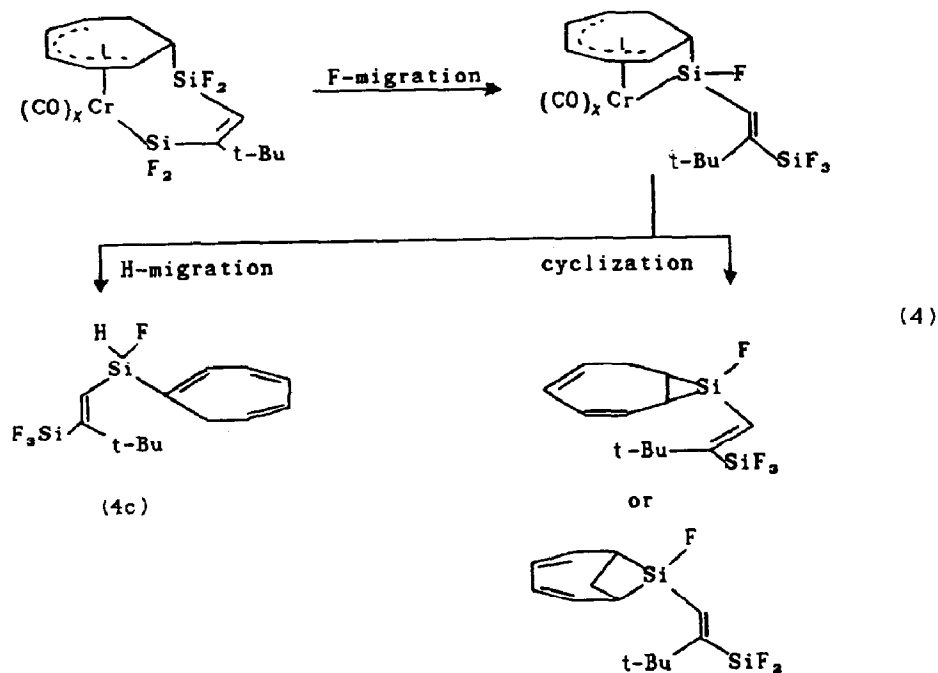
Cycloaddition reactions of **1** with norbornadiene mediated by $M(\text{CO})_6$, $M = \text{Cr}$ and Mo

Run	Reactants	conditions	Products (% yield)
1	 $\text{Mo}(\text{CO})_4$ + 1	-30°C , $h\nu$	 VIIIa, VIIIb (30%)
2	VIIIa/VIIIb	120°C	 6a (80%)  6c (5%)
3	 $\text{Cr}(\text{CO})_4$ + 1	-30°C , $h\nu$	6a (12%)  6b (13%)

atom from one silicon to the other has taken place. The resonance assigned to SiF further splits into a large doublet ($J(\text{H}, \text{F})$ 51.3 Hz) in the non-decoupled ^{19}F NMR spectrum. This is strong evidence of a hydrogen directly bonded to the SiF group. Although this compound has not been isolated pure, it is almost certain from the above characteristic spectral features that **4c** must have been formed via a hydrogen migration from the C_7H_8 ring to the SiF group. The driving force is due partly to the stabilization by establishment of the conjugate triene system, and partly to the instability of the products from the alternative cyclization pathway, which would lead to bicyclic structures involving either silacyclobutane or silacyclopropane bridges (eq. 4).

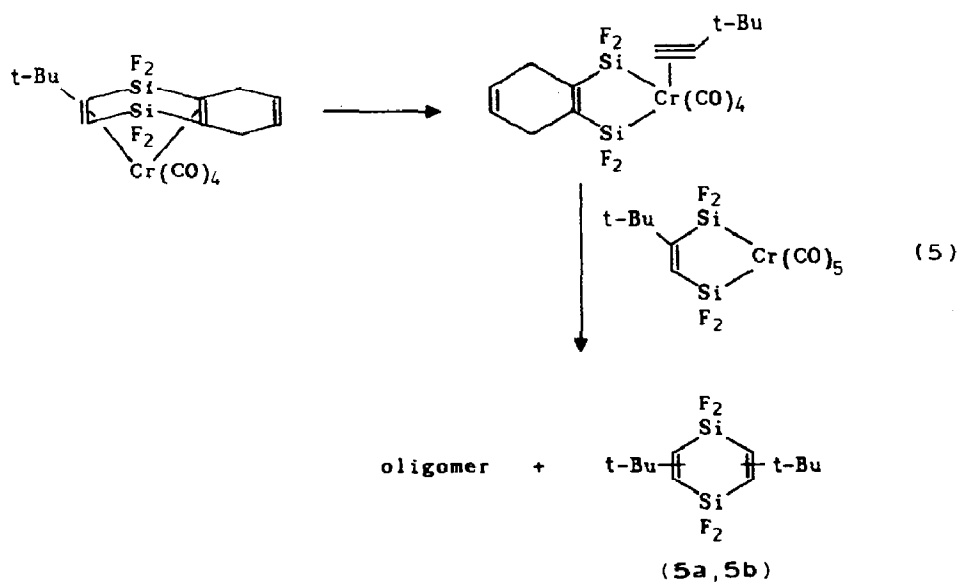
The *trans* disilyl olefin structure in compounds **4** has been determined on the basis of the large $^5J(\text{F}, \text{F})$ coupling constants (15 Hz as compared with 5 Hz for the *cis* disilyl olefins) and from the mechanism of F migration involved in these reactions [4].

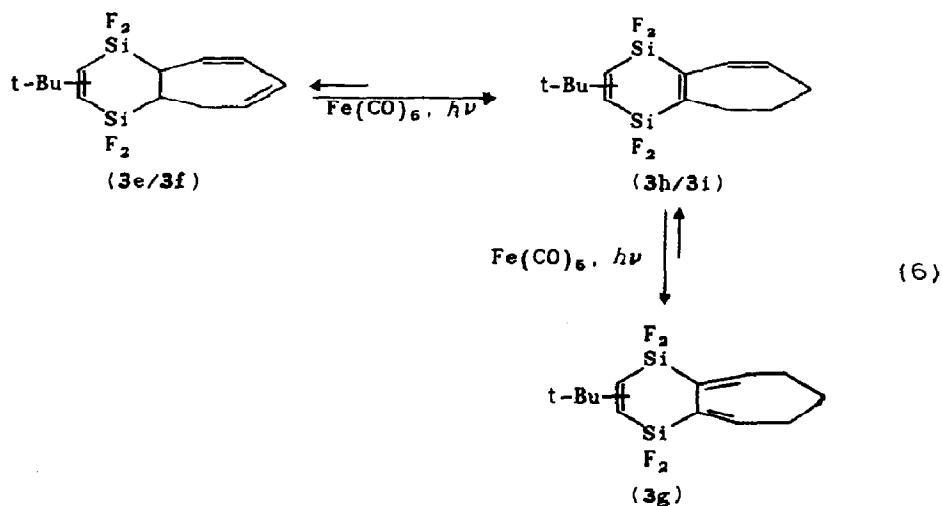
The reactions of $(\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2)\text{Cr}(\text{CO})_6$ with cycloheptadiene unexpectedly yielded the 1,4-disilacyclohexadienes, **5a** and **5b**. While the mechanism of formation of such products is not at all certain, a reaction route involving an alkyne complex intermediate as depicted in eq. 5 [5,9] is suggested.



In connection with the photo-initiated isomerization (eq. 3) previously reported, the equilibria between **3e/3f**, **3h/3i** and **3g** in the presence of $\text{Fe}(\text{CO})_5$ can be rationalized as shown in eq. 6.

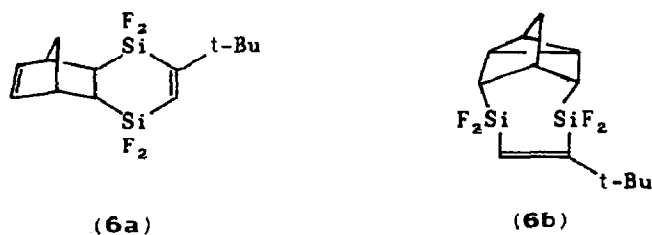
It is clear from these observations that the driving force for the transfer of a double bond in these systems is the higher stability of the vinylsilyl structure compared with the allylsilyl structure [10,4].





One other cyclic diene studied in this work is norbornadiene. Transition metal complexes of norbornadiene have been used as examples for studies of photo-initiated substitution [11–14] and hydrogenation [15,16]. For example, the photo-initiated hydrogenation of norbornadiene mediated by $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ gives norbornadiene preferentially, whereas that mediated by $\text{Mo}(\text{CO})_6$ selectively gives quadricyclane.

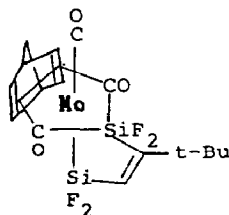
Compound **1** and norbornadiene do not react under photochemical conditions. We have used $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ to mediate the cycloaddition reaction between **1** and norbornadiene. In both cases $(\text{NBD})\text{M}(\text{CO})_4$ was prepared first then allowed to react with **1** photochemically. The reaction of $(\text{NBD})\text{Cr}(\text{CO})_4$ yields the products **6a** and **6b** in approximately 1/1 ratio (total yield 25%) whereas the reaction of $(\text{NBD})\text{Mo}(\text{CO})_4$ gives mainly **6a** (yield 30%).



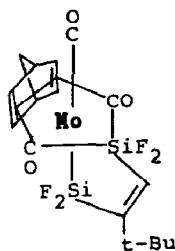
In the case of $(\text{NBD})\text{Mo}(\text{CO})_4$, the reaction intermediate VIII can be isolated at -30°C . This seven-coordinated intermediate has a molecular formula of $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Si}_2\text{F}_4\text{Mo}$ as is shown by its mass spectrum and elemental analysis. The $^{19}\text{F}\{^1\text{H}\}$ spectrum of VIII shows four singlets at 81.13, 108.45, 93.28 and 96.85 ppm with an integration ratio of 1/1/3/3. A COSY experiment shows that there are two isomers in the ratio 1/3 in the sample. Since the two fluorines in each SiF_2 group of the two isomers are chemically equivalent, there is a symmetry plane involving the two Si atoms in each isomer of VIII.

The $^{13}\text{C}\{^1\text{H}\}_{\text{BB}}$ NMR spectrum confirms the existence of two isomers: there are two sets of signals (integration ratio about 1/3) associated with each resonance. The spectrum in the carbonyl region is particularly informative in that it shows for each isomer one triplet and one singlet in an approximate 1/2 integration ratio. Since only the SiF_2 *trans* to a carbonyl group causes significant three-bond F-Si-M-C couplings [17], this spectrum suggests that in each isomer there is one CO *trans* to the SiF_2 group and two CO groups *cis* to the SiF_2 groups.

In all the possible regular structures of the seven-coordinated complex, i.e., monocapped trigonal prism, monocapped octahedron and pentagonal bipyramid, only the structures shown below fit the requirements of a symmetry plane involving two Si atoms and one CO *trans* to an SiF_2 group. In addition, an X-ray diffraction study has revealed that $(\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2)\text{Mo}(\text{CO})_5$ is a pentagonal bipyramid [18].



(VIIIa)



(VIIIb)

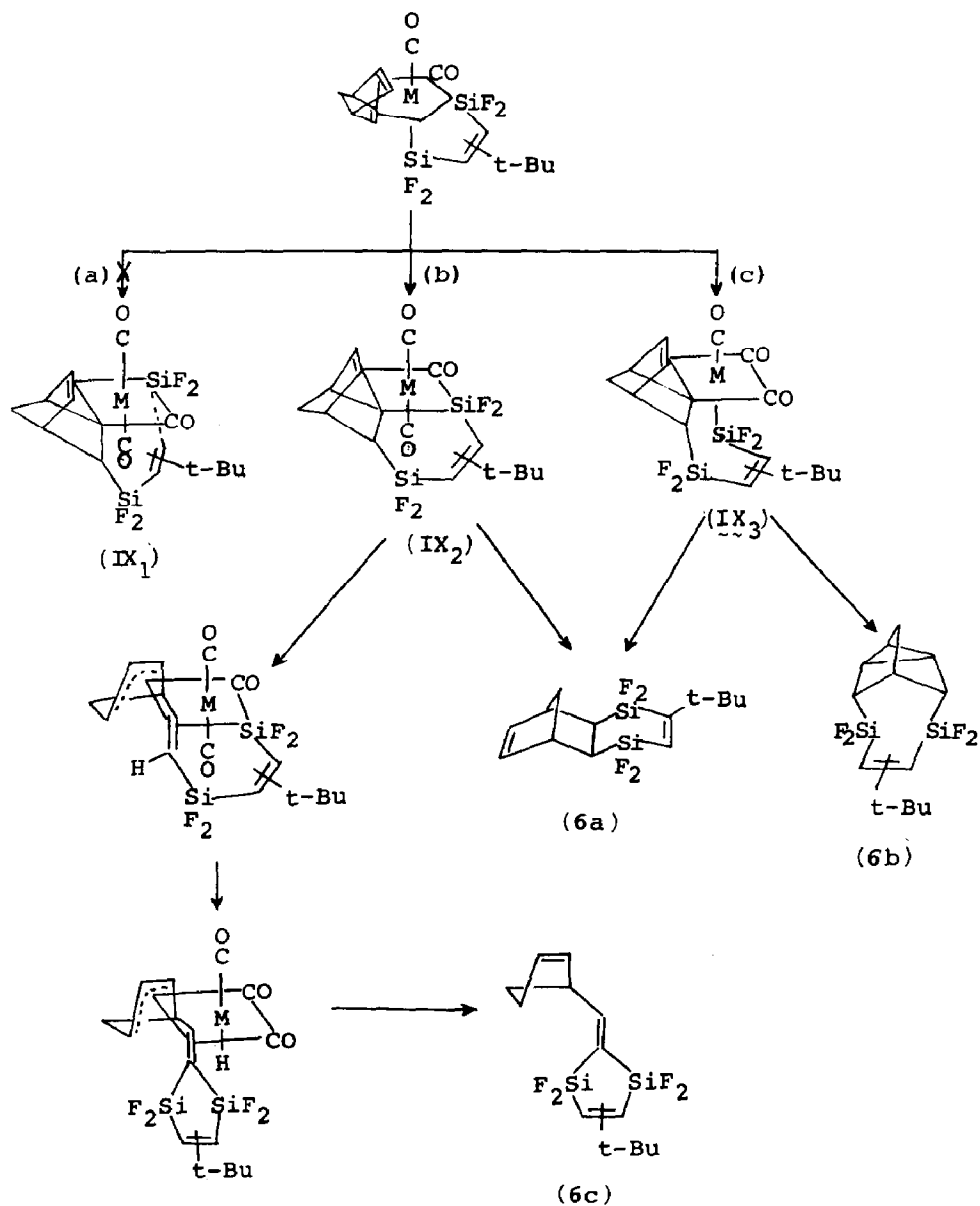
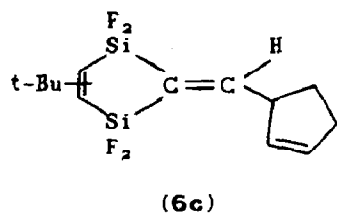
The ^1H NMR spectrum is in good agreement with the structures.

The identification of compounds **6a** and **6b** was carried out by mass spectrometry, elemental analysis, ^1H , ^{19}F and ^{13}C NMR spectroscopy. Although **6b** has not been isolated pure, its spectra can be obtained by subtracting the spectra of **6a** from those of a mixture of **6a** and **6b**. Both **6a** and **6b** show four doublets in the $^{19}\text{F}\{^1\text{H}\}$ spectra which are characteristic of 1,1,4,4-tetrafluoro-1,4-disilacyclic compounds [3,6,7]. The $^{13}\text{C}\{^1\text{H}\}_{\text{BB}}$ spectrum of **6a** shows four resonances of sp^2 carbons, two of which are adjacent to the SiF_2 groups (with subsequent F couplings) and the other two are of the simple $=\text{CH}$ type (and are split into doublets in the $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ spectrum). In addition, there are two sp^3 carbon signals at δ 22.6 and 23.1 also with strong F couplings. These spectral features make the identification of **6a** unequivocal.

The $^{13}\text{C}\{^1\text{H}\}_{\text{BB}}$ spectrum of **6b** reveals that there are only two sp^2 carbons adjacent to the SiF_2 groups and the additional sp^3 carbons that are a requisite for the proposed structure of **6b**. As in the case of **6a**, the resonances at δ 9.75, 10.96 and 11.26 in the ^{13}C spectrum are typical of the three carbons in the bridge-head.

Compound **6a** and a small quantity of **6c** were obtained when intermediate VIII was heated to 120°C . Compound **6c** cannot be isolated but from the AA'XX' pattern in the $^{19}\text{F}\{^1\text{H}\}$ spectrum, which is characteristic of the alkylidenedisilacyclopentene moiety [2], and the extremely low field resonance (δ 182.6) in the ^{13}C NMR spectrum, a possible structure with an sp^2 carbon β to two SiF_2 groups [2,19] is suggested. This indicates that **6c** has the structure $\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2\text{C}=\text{CH}$.

Judging from the rest of the spectrum the most representative structure of **6c** is shown.



Scheme 2

The position of the *t*-butyl group cannot be determined on the basis of the present data.

A plausible reaction mechanism is shown in Scheme 2.

The intermediate VIIIa or VIIIb can take on one of three possible structures after the initial SiF_2 attack. A molecular model shows that structure IX_1 is unlikely because the two SiF_2 groups are almost *trans* to each other. The molecular model also shows that IX_2 would require a larger central atom than IX_3 in order to bond favorably with all ligand bonding sites. If Mo prefers the structure of IX_2 and Cr prefers IX_3 , then the former gives the products **6a** and **6c**, whereas the latter would lead to a mixture of **6a** and **6b**. These rationalizations are supported by what is observed experimentally. The mechanism involving the similar activation of one C–C bond to form **6c** has previously been postulated to account for the metal-catalyzed rearrangement of norbornadiene [20].

In contrast to the conclusion drawn from the previous study of the metal-mediated hydrogenation of norbornadiene [15,16], our results seem to suggest that the dissociation of one metal–olefin bond is not essential for the formation of nortricyclene and norbornene.

Experimental

Vacuum manipulations in vacuum were carried out on vacuum lines at 10^{-3} torr. For the photochemical preparations a 450 W medium pressure Hg lamp was used. Dienes (Aldrich), metal carbonyls ($\text{M} = \text{Fe}, \text{Cr}, \text{Mo}, \text{W}, \text{Ni}, \text{Strem}$) and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ (Strem) were used as received. The following compounds were prepared by procedures published elsewhere: **1** [21], $\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2\text{M}(\text{CO})_n$ ($\text{M} = \text{Ni}, n = 2$; $\text{M} = \text{Fe}, n = 4$; $\text{M} = \text{Cr}, \text{Mo}, \text{W}, n = 5$) [22,23]. $\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)\text{CO}$ [7], $(\eta^4\text{-norbornadiene})\text{M}(\text{CO})_4$ ($\text{M} = \text{Cr}, \text{Mo}$) [12].

Spectra. All mass spectra were recorded on a JEOL JMS-100 Mass spectrometer operating at 12 eV. The NMR spectra were recorded on a JEOL FX-100 spectrometer operating at 99.55, 93.65 and 25.0 MHz for the ^1H , ^{19}F and ^{13}C spectra, respectively, and a Bruker AM 400 spectrometer operating at 400.0, 376.5, 100.0 MHz for ^1H , ^{19}F and ^{13}C spectra, respectively. Chemical shifts of ^1H and ^{13}C spectra are expressed as δ values, ^{19}F chemical shifts were measured in ppm upfield (being positive) from the internal standard CCl_3F . In the ^{13}C NMR data, the spectral multiplicity after each chemical shift is due to the coupling with heteronuclei, whereas the coupling patterns in $^{13}\text{C}\{^1\text{H}\}_{\text{CW}}$ are included in parentheses.

Preparation of $\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-diene})$. The $(\eta^4\text{-diene})$ disilametallacycle complexes with diene = C_6H_8 and $\text{M} = \text{Fe}, \text{Mo}, \text{W}$ (I, II, III), have been reported previously [1–3]. In the case of $\text{M} = \text{Co}$, the procedure was typically as follows: about 2.0 mmol of $\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)\text{CO}$ and 4.0 mmol of a cyclic diene were transferred into a quartz reaction tube with 10 ml of degassed benzene as solvent. The solution was irradiated at 0°C and degassed every 3 h. The progress of the reaction was followed by ^{19}F NMR spectra. After removal of solvent and excess diene, the desired product was obtained by vacuum distillation at 70°C .

(1) IVa/IVb from the reaction with cyclohexa-1,3-diene, yield 40%. Anal. Found: C, 48.63; H, 5.91; F, 18.20. $\text{C}_{17}\text{H}_{23}\text{CoF}_4\text{Si}_2$ calcd.: C, 48.80; H, 5.50; F, 18.18%. Mass spectrum of IVa/IVb: 418 (M^+ , $\text{C}_{17}\text{H}_{23}\text{Si}_2\text{F}_4\text{CO}^+$), 338 ($\text{C}_{11}\text{H}_{15}\text{Si}_2\text{F}_4\text{Co}^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 124 ($\text{C}_5\text{H}_5\text{Co}^+$), 80 (C_6H_8^+), 57 (C_4H_9^+). ^1H NMR: δ 1.08 (s),

9H, *t*-Bu; 1.74 (m), 4H, (CH₂)₂; 2.80 (m), 2H, Co-bonded HC=CH; 5.68 (m), 2H, free HC=CH; 4.93 (s), 5H, η⁵-C₅H₅; 6.49 (t, t) 1H, =CHSiF₂. ¹⁹F{¹H} NMR: 87.85 (d), 89.68 (d); 92.88 (d), 94.86 (d); two SiF₂ of IVa. 100.57 (d), 101.85 (d), 112.51 (d), 114.22 (d); two SiF₂ of IVb. ¹³C NMR: δ 184.0 t(t), =C(*t*-Bu)SiF₂; 142.15 t(d, t), =CHSiF₂; 130.48 s(d) and 127.85 s(d), free HC=CH of IVa and IVb; 88.24 s(d), η³-C₅H₅; 53.55 s(d) and 51.21 s(d), Co-bonded HC=CH of IVa and IVb; 37.32 s(s), C(CH₃)₃; 29.06 s(q), C(CH₃)₃; 24.36 s(t) and 21.15 s(t), CH₂-CH₂.

(ii) VIa/VIb from the reaction with cyclohepta-1,3-diene, yield 55%. Anal. Found: C, 49.58; H, 5.39; F, 17.80. C₁₈H₂₅CoF₄Si₂ calcd.: C, 50.0; H, 5.79; F, 17.59%. Mass spectrum of VIa/VIb: 432 (*M*⁺, C₁₈H₂₅Si₂F₄Co⁺), 338 (C₁₁H₁₅Si₂F₄Co⁺), 215 (C₆H₁₁Si₂F₄⁺), 124 (C₅H₅Co⁺), 94 (C₇H₁₀⁺), 57 (C₄H₉⁺). ¹H NMR: δ 1.04 (s), 9H, *t*-Bu; 1.94 (c), 6H, (CH₂)₃; 2.62 (m), 2H, Co-bonded HC=CH; 4.52 (s), 5H, η⁵-C₅H₅; 6.10 (m) and 6.46 (m), 2H, free HC=CH; 6.60 (m), 1 H, =CHSiF₂. ¹⁹F{¹H} NMR: 90.53 (d), 92.99 (d); 113.52 (d), 114.23 (d); two SiF₂ of VIa. 86.03 (d), 88.39 (d); 101.57 (d), 102.10 (d); two SiF₂ of VIb. ¹³C NMR: δ 183.0 t(t), =C(*t*-Bu); 142.73 t(d, t), =CHSiF₂; 133.36 s(d), and 124.68 s(d), free HC=CH of VIa and VIb; 88.83 s(d), η⁵-C₅H₅; 56.42 s(d) and 61.87 s(d), Co-bonded HC=CH of VIa and VIb; 37.61 s(s), C(CH₃)₃; 31.87 s(t), CH₂CH₂CH₂; 29.23 s(q), C(CH₃)₂; 25.49 s(t), CH₂CH₂CH₂.

(iii) VIIa/VIIb from the reaction with cycloheptatriene, yield 40%. Anal. Found: C, 50.10; H, 5.19; F, 17.85. C₁₈H₂₃CoF₄Si₂ calcd.: C, 50.23; H, 5.35; F, 17.67%. Mass spectrum of VIIa/VIIb: 430 (*M*⁺, C₁₈H₂₃Si₂F₄Co⁺), 338 (C₁₁H₁₅Si₂F₄Co⁺), 215 (C₆H₁₁Si₂F₄⁺), 124 (C₅H₅Co⁺), 92 (C₇H₈⁺), 57 (C₄H₉⁺). ¹H NMR: δ 1.01 (s), 9H, *t*-Bu; 2.26 (t), 2H, CH₂; 2.64 (m) and 3.00 (m), 2H, Co-bonded HC=CH of VIIa and VIIb; 4.52 (s), 5H, η⁵-C₅H₅; 5.50 (m) and 5.73 (m), 2H, CH=CHCH₂; 5.79 (m) and 6.48 (m), 2H, CH=CHCH=CHCH₂; 6.55 (m), 1 H, =CHSiF₂. ¹⁹F{¹H} NMR: 86.96 (d), 88.03 (d), 91.13 (d), 92.73 (d); two SiF₂ of VIIa. 99.88 (d), 100.84; 111.74 (d), 112.91 (d); two SiF₂ of VIIb. ¹³C NMR: δ 183.39 t(t), =C(*t*-Bu); 143.43 t(d, t), =CHSiF₂, 136.05 s(d) and 128.20 s(d), free HC=CH-CH=CHCH₂; 130.66 s(d) and 125.09 s(d), free HC=CHCH=CHCH₂; 87.95 s(d), η⁵-C₅H₅; 57.07 s(d) and 55.31 s(d), Co-bonded HC=CH; 37.62 s(s), C(CH₃)₃; 29.30 s(q), C(CH₃)₃; 29.28 s(t), CH₂.

(iv) Va/Vb from the reaction Fe(CO)₅, **1** and cyclohepta-1,3-diene, yield 55% (preparations were similar to those reported for the reaction with cyclohexa-1,3-diene [1,3]). Anal. Found: C, 43.01; H, 4.31; F, 18.21. C₁₅H₂₀F₄FeO₂Si₂ calcd.: C, 42.86; H, 4.76; F, 18.09%. Mass spectrum of Va/Vb: 420 (*M*⁺, C₁₅H₂₀O₂Si₂F₄Fe⁺), 392 (C₁₄H₂₀O₂Si₂F₄Fe⁺), 364 (C₁₃H₂₀Si₂F₄Fe⁺), 308 (C₁₃H₂₀Si₂F₄⁺), 215 (C₆H₁₁Si₂F₄⁺), 206 (C₉H₁₀O₂Fe⁺), 178 (C₈H₁₀OFe⁺), 150 (C₇H₁₀Fe⁺), 94 (C₇H₁₀⁺), 57 (C₄H₉⁺). ¹⁹F{¹H} NMR: 87.79 (d), 95.37 (d); 99.42(d), 103.09 (d); two SiF₂ of Va. 90.08 (d), 92.87 (d); 99.17 (d), 107.59 (d); two SiF₂ of Vb. ¹³C NMR of Va/Vb: δ 212.43 s(s), CO; 184.72 m(m), =C(*t*-Bu); 145.21 m(d, m), =CHSiF₂; 89.49 s(d) and 77.42 s(d), HC=CHCH=CH; 67.92 s(d) and 60.31 s(d), HC=CHCH=CH; 38.50 s(s), C(CH₃)₃; 29.88 s(q), C(CH₃)₃; 28.79 s(t), CH₂CH₂CH₂; 23.66 s(t), CH₂CH₂CH₂.

Preparation and identification of **2a**, **3a**, **3b**, **5a** and **5b** have been reported previously [1,6,22].

Preparation of 3c and 3d. A mixture of 0.43 g (2.0 mmol) of **1**, 0.38 (4.0 mmol) of cyclohepta-1,3-diene and a catalytic amount of Va/Vb in 0.5 ml of isooctane

solution was transferred into a reaction tube and heated at 140 °C for 1 h. After the solvent and the excess of reagents had been removed, vacuum distillation of the residue at 90 °C yielded 0.5 g (1.6 mmol) of **3c**, yield 80%.

Compound **3d** was obtained in 80% purity by treating 0.5 g (1.2 mmol) of $F_2Si(t-Bu)C=CHSiF_2Cr(CO)_5$ and 0.5 g (5.4 mmol) cyclohepta-1,3-diene in 20 ml of n-pentane solution. The solution was subjected to irradiation at -50 °C for 72 h. After filtration and removal of solvent, vacuum distillation of the residue at 90 °C gave a mixture of **3d** and **3c**, in 48 and 12% yields, respectively. Anal. Found: C, 50.56; H, 6.81; F, 24.55. $C_{13}H_{20}F_4Si_2$ calcd.: C, 50.65; H, 6.49; F, 24.67%. Mass spectrum of **3c**: 308 (M^+ , $C_{13}H_{20}Si_2F_4^+$), 293 ($C_{12}H_{17}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 94 ($C_7H_{10}^+$), 57 ($C_4H_9^+$). 1H NMR: δ 1.16 (s), 9H, t-Bu; 1.5 ~ 2.5 (c), 8H, $HC-CH(CH_2)_3$; 5.84 (m), 2H, $HC=CH$; 6.52 (m), 1H, $=CHSiF_2$. $^{19}F\{^1H\}$ NMR of **3c**: 129.83 (d), 137.98 (d), $=CHSiF_2$; 143.38 (d), 145.46 (d), $=C(t-Bu)SiF_2$. ^{13}C NMR of **3c**: δ 175.01 m(m), $=C(t-Bu)$; 134.82 s(d) and 126.62 s(d), $HC=CH$; 133.65 t(d, t), $=CHSiF_2$; 39.37 s(s), $C(CH_3)_3$; 29.59 s(q), $C(CH_3)_3$; 29.36 s(t), $=CHCH_2$; 28.89 s(t), $=CHCH_2(CH_2)_2$; 25.37 t(d, t), $F_2SiCHCHSiF_2$.

All spectral data for **3d** were obtained by subtracting the spectra of **3a**. Mass spectrum of **3d**: similar to that of **3c**. 1H NMR of **3d**: δ 1.15 (s), 9H, t-Bu; 1.2-2.7 (c), 8H, all saturated H in the 7-membered ring; 5.30 (c) and 5.50 (c), 2H, $HC=CH$; 6.52 (t), 1H, $=CHSiF_2$. $^{19}F\{^1H\}$ NMR of **3d**: 137.66 (d), 140.33 (d), $=CHSiF_2$; 135.23 (d), 142.76 (d), $=C(t-Bu)SiF_2$. ^{13}C NMR of **3d**: δ 174.01 m(m), $=C(t-Bu)$; 134.60 t(d, t), $=CHSiF_2$; 134.41 s(d) and 122.7 s(d), $HC=CH$; 39.21 s(s), $C(CH_3)_3$; 29.61 s(t), $(CH_2)_3$; 29.12 s(q), $C(CH_3)_3$; 26.50 t(d, t), $F_2Si-CH-CH-SiF_2$.

Preparation of 3e, 3f, 3g, 3h and 3i. A 10-ml n-pentane solution containing 0.86 g (4.0 mmol) of **1** and 0.93 g (4.0 mmol) $(\eta^4C_7H_8)Fe(CO)_3$ in a quartz tube was degassed and irradiated at 0 °C for 25 h. The solution was degassed every 5 h. After removal of solvent, vacuum distillation, of the residue, at 90 °C gave a yellowish liquid containing 0.3 g (1.0 mmol) of **3e** and an equal amount of **3f**, with total yield 50%. Vacuum distillation at 130 °C gave 0.71 g (1.6 mmol) of a 1/1 mixture **3e'**/**3f'**, yield 40%.

A 10-ml isooctane solution containing 0.45 g (1.0 mmol) of **3e'**/**3f'** was heated in a sealed tube at 150 °C for 20 h. After removal of solvent, vacuum distillation of the residue at 130 °C gave 0.36 g (0.8 mmol) of **3g'**, yield 80%.

A 10-ml isooctane solution containing 0.45 g (1.0 mmol) of **3g'** and 1.3 g (5.0 mmol) of triphenylphosphine was heated at 150 °C for 24 h. Vacuum distillation at 90 °C gave 0.27 g (0.9 mmol) of a mixture of **3g** (0.22 g, 0.72 mmol) and **3h**/**3i** (0.05 g, 0.18 mmol). Mass spectrum of **3e**/**3f**: 306 (M^+ , $C_{13}H_{18}Si_2F_4^+$), 291 ($C_{12}H_{15}Si_2F_4^+$), 278 ($C_{11}H_{14}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of **3e**/**3f**: 129.09 (d, d), 135.80 (d); 135.20 (d, d), 137.73 (d); $=CHSiF_2$ and $=C(t-Bu)SiF_2$, respectively of **3e** or **3f**. 134.87 (d, d), 141.39 (d); 142.14 (d, d), 143.86 (d): $=CHSiF_2$ and $=C(t-Bu)SiF_2$, respectively of **3f** or **3e**. ^{13}C NMR of **3e**/**3f**: δ 172.27 m(m), $=C(t-Bu)$; 132.90 m(d, m), $=CHSiF_2$; 133.42 s(d), 133.06 s(d), 128.44 s(d), 126.62 s(d), 125.98 s(d) and 125.21 s(d), $HC=CHCH=CH$ of **3e** and **3f**, 39.73 s(s), $C(CH_3)_3$; 31.58 t(d, t), $F_2SiCH-CH=$; 31.05 s(t), CH_2 ; 29.77 s(q) and 29.24 s(q), $C(CH_3)_3$ of **3e** and **3f**; 21.45 t(d, t), $F_2SiCHCH_2$. Mass spectrum of **3e'**/**3f'**: 446 (M^+ , $C_{16}H_{18}O_3Si_2F_4Fe^+$), 418 ($C_{15}H_{18}O_2Si_2F_4Fe^+$), 390 ($C_{14}H_{18}OSi_2F_4Fe^+$), 362 ($C_{13}H_{18}Si_2F_4Fe^+$), 306 ($C_{13}H_{18}Si_2F_4^+$), 291

($C_{12}H_{15}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 204 ($C_9H_8O_2Fe^+$), 176 ($C_8H_8OFe^+$), 148 ($C_7H_8Fe^+$), 92 ($C_7H_8^+$), 57 ($C_4H_9^+$). $^{19}F\{^1H\}$ NMR of $3e'/3f'$: 128.04 (d, d), 133.04 (d); 134.44 (d, d), 139.12 (d); $=CHSiF_2$ and $=C(t-Bu)SiF_2$, respectively of $3e'$ or $3f'$, 137.97 (d, d), 140.28 (d); 141.40 (d, d), 145.43 (d); $=CHSiF_2$ and $=C(t-Bu)SiF_2$, respectively of $3f'$ or $3e'$. ^{13}C NMR of $3e'/3f'$: δ 210.52 s(s), CO; 172.21 m(m), $=C(t-Bu)$; 134.70, m(d, m), $=CHSiF_2$; 90.64 s(d) and 82.73 s(d), $HC=CHCH=CH$; 59.77 s(d) and 53.61 s(d), $HC=CHCH=CH$; 40.62 s(s) and 39.67 s(s), $C(CH_3)_3$ of $3e'$ and $3f'$; 29.41 s(q), $C(CH_3)_3$; 25.78 s(t), CH_2 ; 24.96 t(c), HCC .

Mass spectrum of $3g'$ is similar to that of $3e'/3f'$. $^{19}F\{^1H\}$ NMR of $3g'$: 127.48 (d), 144.36 (d); 134.34 (d), 149.21 (d); $=CHSiF_2$ and $=C(t-Bu)SiF_2$, respectively. ^{13}C NMR of $3g'$: δ 209.35 s(s), CO; 171.56 m(m), $=C(t-Bu)$; 131.13 t(d, t), $=CHSiF_2$; 90.06 m(m), $F_2SiCCSiF_2$; 66.74 s(d) and 66.62 s(d), $HC=CC=CH$; 40.25 s(s), $C(CH_3)_3$; 29.36 s(q), $C(CH_3)_3$; 28.30 s(t), $CH_2CH_2CH_2$; 23.79 s(t), $CH_2CH_2CH_2$.

Mass spectrum of a mixture of $3g$ (80%) and $3h/3i$ (20%): 306 (M^+ , $C_{13}H_{18}Si_2F_4^+$), 291 ($C_{12}H_{15}Si_2F_4^+$), 278 ($C_{11}H_{14}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). 1H NMR of the mixture of $3g$ (80%) and $3h/3i$ (20%): δ 1.17 (s), 9H, t-Bu; 2.02 (c), 2.24 (c), 2.44 (c), 6H, $(CH_2)_3$ of $3g$ and $3h/3i$; 6.16 (c), 2H, all $=CH$ of $3g$ and $3h/3i$; 6.64 (m) 1H, $=CHSiF_2$. $^{19}F\{^1H\}$ NMR of $3g$ (80%) and $3h/3i$ (20%): 136.09 (s), $=CHSiF_2$; 142.93 (s), $=C(t-Bu)SiF_2$ of $3g$, 137.90 (t), $=CHSiF_2$; 145.51 (t), $=C(t-Bu)SiF_2$ of $3h$ or $3i$. 138.84 (t), $=CHSiF_2$; 144.98 (s), $=C(t-Bu)SiF_2$ of $3i$ or $3h$. ^{13}C NMR of $3g$ (80%) and $3h/3i$ (20%): δ 173.96 m(m), $=C(t-Bu)$; 155.86 t, t(t, t) and 155.09 t, t (t, t), $HC=CC=CH$ of $3g$ and $=CHC=CCH_2$ of $3h/3i$; 150.64 s(d) and 150.23 s(d), $HC=CC=CH$ or $3g$; 140.39 s(d), $=CH(CH_2)_3$ of $3h/3i$; 135.0 m(d, m) $=CHSiF_2$; 125.86 s(d) and 125.27 s(d), $HC=CH(CH_2)_3$ of $3h/3i$; 40.08 s(s), $C(CH_3)_3$; 32.40 s(t), 31.93 s(t), 31.13 s(t), all CH_2 ; 29.82 s(q), $C(CH_3)_3$.

Preparation of 4a, 4b and 4c. A 10-ml n-pentane solution containing 0.5 g (1.2 mmol) of $F_2Si(t-Bu)C=CHSiF_2Cr(CO)_5$ and 0.8 g (10 mmol) of cyclohexa-1,3-diene was degassed and sealed in a reaction tube. The solution was heated to 70 °C for 1 h. After filtration and removal of solvent and excess reagent, vacuum distillation at 80 °C gave a small amount of **4a**, yield ~ 10%. Compound **4b** was prepared with cyclohepta-1,3-diene by the same procedures, the yield was ~ 12%. Compound **4c** was prepared photochemically with cycloheptatriene at -50 °C, in ~ 25% yield.

Compound **4b** was obtained together with **5a** and **5b**; further purification was unsuccessful. Compound **4c** was obtained in a mixture together with **3e** and **3f**. Adding $Fe(CO)_5$ to the mixture and irradiation at 0 °C for 3 h converted $3e/3f$ into $3e'/3f'$. Vacuum distillation at 79 °C gave a small quantity of **4c** with 80% purity.

Mass spectrum of **4a**: 294 (M^+ , $C_{12}H_{18}Si_2F_4^+$), 279 ($C_{11}H_{15}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). 1H NMR of **4a**: δ 1.12 (s), 9H, t-Bu; 1.85 (br, c), 2H, CH ; 2.5 (br), 4H, CH_2 ; 5.85 (c), 2H, $HC=CH$; 6.21 (m), 1H, $=CHSiF_2$. $^{19}F\{^1H\}$ NMR of **4a**: 136.24 (d), SiF_3 ; 126.28 (q), SiF .

Mass spectrum of **4b**: 308 (M^+ , $C_{13}H_{20}Si_2F_4^+$), 293 ($C_{12}H_{17}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). 1H NMR of **4b**: (obtained by subtracting the spectra of **5a/5b**) δ 1.10 s(s), 9H, t-Bu; 1.85 (br, c), 2H, CH ; 1.9–2.3 (br), 6H, $(CH_2)_3$; 5.5 (c), 2H, $CH=CH$; 6.35 (m), 1H, $=CHSiF_2$. $^{19}F\{^1H\}$ NMR of **4b**: 137.5 (d), SiF_3 ; 125.4 (q), SiF .

Mass spectrum of **4c**: 306 (M^+ , $C_{13}H_{18}Si_2F_4^+$), 291 ($C_{12}H_{15}Si_2F_4^+$), 215 ($C_6H_{11}Si_2F_4^+$), 57 ($C_4H_9^+$). 1H NMR of **4c**: δ 1.14 s(s), 9H, t-Bu; 2.40 (d), 2H,

CH_2 ; 5.0 (d), SiFH ; 5.5–5.8 (br), 5H, all olefin H in the ring; 6.23 (m), $=\text{CHSiF}_2$. $^{19}\text{F}\{^1\text{H}\}$ NMR of **4c**: 135.5 (d), SiF_3 ; 173.8 (q), SiF ; $^2J(\text{H}, \text{F})$ 51.3 Hz.

Preparation of 2b. To 10 ml of benzene, was added 0.67 g (1.8 mmol) of $\text{F}_2\text{Si}(\text{t-Bu})\text{C}=\text{CHSiF}_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)\text{CO}$ and 0.37 g (4.0 mmol) of cyclohepta-1,3-diene. The solution was degassed and irradiated at 30 °C for 3 days. The mixture was degassed every 5 h. After removal of solvent and excess reagent, vacuum distillation at 80 °C gave 0.39 g of **2b**, yield 70%. Mass spectrum of **2b**: 308 (M^+ , $\text{C}_{13}\text{H}_{20}\text{Si}_2\text{F}_4^+$), 293 ($\text{C}_{12}\text{H}_{17}\text{Si}_2\text{F}_4^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 94 (C_7H_8^+), 57 (C_4H_9^+). $^{19}\text{F}\{^1\text{H}\}$ NMR of **2b**: 129.43 (d), 128.18 (d); $=\text{CHSiF}_2$; 137.60 (d), 138.04 (d); $=\text{C}(\text{t-Bu})\text{SiF}_2$. ^{13}C NMR of **2b**: δ 166.46 t, t(t, t), $=\text{C}(\text{t-Bu})$; 132.82 t(d, t), $=\text{CHSiF}_2$; 134.70 s(d) and 126.74 s(d), $\text{HC}=\text{CH}$; 39.31 s(s), $\text{C}(\text{CH}_3)_3$; 29.47 s(q), $\text{C}(\text{CH}_3)_3$; 27.07 s(t), $\text{CH}_2\text{CH}_2\text{CH}_2$; 26.95 s(t) and 25.49 s(t), $\text{CH}_2\text{CH}_2\text{CH}_2$.

Preparation of VIIIa/VIIIb. To 15 ml of n-hexane, 0.2 g (0.7 mmol) of (η^4 -norbornadiene) $\text{Mo}(\text{CO})_4$ and 0.3 g (1.4 mmol) of **1** were added. The solution was degassed and irradiated at -30 °C for 3 days. After removal of solvent and excess reagents, about 0.1 g (0.2 mmol) of VIIIa/VIIIb was obtained, yield 30%. Mass spectrum of VIIIa/VIIIb: 486 (M^+ , $\text{C}_{16}\text{H}_{18}\text{O}_3\text{Si}_2\text{F}_4\text{Mo}^+$), 458 ($\text{C}_{15}\text{H}_{18}\text{O}_2\text{Si}_2\text{F}_4\text{Mo}^+$), 430 ($\text{C}_{14}\text{H}_{18}\text{OSi}_2\text{F}_4\text{Mo}^+$), 306 ($\text{C}_{13}\text{H}_{18}\text{Si}_2\text{F}_4^+$), 272 ($\text{C}_{10}\text{H}_8\text{O}_3\text{Mo}^+$). ^1H NMR spectrum of VIIIa/VIIIb: δ 1.15 (s) and 1.20 (s), t-Bu of VIIIa and VIIIb; 1.26 (s), CH_2 ; 2.98 (c), CH ; 3.56 (d) and 4.80 (d), all $\text{HC}=\text{CH}$ of VIIIa and VIIIb; 7.25 (t, t), $=\text{CHSiF}_2$. $^{19}\text{F}\{^1\text{H}\}$ NMR of VIIIa/VIIIb: 81.13 (s), $=\text{CHSiF}_2$; 108.45 (s), $=\text{C}(\text{t-Bu})\text{SiF}_2$ of VIIIa or VIIIb, 93.28 (s), $=\text{C}(\text{t-Bu})\text{SiF}_2$; 96.85 (s), $=\text{CHSiF}_2$ of VIIIb or VIIIa. ^{13}C NMR of VIIIa/VIIIb: δ 215.53 t(t) and 214.92 t(t), CO (*trans* to SiF_2) of VIIIa and VIIIb; 212.11 s(s) and 211.95 s(s), CO (*cis* to SiF_2) of two isomers; 186.38 m(m) and 187.70 m(m), $=\text{C}(\text{t-Bu})$ of two isomers; 151.13 m(dm) and 150.41 m(dm), $=\text{CHSiF}_2$ of two isomers; 77.04 s(d) and 75.20 s(d), norbornadiene $=\text{CH}$ (on same side of axial SiF_2); 63.95 s(t), s(t), CH_2 ; 58.70 s(d), norbornadiene $=\text{CH}$ (on opposite side of axial SiF_2); 48.34 s(d) and 48.17 s(d), CH ; 38.76 s(s) and 37.91 s(s), $\text{C}(\text{CH}_3)_3$ of two isomers; 30.12 s(q) and 29.87 s(q), $\text{C}(\text{CH}_3)_3$ of two isomers.

Preparation of 6a. About 0.1 g (0.2 mmol) of VIIIa/VIIIb in 5 ml of n-hexane was degassed and heated at 120 °C in a sealed tube for 3 h. Molecular distillation under vacuum at 90 °C gave about 50 mg (0.16 mmol) of **6a**, yield 80%. A trace quantity of **6c** was also obtained, yield ~ 5%.

Mass spectrum of **6a**: 306 (M^+ , $\text{C}_{13}\text{H}_{18}\text{Si}_2\text{F}_4^+$), 291 ($\text{C}_{12}\text{H}_{15}\text{Si}_2\text{F}_4^+$), 215 ($\text{C}_6\text{H}_{11}\text{Si}_2\text{F}_4^+$), 92 (C_7H_8^+). ^1H NMR of **6a**: δ 1.14 (s), 9H, t-Bu; 1.55 (s), 2H, $\text{CH}-\text{SiF}_2$; 1.83 (AB), 2H, CH_2 ; 3.34 (m) and 3.30 (m), 2H, $\text{CH}-\text{CH}_2$; 6.10 (c), 2H, $\text{HC}=\text{CH}$; 6.48 (m), $=\text{CHSiF}_2$. $^{19}\text{F}\{^1\text{H}\}$ NMR of **6a**: 126.84 (d), 132.43 (d), $=\text{C}(\text{t-Bu})\text{SiF}_2$; 135.23 (d), 140.60 (d), $=\text{CHSiF}_2$. ^{13}C NMR of **6a**: δ 175.0 m(m), $=\text{C}(\text{t-Bu})$; 136.39 t(d, t), $=\text{CHSiF}_2$; 136.37 s(d) and 135.54 s(d), $\text{HC}=\text{CH}$; 51.05 s(t), CH_2 ; 45.41 s(d) and 45.13 s(d), $\text{HCCH}=\text{CHCH}$; 39.63 s(s), $\text{C}(\text{CH}_3)_3$; 29.15 s(q), $\text{C}(\text{CH}_3)_3$; 23.10 t(d, t) and 22.65 t(d, t), $\text{F}_2\text{SiCHCHSiF}_2$.

Preparation of 6b. (η^4 -Norbornadiene) $\text{Cr}(\text{CO})_4$, when subjected to the same procedures as in the preparation of **6a**, gave a mixture of **6a** and **6b** (approximately 1/1 total yield 25%). Since **6b** cannot be obtained pure, the spectral data are obtained by subtracting the spectra of **6a** from the spectra of the mixture.

Mass spectrum of **6b**; Similar to that of **6a**. ^1H NMR of **6b**: δ 0.9 ~ 1.1 (br), three CH in the three-membered ring; 1.15 (s), t-Bu; 1.57 (br, c), two F_2SiCH ; 1.85

(AB), CH_2 ; 2.45 (c), $\text{F}_2\text{SiCHCHCHSiF}_2$; 6.62 (m), $=\text{CHSiF}_2$. $^{19}\text{F}\{^1\text{H}\}$ NMR of **6b**: 127.40 (d), 132.14 (d), $=\text{C}(\text{t-Bu})\text{SiF}_2$; 135.57 (d), 140.13 (d), $=\text{CHSiF}_2$. ^{13}C NMR spectrum of **6b**: δ 174.6 m(m), $=\text{C}(\text{t-Bu})$; 136.5 m(d, m), $=\text{CHSiF}_2$; 48.7 s(t), CH_2 ; 48.5 s(d), $\text{F}_2\text{SiCHCHCHSiF}_2$ 39.8 s(s), $\text{C}(\text{CH}_3)_3$; 29.5 s(q), $\text{C}(\text{CH}_3)_3$; 21.2 t(d, t), and 21.1 t(d, t), two F_2SiCH ; 11.3 s(d), 10.9 s(d) and 9.7 s(d), three CH in the three-membered ring.

Acknowledgement

We thank the National Science Council and Ministry of Education for financial support of this work. CHL thanks the Institute of Nuclear Energy Research for a research fellowship.

References

- 1 C.H. Lin, C.Y. Lee, and C.S. Liu, *J. Am. Chem. Soc.*, 108 (1986) 1323.
- 2 C.H. Lin, C.Y. Lee, and C.S. Liu, *Organometallics*, 6 (1987) 1861.
- 3 C.Y. Lee, C.H. Lin, and C.S. Liu, *Organometallics*, 6 (1987) 1869.
- 4 C.H. Lin, C.Y. Lee, and C.S. Liu, *Organometallics*, 6 (1987) 1878.
- 5 Y.C. Chen, C.H. Lin, C.Y. Lee, and C.S. Liu, *Organometallics*, 6 (1987) 1882.
- 6 T.T. Jzang, C.Y. Lee, and C.S. Liu, *Organometallics*, in press.
- 7 T.T. Jzang, and C.S. Liu, *Organometallics*, in press.
- 8 C.H. Lin, Ph.D. Thesis, National Tsing Hua University, 1985.
- 9 D. Seyferth, M.L. Shannon, S.C. Vick, and T.F. Lim, *Organometallics*, 4 (1985) 47.
- 10 J. Slutsly, and H.J. Kwart, *H.J. Am. Chem. Soc.*, 95 (1973) 8678.
- 11 G. Platbrood, and L.J. Wilputte-Steindrt, *J. Organomet. Chem.*, 85 (1975) 199.
- 12 R.B. King, and T.F. Korenowski, *Inorg. Chem.*, 10 (1971) 1188.
- 13 D.J. Darensbourg, and H.H. Nelson, *J. Am. Chem. Soc.*, 99 (1977) 896.
- 14 D.J. Darensbourg, and H.H. Nelson, *J. Am. Chem. Soc.*, 96 (1974) 6511.
- 15 M.A. Schroeder, and M.S. Wrighton, *J. Organomet. Chem.*, 74 (1974) C29.
- 16 E.N. Frankel, E. Selke, and C.A. Glass, *C.A.J. Am. Chem. Soc.*, 90 (1968) 2446.
- 17 W.P. Lin, Thesis, National Tsing Hua University, 1982.
- 18 T.H. Sheu, Y. Chi, and C.S. Liu, *Inorg. Chem.*, 20 (1981) 199.
- 19 T.H. Sheu, Y. Chi, and C.S. Liu, *J. Am. Chem. Soc.*, 104 (1982) 1594.
- 20 M.F. Howthorne, D.M. Speckman, and C.B. Knobler, *Organometallics*, 4 (1985) 1692.
- 21 C.S. Liu, J.L. Margrave, J.C. Thompson, *Can. J. Chem.*, 50 (1972) 465.
- 22 C.W. Cheng, and C.S. Liu, *J. Am. Chem. Soc.*, 97 (1975) 6746.
- 23 Y. Chi, and C.S. Liu, *Inorg. Chem.*, 20 (1981) 3456.