Preparation and Reactivities of (η^3-1- and 2-Trimethylsiloxyallyl)$Fe(CO)_2NO$ Complexes. Intermediates Functioning as Equivalents of β- and α-Acyl Carbocations and Acyl Carbanions

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(η^3-1- and 2-Trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes were prepared by the reaction of the corresponding siloxyallylic halides with $Bu_4N[Fe(CO)_3NO]$. These complexes reacted with both of carbon nucleophiles and carbon electrophiles preferentially at the less hindered sites of the allylic ligands. In these reactions, (η^3-1-trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes served as synthetically equivalent synthons for both of β-acyl carbocations and β-acyl carbanions and (η^3-2-trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes as both of α-acyl carbocations and α-acyl carbanions. The stereochemical courses of the reactions are described.

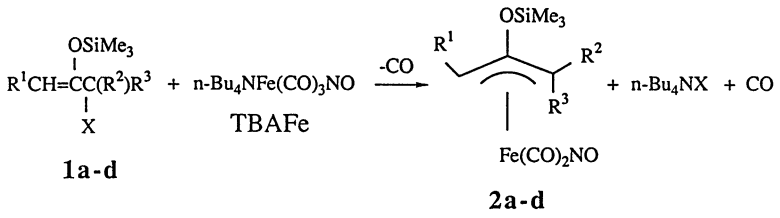
π-Allyl transition metal complexes have been shown to be useful intermediates in organic synthesis.[1] In most cases, these complexes have been used as a synthetically equivalent synthon for allylic carbocations. An exceptional case is π-allyl nickel complexes. They react with carbon electrophiles such as organic halides in polar media to produce alkylated allyl compounds.[2] However, the synthetic applicability of π-allyl iron complexes has been less explored, compared with the other transition metal complexes such as π-allyl nickel and palladium complexes. Nicholas et al. have reported that cationic π-allyl iron complexes of the type, (η^3-allyl)$Fe(CO)_4BF_4$, react with carbon nucleophiles preferentially at the less hindered site of the allylic ligands to produce alkylated allyl compounds.[3] Roustan et al. have shown that allylic acetates and halides couple with carbon nucleophiles in the presence of a catalytic amount of $Na[Fe(CO)_3NO]$ also to produce alkylated allyl compounds.[4] In this catalytic reaction, the attack of nucleophiles occurs preferentially at the leaving group-bearing carbons of the allylic ligands. They proposed that this reaction proceeds via (η^3-allyl)$Fe(CO)_2NO$ complexes. Xu and Zhou have reported a similar type of coupling reactions using n-$Bu_4N[Fe(CO)_3NO]$ as catalyst, but they proposed σ-allyl iron complexes as a key intermediate in this catalytic reaction.[5] However, no systematic studies have so far been made for the reactivities of (η^3-allyl)$Fe(CO)_2NO$ complexes. Previously, we reported a convenient procedure for preparation of the tetrabutylammonium ferrate, n-$Bu_4N^+[Fe(CO)_3NO]^-$ (TBAFe), and have shown that this ferrate complex can be utilized as a useful reagent for the synthesis of a variety of (η^3-allyl)$Fe(CO)_2NO$ complexes.[6] We also found that (η^3-allyl)$Fe(CO)_2NO$ complexes derived from allylic halides react with carbon electrophiles such as allyl, acyl and alkoxycarbonyl halides to give 1,5-dienes and β,γ-unsaturated carbonyl compounds, respectively.[6] In our previous communications,[7] we showed that (η^3-1-trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes react with both of carbon nucleophiles and electrophiles at the same position of the allylic ligands. Therefore, these iron complexes are envisaged to serve as a synthetically equivalent synthon for both of β-acyl carbocations and β-acyl carbanions. Since then, we have extensively investigated the chemical reactivities of iron complexes of this sort. In this paper, we report the preparation of (η^3-1- and 2-trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes and their reactivity features. These complexes have a dual reactivity and react with both of carbon nucleophiles and electrophiles at the same position of the allylic ligands of the complexes, preferentially at the less hindered sites. The stereochemical courses of the reactions are also discussed.

Results and Discussion

Preparation of (η^3-Trimethylsiloxyallyl)$Fe(CO)_2NO$ Complexes. The reaction of 3-halo-2-trimethylsiloxy-1-propenes **1a**—**d** with one equiv of TBAFe in CH_2Cl_2 at room temperature gave (η^3-2-trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes **2a**—**d** with evolution of one equiv of CO. The results are given in Scheme 1 and Table 1. The complexes were fairly stable to air and moisture, and they could be isolated by column chromatography on slica gel.

The structures of **2a**—**d** were established from their spectral data. The IR spectra showed characteristic absorption due to two CO ligands and one NO ligand in 1950—2050 and 1720—1730 cm^{-1} regions, respectively. The ^1H NMR spectra exhibited signals assignable to the allylic ligands. The ^1H NMR spectrum of **2c** revealed that this complex is actually a 1:1 mixture of two isomers in which the allylic ligand has a different configuration; i,e. the one isomer has the *syn*-methyl and *anti*-ethyl configuration and the other isomer has the *syn*-ethyl and *anti*-methyl configuration. The methyl proton signal of the former isomer appeared at a lower field (δ=2.07) than that of the later isomer (δ=1.51). In the case of **2d**, chlorine atom on the allylic ligand was found to be oriented to the anti-direction.

(η^3-1-Trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes

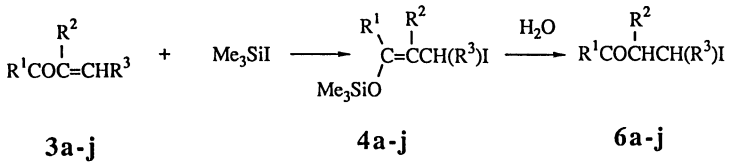


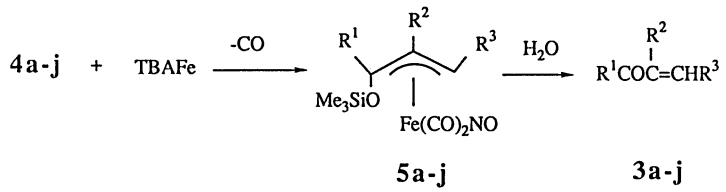
Scheme 1.

Table 1. Preparation of (η^3-2-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes

Allylic halide	Iron complex	Isolated Yield[a)]/%
1a: R^1=R^2=R^3=H, X=Cl	**2a**	57
1b: R^1=H, R^2=R^3=Me, X=Br	**2b**	68
1c: R^1=H, R^2=Me, R^3=Et, X=Br	**2c**	72
1d: R^1=Cl, R^2=R^3=H, X=Cl	**2d**	37

a) Isolated yields based on the allylic halides used.



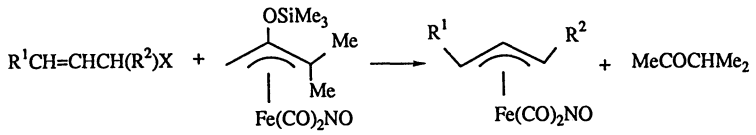


Scheme 2.

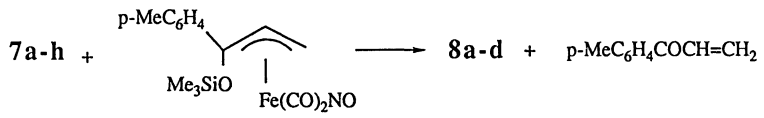
5a—**j** were synthesized by the reaction of TBAFe in CH_2Cl_2 at room temperature with one molar equiv of 3-iodo-1-trimethylsiloxy-1-propenes **4a**—**j**, which had been prepared in situ from α,β-unsaturated carbonyl compounds **3a**—**j** and Me_3SiI. Complexes **5a**—**j** were unable to isolate in pure forms because of their sensitivity to air and moisture. However, formation of the iron complexes was supported by their chemical properties and spectral data.

The reaction of **3a**—**j** with Me_3SiI in CH_2Cl_2, followed by acid hydrolysis, gave the β-iodo ketones and esters **6a**—**j**. This reaction is likely to proceed via silyl enol ethers **4a**—**j**.[8] In separate experiments, **4a**—**j**, which were prepared from **3a**—**j** and Me_3SiI, were first treated with TBAFe, and then hydrolyzed with 4 M (1 M=1 mol dm^{-3}) HCl. This treatment gave quantitatively the starting ketones and esters **3a**—**j**. All of these results can be explained in terms of the reaction pathways shown in Scheme 2. A more direct support for the formation of **5a**—**j** was secured from the IR spectra of the reaction mixtures. The IR spectrum of the reaction mixture obtained from **3a**, Me_3SiI and TBAFe showed the characteristic bands for **5a** at 2060 and 1980 cm^{-1} due to two CO ligands, 1745 cm^{-1} due to the NO ligand, and 870 cm^{-1} due to the O–Si bond of the allylic ligand. Similar spectral data were obtained for **5b**—**j** which were prepared in a similar manner.

Reactions of (η^3-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes. Ligand Exchange. The reactions of (η^3-trimethylsiloxyallyl)Fe(CO)$_2$NO complexes **2b** and **5b** with one equiv of allylic halides, acetates, and carbonates **7a**—**h** in CH_2Cl_2 resulted in the ligand exchange to give (η^3-allyl)Fe(CO)$_2$NO complexes **8a**—**d**. In these reactions, small amounts of ketones **9** and **3b**, which were obtained by hydrolysis of the trimethylsiloxyallylic ligands, were produced as by-products. The results are summarized in Scheme 3 and Table 2. Noteworthy is that allylic acetates and carbonates have little reactivity toward TBAFe, but they react with (η^3-trimethylsiloxyallyl)Fe(CO)$_2$NO complexes to form (η^3-allyl)-Fe(CO)$_2$NO complexes via the ligand exchange reaction. The reactivity in the ligand-exchange reaction



7a-h **2b** **8a-d** **9**



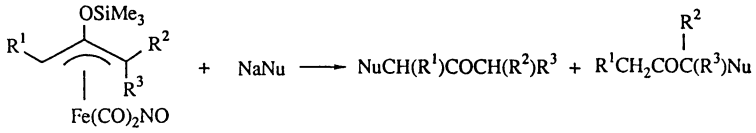
5b **3b**

Scheme 3.

Table 2. Ligand Exchange of (η^3-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes[a)]

Allylic compound			Iron complex	Product	Yield[b)]/%
R^1	R^2	X			
7a: H	H	Br	**2b**	**8a**: R^1=R^2=H	75
7b: Ph	H	Br	**2b**	**8b**: R^1=Ph, R^2=H	68
7b: Ph	H	Br	**5b**	**8b**	73
7c: Ph	H	OAc	**5b**	**8b**	28
7d: Ph	H	OCO_2Me	**5b**	**8b**	56
7e: Me	H	Cl	**2b**	**8c**: R^1=Me, R^2=H	26
7e: Me	H	Cl	**5b**	**8c**	38
7f: Me	H	OAc	**5b**	**8c**	26
7g: $-(CH_2)_3-$		Br	**2b**	**8d**: R^1—R^2=$-(CH_2)_3-$	76
7g: $-(CH_2)_3-$		Br	**5b**	**8d**	71
7h: $-(CH_2)_3-$		OAc	**5b**	**8d**	25

a) Solvent: CH_2Cl_2, Temperature: 40 °C, Time: 5 h. b) Isolated yields based on the allylic compounds used.



2 **10** **11**

Scheme 4.

Table 3. Reaction of the Iron Complexes **2a**—**d** with Carbon Nucleophiles

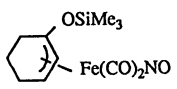
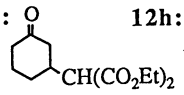
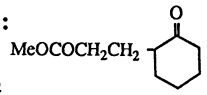
Iron complex	Nucleophile	Substituents on **10** and **11**				Yield[a)]/%	
			R^1	R^2	R^3	**10**	**11**
2a	$NaCH(CO_2Et)_2$	**a**:	H	H	H	57	(**10a**=**11a**)
2a	$NaCH(COMe)CO_2Et$	**b**:	H	H	H	43	(**10b**=**11b**)
2b	$NaCH(CO_2Et)_2$	**c**:	H	Me	Me	46	16
2b	$NaCH(COMe)CO_2Et$	**d**:	H	Me	Me	30	7
2b	$NaCH(CN)_2$	**e**:	H	Me	Me	18	6
2c	$NaCH(CO_2Et)_2$	**f**:	H	Me	Et	52	16
2c	$NaCH(COMe)CO_2Et$	**g**:	H	Me	Et	40	9
2c	$NaCH(CN)_2$	**h**:	H	Me	Et	46	4
2d	$NaCH(CO_2Et)_2$	**a**:	H	H	H	53	(**10a**=**11a**)
2d	$NaCH(COMe)CO_2Et$	**b**:	H	H	H	43	(**10b**=**11b**)

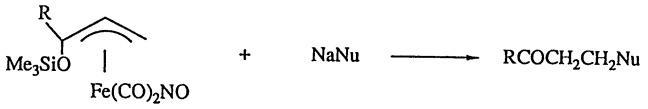
a) Isolated yields based on the iron complexes used.

Table 4. Reaction of the Iron Complexes **5** with Carbon Nucleophiles in THF

Iron complex	Nucleophile	Product	Yield[a]/%
5a: R=Ph	$NaCH(CO_2Et)_2$	**12a**: R=Ph, Nu=$CH(CO_2Et)_2$	95
5a:	$NaCH(COMe)CO_2Me$	**12b**: R=Ph, Nu=$CH(COMe)CO_2Me$	42
5d: R=Et	$NaCH(CO_2Et)_2$	**12c**: R=Et, Nu=$CH(CO_2Et)_2$	75
5e:[b]	$NaCH(CO_2Et)_2$	**12d**:[b]	90
5h: R=MeO	$NaCH(CO_2Et)_2$	**12e**: R=MeO, Nu=$CH(CO_2Et)_2$	95
5h:	$NaCH(COMe)CO_2Me$	**12f**: R=MeO, Nu=$CH(COMe)CO_2Me$	60
5h:	$NaCH(CN)_2$	**12g**: R=MeO, Nu=$CH(CN)_2$	92
5h:	1-morphilinocyclohexene	**12h**:[b]	89

a) Isolated yields based on the iron complexes used.

b) **5e**:  **12d**:  **12h**: 



5a,d,e,h **12a-h**

Scheme 5.

implies that the stability of (η^3-allyl)$Fe(CO)_2NO$ complexes depends upon substituents on the allylic ligands and decreases in the order: alkyl, aryl>2-trimethylsiloxy>1-trimethylsiloxy.

Reactions with Carbon Nucleophiles. The iron complexes **2a**—**d** reacted with carbon nucleophiles such as $NaCH(CO_2Et)_2$, $NaCH(COMe)CO_2Et$ and $NaCH(CN)_2$ in THF at room temperature to give α-alkylated ketones **10a**—**h** along with small amounts of the regioisomers **11a**—**h** (**10a**=**11a**, **10b**=**11b**) after acid hydrolysis of the reaction mixtures. The results are shown in Scheme 4 and Table 3. In these reactions, the attack of carbon nucleophiles occurred predominantly at the less hindered sites of the allylic ligands. In the cases of **2d**, the reductive elimination of chlorine atom occurred concurrently to give the corresponding α-alkylated products. Consequently, the iron complexes **2a**—**d** can be regarded as a synthetically equivalent synthon for α-acyl carbocations.

The iron complexes **5a,d,e,h** also reacted with carbon nucleophiles in THF at room temperature to give β-alkylated ketones **12a,d,e,h** after acid hydrolysis of the reaction mixtures. The results are shown in Scheme 5 and Table 4. The regioselectivity in these reactions was extremely high, so that the nucleophiles reacted only at the less hindered sites of the allylic ligands, giving a single product in every case. Thus, the iron complexes **5a,d,e,h** can be regarded as a synthetically equivalent synthon for β-acyl carbocations.

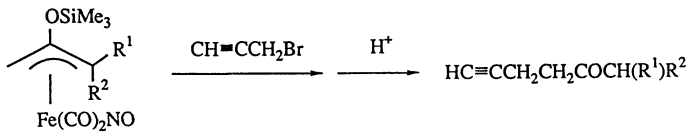
Reactions with Carbon Electrophiles. Iron complexes **2a**—**c** reacted with 2-propynyl bromide in *N,N*-dimethylformamide (DMF) or *N*-methyl-2-pyrrolidinone (NMP) at 80 °C. In these reactions, the attack of 2-propynyl bromide occurred regioselectively also at the less hindered sites of the allylic ligands of the iron complexes. The acid hydrolysis of the reaction mixtures gave 3-butynyl ketones **13a**—**c** as sole isolable products. The results are given in Scheme 6 and Table 5.

Treatment of 3-halo-2-trimethylsiloxy-1-propenes **1a**—**c** with a half molar equiv of TBAFe in toluene at 110 °C, followed by acid hydrolysis of the reaction mixtures, gave two regioisomeric mixtures of 1,4-diketones, **14a**—**c** and **15a**—**c** (**14a**=**15a**). The results

Table 5. Reaction of the Iron Complexes **2a**—**c** with 2-Propynyl Bromide in DMF

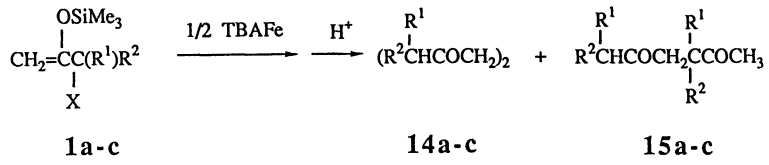
Complex **2**	Product	Yield[a]/%
2a	**13a**	18
2b	**13b**	65
2b	**13b**	63[b]
2c	**13c**	55

a) Isolated yields based on the substrates **1** used.
b) NMP was used as solvent.



2a-c **13a-c**

Scheme 6.



1a-c **14a-c** **15a-c**

Scheme 7.

Table 6. Formation of 1,4-Diketones

Substrate	Products: Yield[a]/%	
	14	**15**
1a	**14a**: 28	**(14a=15a)**
1b	**14b**: 69	**15b**: 22
1c	**14c**: 62	**15c**: 12

a) Isolated yields based on the substrates **1** used.

are shown in Scheme 7 and Table 6.

This reaction probably proceeds via an electrophilic attack of **1a—c** toward the intermediary produced iron complexes **2a—c**. With **1b,c**, the formation of **14b,c** predominated, indicating that a coupling at the less hindered sites of both of **1a—c** and **2a—c** is favored. Mechanistically, this reaction may involve an oxidative addition of the C–X bonds of **1a—c** on the Fe atom of the iron complexes **2a—c** as a key step. The detailed mechanistic feature of the reaction of the allylic iron complexes with allylic halides will be discussed later.

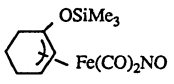
The above results strongly imply that the iron complexes **2a—c** serve as a synthetically equivalent synthon for α-acyl carbanions. Previously, Hegedus and Stiverson have demonstrated that η^3-2-methoxyallyl nickel complexes also serve as a synthetically equivalent synthon for α-acyl carbanions.[9]

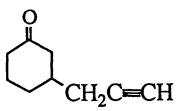
The iron complexes **5a—g,i,j**, which were prepared in situ from **3a—g,i,j**, Me_3SiI and TBAFe, reacted regioselectively with 2-propynyl bromides in DMF or NMP at 80 °C to give β-propynylated ketones and esters **16a—g,i,j**, after acid hydrolysis of the reaction mixtures. The results are given in Scheme 8 and Table 7. The yields of the products were appreciably improved by pretreating **5a—g,i,j** with one equiv of triphenyl phos-

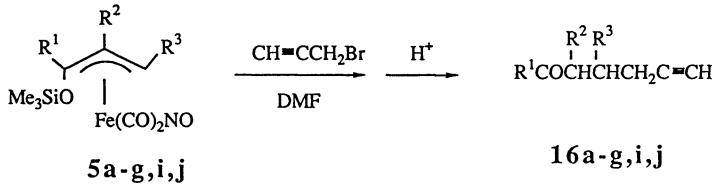
Table 7. Reaction of (η^3-1-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes with 2-Propynyl Bromide in DMF[a]

	Complex			Additive	Product	Yield[b]/%
	R^1	R^2	R^3			
5a:	C_6H_5	H	H	None	**16a**	81
5a:				$P(OPh)_3$	**16a**	93
5b:	*p*-$CH_3C_6H_4$	H	H	None	**16b**	35
				$P(OPh)_3$	**16b**	83
				$P(OPh)_3$	**16b**	80[c]
5c:	*p*-ClC_6H_4	H	H	None	**16c**	66
				$P(OPh)_3$	**16c**	87
5d:	C_2H_5	H	H	$P(OPh)_3$	**16d**	58
5e:	$-(CH_2)_3-$	H	—[d]	$P(OPh)_3$	**16e**[e]	56
5f:	C_6H_5O	H	H	None	**16f**	12
				$P(OPh)_3$	**16f**	50
5g:	CH_3O	H	C_6H_5	None	**16g**	30
				$P(OPh)_3$	**16g**	62
5i:	C_6H_5	CH_3	H	$P(OPh)_3$	**16i**	76
5j:	C_6H_5O	CH_3	H	$P(OPh)_3$	**16j**	73

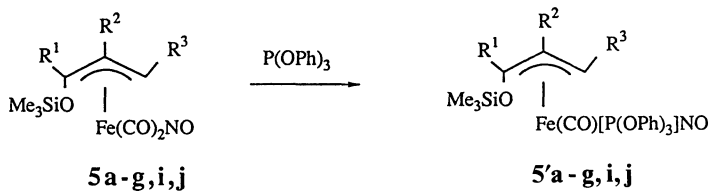
a) Reaction conditions: **5**; 2 mmol, $CH{\equiv}CCH_2Br$; 4 mmol, $P(OPh)_3$; 2 mmol, Temp; 80 °C, Time; 15 h.
b) Isolated yields based on iron complexes used.
c) NMP was used as solvent.

d) **5e**: 

e) **16e**: 

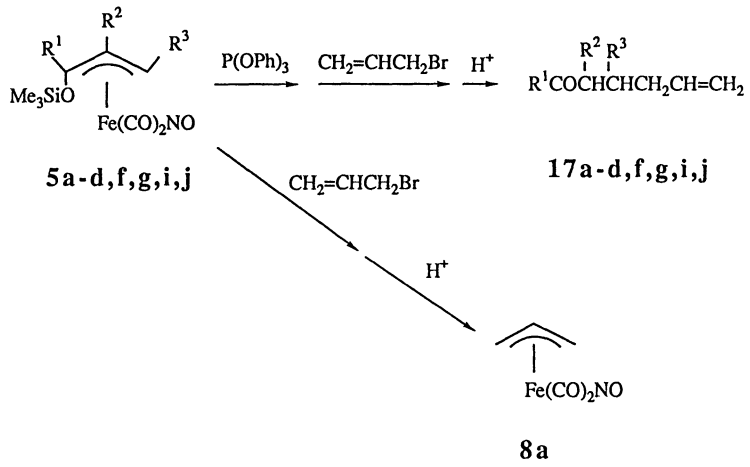


5a-g,i,j **16a-g,i,j**



5a-g,i,j **5'a-g,i,j**

Scheme 8.



Scheme 9.

phite before adding 2-propynyl bromide to the reaction mixtures. In these cases, it is conceivable that the iron complexes **5** are first converted into the corresponding (η^3-1-trimethylsiloxyallyl)Fe(CO)[P(OPh)$_3$]NO complexes **5′**, although they were not isolated in pure forms.

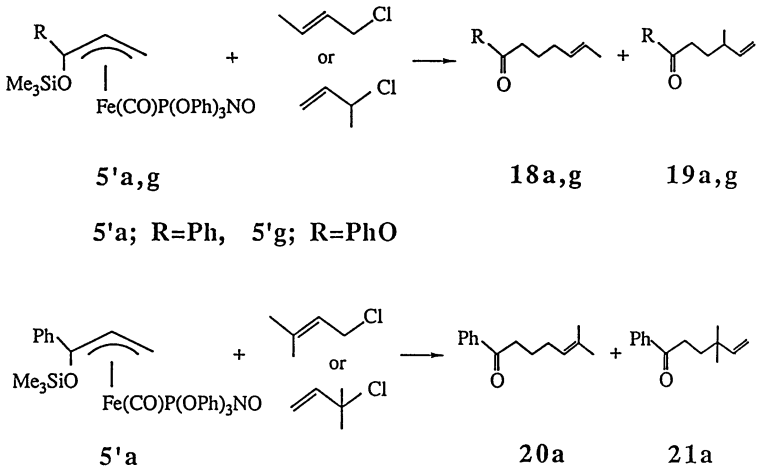
Table 8. Reaction of (η^3-1-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes with Allyl Bromide in the Presence of P(OPh)$_3$ in DMF[a)]

	Complex			Product	Yield/%
	R^1	R^2	R^3		
5a:	C_6H_5	H	H	**17a**	61
5a:		H	H	**17a**	66[b)]
5b:	*p*-$CH_3C_6H_4$	H	H	**17b**	48
5c:	*p*-ClC_6H_4	H	H	**17c**	52
5d:	C_2H_5	H	H	**17d**	25
5f:	C_6H_5O	H	H	**17f**	48
5g:	CH_3O	H	C_6H_5	**17g**	30
5i:	C_6H_5	CH_3	H	**17i**	60
5j:	C_6H_5O	CH_3	H	**17j**	42

a) Reaction conditions: **5**; 2 mmol, CH_2=$CHCH_2Br$; 4 mmol, P(OPh)$_3$; 2 mmol, Temp; 80 °C, Time; 15 h. b) NMP was used as solvent.

The iron complexes **5a**—**d**,**f**,**g**,**i**,**j** also reacted in DMF or NMP with allyl bromide after treating the complexes with triphenyl phosphite to give β-allylated ketones and esters **17a**—**d**,**f**,**g**,**i**,**j**. In the absence of triphenyl phosphite, the complexes did not react with allyl bromide at room temperature, but the ligand-exchange reaction occurred to give (η^3-allyl)Fe(CO)$_2$NO complex **8a**. The results are shown in Scheme 9 and Table 8. When the reaction was carried out at 80 °C, 1,5-hexadiene was obtained by the coupling of the allyl ligand of the complex **8a**.

All the above results strongly support the assumption that the actual reactive complexes in the reactions of the iron complexes **5** in the presence of triphenyl phosphite are **5′**, and indicate that the nucleophilic reactivity of the iron complexes **5** is increased by converting the electron-withdrawing CO ligand in the complexes to the electron-donating P(OPh)$_3$ ligand. A more detailed mechanistic feature for the reaction of the iron complexes with allylic halides was obtained from the following experiments.

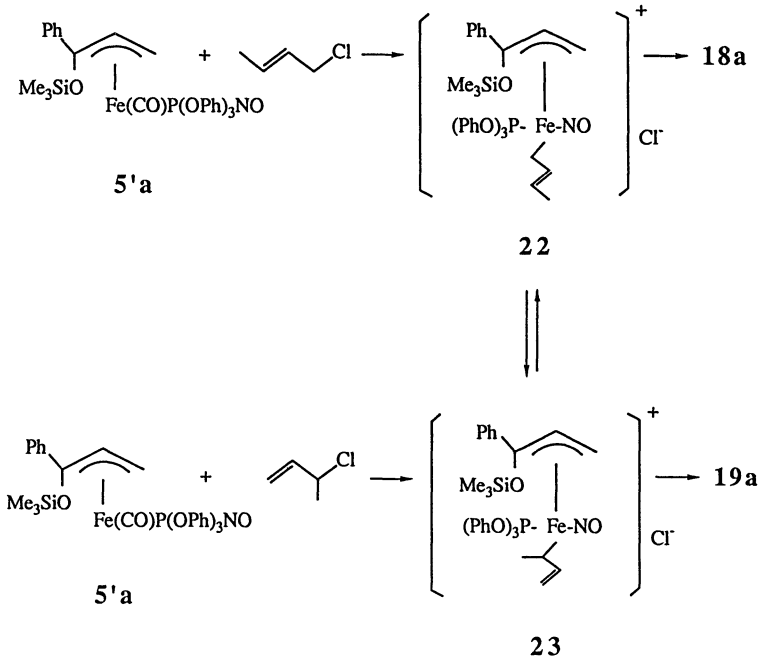


Scheme 10.

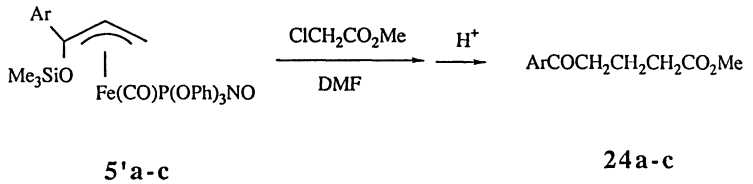
Table 9. Reaction of the Iron Complexes **5'a** and **5'g** with Allylic Chlorides in DMF

Iron complex	Allylic halide	Yield of products[a]/%	Ratio of **18**/**19** or **20**/**21**
5'a	1-Chloro-2-butene	51	38/13
5'a	3-Chloro-1-butene	48	34/14
5'g	1-Chloro-2-butene	43	32/11
5'g	3-Chloro-1-butene	50	36/14
5'a	1-Chloro-3-methyl-2-butene	58	56/ 2
5'a	3-Chloro-3-methyl-1-butene	52	50/ 2

a) Isolated yields based on the iron complexes used.



Scheme 11.



Scheme 12.

The reaction of **5'a** and **5'g** with 1-chloro-2-butene and 3-chloro-1-butene in DMF afforded a mixture of δ,ε-unsaturated ketones **18a** and **19a** and a mixture of **18g** and **19g**, respectively, essentially in the same ratio from both of the allylic halides. The reaction of **5'a** with 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene also afforded a mixture of two unsaturated ketones **20a** and **21a** almost in the same ratio. The results are given in Scheme 10 and Table 9. These results can be accounted for in terms of the reaction pathway shown in Scheme 11. The first step is the oxidative addition of allylic halides on the Fe atom of the iron complexes to form iron complexes **22** and **23** which are in equilibrium with each other. The reductive elimination of two allylic moieties gives the products.

The other example for the electrophilic addition on the iron complexes is the reaction of methyl chloroacetate with **5'a**—**c** in DMF. This reaction gave δ-keto esters **24a**—**c** in moderate yields. The results are given in Scheme 12 and Table 10.

All the above results indicate that the iron complexes **5** and **5'** serve as a synthetically equivalent synthon for β-acyl carbanions. Since β-acyl carbanions are useful intermediates in organic synthesis, several methods have already been developed for the generation of these inter-

Table 10. Reaction of (η^3-1-Trimethylsiloxyallyl)-Fe(CO)[P(OPh)$_3$]NO Complexes with Methyl Chloroacetate in DMF

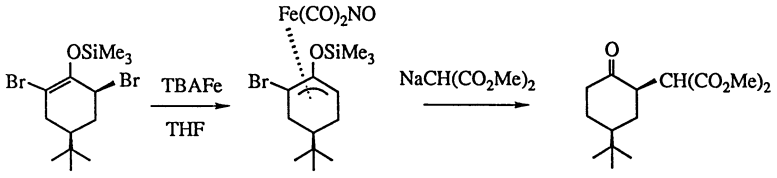
Complex	Product	Yield/%
5'a: Ar=C_6H_5	**24a**	32
5'b: Ar=*p*-$CH_3C_6H_4$	**24b**	48
5'c: Ar=*p*-ClC_6H_4	**24c**	28

Reaction conditions: **5'**; 2 mmol, $ClCH_2CO_2Me$; 4 mmol, Temp; 80 °C, Time 15 h.

mediates.[10–14] An approach is the desilylative ring cleavage of siloxycyclopropanes with metal salts.[12] The other approach is based on the preparation of heteroatom-substituted allylic carbanions.[13,14] By utilizing our method, carbon electrophiles can be introduced at β-position of α,β-unsaturated ketones and esters with high regioselectivity via (η^3-1-trimethylsiloxyallyl)Fe(CO)[P(OPh)$_3$]NO complexes in a one-pot manner.

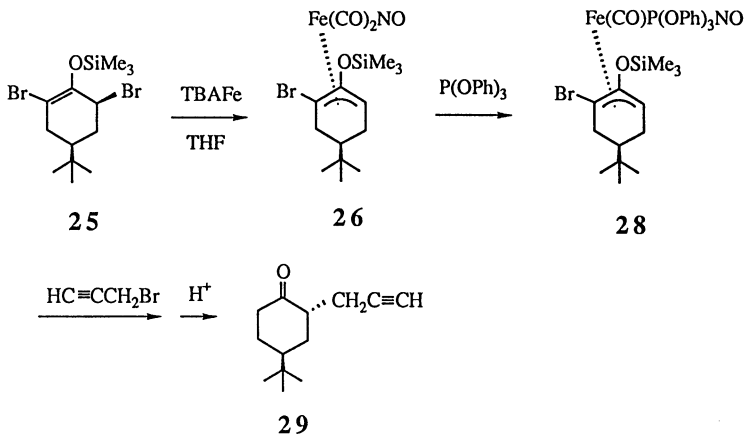
Stereoselectivities. 2,6-Dibromo-4-(*t*-butyl)-1-trimethylsiloxycyclohexene (**25**) was converted to the iron complex **26** by treating with TBAFe in THF. This complex reacted smoothly with $NaCH(CO_2Me)_2$ in THF at room temperature to give exclusively *cis*-4-*t*-butyl-2-[bis(methoxycarbonyl)methyl]cyclohexanone (**27**) in a 76% yield (Scheme 13). The ^{1}H NMR spectrum of **25** showed that the hydrogen atom on C-6 was oriented to the axial direction; its proton appeared as a double doublet centered at δ=4.72 (J=12.01 and 5.24 Hz). The ^{1}H NMR spectrum of the final product showed that the $CH(CO_2Me)_2$ group on C-2 of **27** was oriented to the equatorial direction and the hydrogen atom on the same carbon to the axial direction; the proton signal on C-2 appeared as a triple doublet centered at δ=3.22 (J=13.29, 9.26, and 5.23 Hz). This result suggests that 1) the ferrate ion of TBAFe attacks the C-6 carbon of **25** via a SN_2 like process with inversion of configuration at the reaction center to form iron complex **26**, and 2) the attack of the nucleophile on the allylic ligand of **26** occurs from the opposite side of the coordinated Fe atom and causes inversion of the configuration at the reaction center. During this reaction, the reductive elimination of bromine atom occurs to produce **27**. Trost et al. have proposed a similar stereochemical course for the Pd-catalyzed reaction of *cis*-3-acetoxy-5-(methoxycarbonyl)cyclohexene with carbon nucleophiles.[2,15]

The reaction of the iron complex **26** with 2-propynyl bromide gave *trans*-4-(*t*-butyl)-2-(2-propynyl)cyclohexanone (**29**) in a 36% yield when the reaction was carried out in DMF at 75 °C after treating **26** with triphenyl phosphite (Scheme 14). The ^{1}H NMR spectrum showed that the propynyl group on C-2 of **29** was oriented to the axial direction and the hydrogen atom on the same carbon to the equatorial direction; the proton signal of the hydrogen on C-2 appeared as a qd pattern centered at δ=2.45 (J=7.66 and 4.42 Hz). In this reaction, **26** produced from **25** is first converted to the triphenyl phosphite complex **28**, and then react with



25 26 27

Scheme 13.



25 26 28 29

Scheme 14.

2-propynyl bromide to produce **29**. The final step occurs via the oxidative addition of 2-propynyl bromide on Fe atom of **28** and subsequent reductive elimination of the organic moieties.[1] As a result, the configuration of C-2 of **25** is inverted.

Experimental

General. IR spectra were taken on a Shimadzu IR 24 spectrometer. NMR spectra were recorded with a Hitachi 24B or a JEOL FT-270 in $CDCl_3$ using tetramethylsilane as an internal standsard. Column chromatography was carried out with a Wako-gel C-200 (Wako Pure Chemical Industries). GLC analyses were performed on a Shimadzu GC 4CPF chromatograph using a column packed with SE 30 (10%) (3 mm×1 m). Elemental analyses were carried out on a Yanaco MT-3 elemental analyzer.

Materials. Tetrabutylammonium tricarbonylnitrosylferrate (TBAFe), $Bu_4N[Fe(CO)_3NO]$, was prepared by modification of the method previously reported.[6]

A solution of $Fe(CO)_5$ (60 mmol) in CH_2Cl_2 (20 cm^3) was added to a mixture of $NaNO_2$ (60 mmol) and Bu_4NBr (60 mmol) in water (20 cm^3). The resulting mixture was stirred under argon at room temperature for 2 h. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave $Bu_4N[Fe(CO)_3NO]$ (TBAFe) as yellow crystals in 86% yield; mp 56—56.5 °C; IR (KBr) 1980, 1850 cm^{-1} (CO), 1630 cm^{-1} (NO). Found: C, 55.60; H, 8.96; N 6.58%. Caled for $C_{19}H_{36}N_2O_4Fe$: C, 55.35; H, 8.80; N, 6.79%.

1-Penten-3-one, 2-cyclohexen-1-one, 3-bromo-1-phenyl-1-propene, methyl acrylate, methyl cinnamate, 1-chloro-2-butene, 3-chloro-1-butene, and 1-chloro-3-methyl-2-butene were commercial products and purified before use.

3-Chloro-2-trimethylsiloxy-1-propene (**1a**),[16] 3-bromo-3-methyl-2-trimethylsiloxy-1-butene (**1b**),[17] 3-bromo-3-methyl-2-trimethylsiloxy-1-pentene (**1c**),[17] 1,3-dichloro-2-trimethylsiloxy-1-propene (**1d**),[18] *cis*-2,6-dibromo-4-*t*-butyl-1-(trimethylsiloxy)cyclohexene (**25**),[18] and 3-chloro-3-methyl-1-butene[19] were prepared by the literature methods.

1a: Bp 61—63 °C/35 mmHg (1 mmHg=133.322 Pa); IR (neat) 2960, 2900, 1635, 1315, 1260, 1225, 1160, 1030, 915, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.40 (9H, s), 3.92 (2H, t, J=0.9 Hz), 4.28 (1H, dt, J=2.0, 0.9 Hz), 4.50 (1H, dt J=2.0, 0.9 Hz).

1b: Bp 79 °C/22 mmHg; IR(neat) 1620, 1060, and 875 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.40 (9H, s), 1.95 (6H, s), 4.10 (1H, d, J=2.0 Hz), 4.60 (1H, d, J=2.0 Hz).

1c: Bp 80—82 °C/15 mmHg; IR (neat) 1620, 1060, and 875 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.40 (9H, s), 1.04 (3H, t J=7.0 Hz), 1.95 (3H, s), 2.17 (2H, q, J=7.0 Hz), 4.20 (1H, d, J=2.0 Hz), 4.53 (1H, d, J=2.0 Hz).

1d: Bp 55—56 °C/5 mmHg; IR (neat) 1620, 1310, 1246, 1212, 980, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.34 (9H, s), 3.89 (2H, s), 5.70 (1H, s).

25: Bp 98—100 °C/2 mmHg; IR (neat) 1620, and 868 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.25 (9H, s), 0.87 (9H, s), 1.74 (1H, m), 1.92 (1H, m), 2.14 (1H, m), 2.38 (1H, dd, J=16.92, 11.28 Hz), 2.52 (1H, dd, J=16.92, 6.64 Hz), 4.61 (1H, dd, J=12.02, 5.04 Hz). ^{13}C NMR ($CDCl_3$) δ=0.98, 27.1, 34.3, 36.2, 40.8, 52.0, 108.9, 145.9. The proton signal of CHBr at C-6 appeared at δ=4.61 (dd, J=12.02, 5.04 Hz), confirming that this material has the assigned configuration.

Phenyl vinyl ketone (**3a**),[20] *p*-tolyl vinyl ketone (**3b**),[20] *p*-chlorophenyl vinyl ketone (**3c**),[20] 2-methyl-1-phenyl-2-propen-1-one (**3i**),[20] Phenyl acrylate (**3f**),[21] and phenyl methacrylate (**3j**)[21] were also prepared by the method of the literatures.

3a: IR(neat) 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.72 (1H, dd, J=3.0, 10.3 Hz), 6.25 (1H, dd, J=3.0, 17.2 Hz), 7.06 (1H, dd, J=10.3, 17.2 Hz), 7.33 (3H, m), 7.76 (2H, m).

3b: IR (neat) 1676 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.31 (3H, s), 5.72 (1H, dd, J=2.7, 10.3 Hz), 6.27 (1H, dd, J=2.7, 17.1 Hz), 7.00 (1H, dd, J=10.3, 17.1 Hz), 7.08 (2H, d, J=7.9 Hz), 7.67 (2H, d, J=7.9 Hz).

3c: IR (neat) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.73 (1H, dd, J=2.4, 10.8 Hz), 6.23 (1H, dd, J=2.4, 17.3 Hz), 6.98 (1H, dd, J=10.8, 17.3 Hz), 7.28 (2H, d, J=8.3 Hz), 7.73 (2H, d J=8.3 Hz).

3f: IR (neat) 1726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=5.88 (1H, m), 6.29 (2H, m), 7.02 (5H, m).

3i: IR (neat) 3030, 2940, 1646 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.01 (3H, s), 5.52 (1H, d, J=1.0 Hz), 5.78 (1H, d, J=1.0 Hz), 7.28 (3H, m), 7.58 (2H, m).

3j: IR (neat) 1724 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.95 (3H, s), 5.57 (1H, d, J=1.0 Hz), 6.10 (1H, d, J=1.0 Hz), 7.02 (5H, m).

Preparation of (η^3-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes. General Procedure. A mixture of one of 3-halo-2-trimethylsiloxy-1-propenes (**1**) (2 mmol) and $Bu_4N[Fe(CO)_3NO]$ (TBAFe, 2 mmol) in CH_2Cl_2(5 cm^3) was stirred at room temperature for 2 h. During this period, one molar equiv of CO to TBAFe evolved. The solvent was removed under reduced pressure. Chromatography of the residue on silica gel with pentane solvent gave the corresponding (η^3-2-trimethylsiloxyallyl)Fe(CO)$_2$NO complex.

2a: IR (neat) 2020 and 1955 cm^{-1} (CO), 1720 cm^{-1} (NO), 835 cm^{-1} (OSi); ^{1}H NMR ($CDCl_3$) δ=0.18 (9H, s, $SiMe_3$), 3.47 (2H, d, J=4.0 Hz, *anti*-H), 3.90 (2H, d, J=4.0 Hz, *syn*-H). ^{13}C NMR ($CDCl_3$) δ=0.0, 51.0, 136, 218.

2b: IR (neat) 2010 and 1945 cm^{-1} (CO), 1725 cm^{-1} (NO), 845 cm^{-1} (OSi); ^{1}H NMR ($CDCl_3$) δ=0.17 (9H, s, $SiMe_3$), 1.53 (3H, s, *anti*-Me), 2.07 (3H, s, *syn*-Me), 3.51 (1H, d, J=4.2 Hz, *anti*-H), 3.98 (1H, d, J=4.2 Hz, *syn*-H). ^{13}C NMR ($CDCl_3$) δ=0.0, 24.1 (*anti*-CH_3), 28.3 (*syn*-CH_3), 46.8, 86.9, 136, 220.

2c: IR (neat) 2030 and 1950 cm^{-1} (CO), 1720 cm^{-1} (NO), 845 cm^{-1} (OSi). The ^{1}H NMR spectrum showed that this complex contains two isomers with respect to the configuration of the alkyl substituents on the allylic ligand in a 1 : 1 ratio. For the *anti*-methyl and *syn*-ethyl isomer; ^{1}H NMR ($CDCl_3$) δ=0.19 (9H, s, $SiMe_3$), 1.33 (3H, t, J=7.0 Hz, *syn*-$CH_2\underline{CH_3}$), 1.51 (3H, s, *anti*-CH_3), 2.53 (2H, q, J=7.0 Hz, *syn*-$\underline{CH_2}CH_3$), 3.47 (1H, d, J=4.2 Hz, *anti*-H), 4.00 (1H, d, J=4.2 Hz, *syn*-H). ^{13}C NMR, ($CDCl_3$) δ=0.0 ($OSi\underline{Me_3}$), 16.8 (*syn*-CH_2 $\underline{CH_3}$), 23.9 (*anti*-$\underline{CH_3}$), 33.6 (*syn*-$\underline{CH_2}CH_3$), 46.8, 87.2, 137, 219. For the *syn*-methyl and *anti*-ethyl isomer; ^{1}H NMR($CDCl_3$) δ=0.19 (9H, s, $SiMe_3$), 1.19 (3H, t, J=7.0 Hz, *anti*-$CH_2\underline{CH_3}$), 1.75 (2H, q, J=7.0 Hz, *anti*-$\underline{CH_2}CH_3$), 2.09 (3H, s, *syn*-CH_3) 3.61 (1H, d, J=4.2 Hz, *anti*-H), 4.10 (1H, d, J=4.2 Hz, *syn*-H). ^{13}C NMR($CDCl_3$) δ=0.0 ($OSi\underline{Me_3}$), 15.0 (*anti*-$CH_2\underline{CH_3}$), 28.5 (*syn*-$\underline{CH_3}$), 31.5 (*anti*-$\underline{CH_2}CH_3$), 46.8, 87.2, 137, 219.

2d: IR (neat) 2030 and 1965 cm^{-1} (CO), 1725 cm^{-1} (NO), 840 cm^{-1} (OSi); ^{1}H NMR ($CDCl_3$) δ=0.30 (9H, s, $SiMe_3$), 3.84 (1H, d, J=2.5 Hz, *anti*-H), 3.92 (1H, d, J=2.5 Hz, *syn*-H), 5.60 (1H, s, *syn*-$C\underline{H}Cl$). ^{13}C NMR ($CDCl_3$). δ=2.0, 48.5, 60.6, 128, 224.

Preparation of (η^3-1-Trimethylsiloxyallyl)Fe(CO)$_2$NO Com-

plexes. General Procedure. A mixture of one of vinyl ketones **3**, (2 mmol) with Me_3SiI (2.2 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 2 h. This reaction gave one of the corresponding 3-iodo-1-trimethylsiloxy-1-propenes (**4**). Without isolating the siloxypropenes, a solution of TBAFe (2 mmol) in CH_2Cl_2 (2.5 cm^3) was added to each of the above reaction mixtures, and the resulting mixtures were stirred under argon atmosphere at room temperature for 2 h. During this period, one equiv of CO to TBAFe evolved.

The iron complexes **5a**—**j** thus produced were unable to isolate in pure forms because of their high sensitivity to moisture and air. But, support for the formation of **5a**—**j** was furnished by IR spectra of the reaction mixtures and their chemical transformation as described in text.

Ligand Exchange of (η^3-Allyl)Fe(CO)$_2$NO Complexes. A Typical Procedure. A mixture of (η^3-2-trimethylsiloxyallyl)-Fe(CO)$_2$NO complex **2b** (2 mmol) prepared in situ and allyl bromide **7a** (2 mmol) in CH_2Cl_2 (5 cm^3) was refluxed with stirring for 2 h. After cooling, the reaction mixture was chromatographed on silica gel. Elution with hexane gave the iron complex **8a** and subsequent elution with hexane–ethyl acetate (95/5) gave 3-methyl-2-butanone (**9**).

8a: IR (neat) 2030, 1980, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.12 (2H, d, J=12.0 Hz), 3.96 (2H, d, J=6.0 Hz), 5.72 (1H, m).

8b: IR (neat) 2030, 1970, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.91 (1H, d, J=11 Hz), 3.85 (1H, d, J=6.0 Hz), 4.90 (2H, m), 7.20 (5H, m).

8c: IR (neat) 2030, 1970, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.95 (3H, d, J=5.0 Hz), 2.76 (1H, d, J=12.0 Hz), 3.68 (1H, d, J=6.0 Hz), 4.1 (2H, m).

8d: IR (neat) 2030, 1970, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.6—2.7 (m, 6H), 4.5—5.7 (m, 3H).

These spectral data of the iron complexes were essentially identical with those of the same complexes previously reported.[6]

Reaction of (η^3-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes with Carbon Nucleophiles. General Procedure. Iron complexes **2a**—**d** (2 mmol) were prepared from 3-halo-2-trimethylsiloxy-1-propenes and TBAFe by the procedure described above. These complexes were used without isolation for the following reactions.

A mixture of an iron complex and one equiv of a carbon nucleophile in THF was stirred at room temperature for 15 h. The resulting mixture was extracted with ether. The extract was washed successively with 4 M hydrochloric acid and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure. Chromatography of the residue with hexane–ethyl acetate (9/1) gave the corresponding mixture of each one of α-alkylated ketone **10a**—**h** and **11c**—**h**.

Similarly, treatment of mixtures of (η^3-1-trimethylsiloxyallyl)Fe(CO)$_2$NO complexes **5** and carbon nucleophiles gave the corresponding β-alkylated ketones and esters **12a**—**h**.

10a: IR (neat) 1745, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (6H, t, J=7.0 Hz), 2.16 (3H, s), 2.91 (2H, d, J=7.0 Hz), 3.72 (1H, t, J=7.0 Hz), 4.17 (4H, q, J=7.0 Hz). Found: C, 55.32; H, 7.46%. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46%.

10b: IR (neat) 1745, 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (3H, t, J=7.0 Hz), 2.10 (3H, s), 2.22 (3H, s), 2.87 (2H, d, J=7.0 Hz), 3.83 (1H, t, J=7.0 Hz), 4.09 (2H, q, J=7.0 Hz). Found: C, 57.98; H, 7.41%. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58%.

10c: IR (neat) 1740, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.09 (6H, d, J=7.0 Hz), 1.25 (6H, t, J=7.0 Hz), 2.62 (1H, m), 2.90 (2H, d, J=7.0 Hz), 3.71 (1H, t, J=7.0 Hz), 4.14 (4H, q, J=7.0 Hz). Found: C, 58.78; H, 7.99%. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25%.

10d: IR (neat) 1745, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10 (6H, d, J=7.0 Hz), 1.27 (3H, t, J=7.0 Hz), 2.28 (3H, s), 2.62 (1H, m), 2.89 (2H, d, J=7.0 Hz), 3.72 (1H, t, J=7.0 Hz), 4.15 (2H, q, J=7.0 Hz). Found: C, 61.63; H, 8.22%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H,8.47%.

10e: IR (neat) 2210, 1710, 1210 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10 (6H, d, J=7.0 Hz), 2.56 (1H, m), 2.85 (2H, d, J=7.0 Hz), 3.48 (1H, t, J=7.0 Hz). Found: C, 63.81; H, 6.72; N, 18.55%. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.66%.

10f: IR (neat) 1745, 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02—1.34 (14H, m), 2.55 (1H, m), 2.90 (2H, d, J=7.0 Hz), 3.71 (1H, t, J=7.0 Hz), 4.10 (4H, q, J=7.0 Hz). Found: C, 60.18; H, 8.61%. Calcd for $C_{13}H_{22}O_5$ C, 60.45; H, 8.59%.

10g: IR (neat) 1745, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90—1.40 (11H, m), 2.31 (3H, s), 2.56 (1H, m), 2.78 (2H, d, J=7.0 Hz), 3.78 (1H, t, J=7.0 Hz), 4.12 (2H, q, J=7.0 Hz). Found: C, 63.09; H, 8.68%. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83%.

10h: IR (neat) 2210, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88—1.46 (8H, m), 2.60 (1H, m), 2.85 (2H, d, J=7.0 Hz), 3.48 (1H, t, J=7.0 Hz). Found: C, 65.77; H, 7.35; N, 16.89%. Calcd for $C_9H_{12}N_2O$: C, 65.77; H, 7.35; N, 17.06%.

11c: IR (neat) 1745, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26 (6H, t, J=7.0 Hz), 1.30 (6H, s), 2.08(3H, s), 3.80 (1H, s), 4.06 (4H, q, J=7.0 Hz). Found: C, 58.95; H, 8.03%. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25%.

11d: IR (neat) 1745, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (3H, t, J=7.0 Hz), 1.30 (6H, s), 2.06 (3H, s), 2.28 (3H, s), 3.72 (1H, s), 4.15 (2H, q, J=7.0 Hz). Found: C,61.47; H, 8.22%. Calcd for $C_{11}H_{18}O_4$ C, 61.66; H, 8.47%.

11e: IR (neat) 2210, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (6H, s), 2.08 (3H, s), 3.45 (1H, s). Found: C,63.76; H, 6.68; N, 18.61%. Calcd for $C_8H_{10}N_2O$: C, 63.98, H, 6.71; N, 18.66%.

11f: IR (neat) 1745, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02—1.33 (14H, m), 2.10 (3H, s), 3.75 (1H, s), 4.08 (4H, q, J=7.0 Hz). Found: C, 60.33; H,8.59%. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.59%.

11g: IR (neat) 1745, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02—1.34 (11H, m), 2.06 (3H, s), 2.28 (3H, s), 3.78 (1H, s), 4.18 (2H, q, J=7.0 Hz). Found: C, 63.11; H, 8.69%. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83%.

11h: IR (neat) 2210, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02—1.34 (8H, m), 2.10 (3H, s), 3.45 (1H, s). Found: C, 65.77; H, 7.22; N, 16.89%. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06%.

12a: IR (neat) 1745, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.09 (6H, t, J=7.0 Hz), 2.10 (2H, q, J=7.0 Hz), 3.10 (2H, t, J=7.0 Hz), 3.30 (1H, t, J=7.0 Hz), 3.98 (4H, q, J=7.0 Hz), 7.09—7.79 (5H, m). Found: C, 65.55; H, 6.78%. Calcd for $C_{16}H_{20}O_5$: C, 65.73; H, 6.90%.

12b: IR (neat) 1745, 1728, 1682 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.04 (2H, q, J=7.0 Hz), 2.10 (3H, s), 3.13 (2H, t, J=7.0 Hz), 3.48 (1H, t, J=7.0 Hz), 3.80 (3H, s), 7.28 (3H, m), 7.70 (2H, m). Found: C, 67.81; H, 6.40%. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50%.

12c: IR (neat) 1745, 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.19 (3H, t, J=7.0 Hz), 1.26 (6H, t, J=7.0 Hz), 2.12 (2H, q, J=7.0 Hz), 2.34 (2H, q, J=7.0 Hz), 2.80 (2H, t, J=7.0 Hz), 3.11 (1H,

t, J=7.0 Hz), 4.02 (4H, q, J=7.0 Hz). Found: C, 58.92; H, 8.28%. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25%.

12d: IR (neat) 1745, 1725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.22 (6H, t, J=7.0 Hz), 1.50—1.98 (5H, m), 2.13—2.25 (4H, m), 3.15 (1H, d, J=7.0 Hz), 4.08 (4H, q, J=7.0 Hz). Found: C, 60.79; H, 7.71%. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87%.

12e: IR (neat) 1746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.18 (6H, t, J=7.0 Hz), 2.08 (2H, q, J=7.0 Hz), 2.91 (2H, t, J=7.0 Hz), 3.34 (1H, t, J=7.0 Hz), 3.49 (3H, s), 4.02 (4H, q, J=7.0 Hz). Found: C, 53.42; H, 7.41%. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37%.

12f: IR (neat) 1745, 1718 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.98 (2H, q, J=7.0 Hz), 2.10 (3H, s), 3.08 (2H, t, J=7.0 Hz), 3.32 (1H, t, J=7.0 Hz), 3.49 (3H, s), 3.59 (3H, s). Found: C, 53.56; H, 6.74%. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98%.

12g: IR (neat) 2120, 1746 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.02 (2H, q, J=7.0 Hz), 2.88 (2H, t, J=7.0 Hz), 3.42 (1H, t, J=7.0 Hz), 3.49 (3H, s). Found: C, 55.02; H, 5.32; N, 18.22%. Calcd for $C_7H_8N_2O_2$: C, 55.26; H, 5.30; N, 18.41%.

12h: IR (neat) 1746, 1726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.20—1.82 (8H, m), 2.10—2.46 (5H, m), 3.46 (3H, s). Found: C, 65.11; H, 8.78%. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

Reaction of (η^3-2-Trimethylsiloxyallyl)Fe(CO)$_2$NO Complexes with 2-Propynyl Bromide. A Typical Procedure. A mixture of 3-chloro-2-trimethylsiloxy-1-propene (**1a**, 2 mmol) and TBAFe (2 mmol) in DMF (or NMP, 10 cm^3) was stirred at room temperature for 2 h, and 2-propynyl bromide (4 mmol) was then added. The resulting mixture was heated at 80 °C for 15 h. The mixture was hydrolyzed with 4 M hydrochloric acid and extracted with ether. The extract was washed with water, dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane–ethyl acetate (95/5) to give α-alkynyl ketones **13a**. Similar treatments of **1b,c** gave **13b,c**.

13a: IR (neat) 3300, 2100, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.89 (1H, t, J=2.0 Hz), 1.98 (2H, td, J=7.0, 2.0 Hz), 2.09 (3H, s), 2.52 (2H, t, J=7.0 Hz). Found: C, 74.72; H, 8.50%. Calcd for C_6H_8O: C, 74.97; H, 8.39%.

13b: IR (neat) 3300, 2120, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.07 (6H, d, J=7.0 Hz), 1.88 (1H, t, J=2.0 Hz), 1.98 (2H, td, J=7.0, 2.0 Hz), 2.54 (1H, m), 2.68 (2H, t, J=7.0 Hz). Found: C, 77.28; H, 9.66%. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74%.

13c: IR (neat) 3300, 2120, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (3H, t, J=7.0 Hz), 1.09 (3H, d, 17.0 Hz), 1.24 (2H, m), 1.89 (1H, t, J=2.0 Hz), 1.98 (2H, td, J=7.0, 2.0 Hz), 2.54 (1H, m), 2.60 (2H, t, J=7.0 Hz). Found: C,78.01; H, 10.05%. Calcd for $C_9H_{14}O$: C,78.21; H, 10.21%.

Formation of 1,4-Diketones via (η^3-1-Trimethylsiloxyallyl)-Fe(CO)$_2$NO Complexes. General Procedure. A mixture of 3-halo-2-trimethylsiloxy-1-propenes **1a—c** (4 mmol) and a half equiv of TBAFe (2 mmol) in toluene (10 cm^3) was heated at 110 °C for 15 h. The mixture was hydrolyzed with 4 M hydrochloric acid and then extracted with ether. The extract was washed with water, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. 1,4-Diketones **14a—c** and **15a—c** were isolated by chromatography of the residue on silica gel with hexane–ethyl acetate (95/5).

14a: IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2. 22 (6H, s), 2.71 (4H, s). Found: C, 63.21; H, 8.78%. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83%.

14b: IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (12H, d, J=7.0 Hz), 2.52 (2H, m), 2.62 (4H, s). Found: C, 70.48; H, 10.48%. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%.

14c: IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92—1.24 (16H, m), 2.52 (2H, m), 2.62 (4H, s). Found: C, 72.63; H, 11.05%. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18%.

15b: IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (6H, d, J=7.0 Hz), 1.12 (6H, s), 2.08 (3H, s), 2.52 (1H, m), 2.64 (2H, s). Found: C, 70.44; H, 10.57%. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66%.

15c: IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90—1.24 (16H, m), 2.08 (3H, s), 2.52 (1H, m), 2.64 (2H, s). Found: C, 72.70; H, 11.15%. Calcd for $C_{12}H_{22}O_2$: C, 72.68, H, 11.18%.

Reaction of (η^3-1-Trimethylsiloxyally1)Fe(CO)$_2$NO Complexes with Organic Halides. General Procedure. A mixture of one of α,β-unsaturated ketones or esters (**3a—g,i,j**, 2 mmol) and Me_3SiI (2.2 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 2 h. A solution of TBAFe (2 mmol) in CH_2Cl_2 (2.5 cm^3) was added, and the resulting mixture was stirred at the same temperature for 2 h. After removal of the solvent under reduced pressure, DMF or NMP (10 cm^3) was added as a new solvent, and an organic halide (4 mmol), 2-propynyl bromide, was added to this solution. The resulting mixture was heated at 80 °C for 15 h, cooled, and extracted with ether (30 cm^3). The extract was washed successively with 4 M hydrochloric acid, aqueous $NaHSO_3$ and water, and then dried over Na_2SO_4. The solvent was removed and the residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (97.5/2.5) gave the β-alkylated ketone or ester, **16a—g,i,j**.

A Typical Procedure of the Reaction in the Presence of P(OPh)$_3$. A mixture of phenyl vinyl ketone (**3a**, 2 mmol) and Me_3SiI (2.2 mmol) in CH_2Cl_2 (10 cm^3) was stirred at room temperature for 2 h. A solution of TBAFe (2 mmol) in CH_2Cl_2 (2.5 cm^3) was added, and the resulting mixture was stirred at the same temperature for 2 h. $P(OPh)_3$ (2.0 mmol) was then added, and the mixture was heated at 50 °C for 1 h. After removal of the solvent under reduced pressure, DMF (10 cm^3) was added as a new solvent, and 2-propynyl bromide (4 mmol) was added to the DMF solution. The mixture was heated at 80 °C for 15 h, cooled, and extracted with ether (30 cm^3). The extract was washed successively with 4 M hydrochloric acid, aqueous $NaHSO_3$ and water, and then dried over Na_2SO_4. The solvent was removed, and the residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (97.5/2.5) gave the β-alkylated ketone **16a** in good yield. In a similar manner, **3a—g,i,j** were converted to the corresponding β-alkylated ketones and esters, **16b—g,i,j**, **17a—d,f,g,i,j**, **18a,g**, **19a,g**, **20a**, **21a**, and **24a—c** via the reactions of the iron complexes **5′** with organic halides, such as 2-propynyl bromide, allyl bromide, and methyl chloroacetate.

16a: Oil; IR (neat) 3300, 2100, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.84—2.00 (3H, m), 2.14—2.40 (2H, m), 3.04 (2H, t, J=6.9 Hz), 7.30—7.38 (3H, m), 7.74—7.88 (2H, m). ^{13}C NMR ($CDCl_3$) δ=17.9, 22.7, 37.0, 69.1, 83.7, 127.9, 128.0, 128.6, 136.9, 199.5. Found: C, 83.32; H, 6.99%. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02%.

16b: Oil; IR(neat) 3300, 2100, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.90 —1.99 (3H, m), 2.11—2.45 (2H, m), 2.41 (3H, s), 3.04 (2H, t, J=6.9 Hz), 7.14 (2H, d, J=8.4 Hz), 7.78 (2H, d, J=8.4 Hz). ^{13}C NMR ($CDCl_3$) δ=17.8, 21.6, 22.9, 36.9, 69.1, 83.7, 128.1, 129.3, 135.8, 202.0. Found: C, 83.61; H, 7.46%. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58%.

16c: Oil; IR(neat) 3300, 2100, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.85—1.99 (3H, m), 2.00—2.30 (2H, m), 3.04 (2H,

t, J=6.9 Hz), 7.33 (2H, d, J=8.0 Hz), 7.84 (2H, d, J=8.0 Hz). Found: C, 69.54; H, 5.31%. Calcd for $C_{12}H_{11}ClO$: C, 69.73; H, 5.37%.

16d: Oil; IR(neat) 3300, 2100, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.06 (3H, t, J=6.9 Hz), 1.63—1.98 (3H, m), 2.00—2.58 (6H, m). Found: C,77.18; H, 9.55%. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74%.

16e: Oil; IR (neat) 3300, 2100, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.66—1.80 (5H, m), 1.92—2.38 (7H, m). Found: C, 79.21; H, 8.56%. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88%.

16f: Oil; IR (neat) 3300, 2100, 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.92—2.02 (3H, m), 2.21—2.33 (2H, m), 2.54 (2H, t, J=6.9 Hz), 7.03—7.10 (5H, m). Found: C, 76.64; H, 6.59%. Calcd for $C_{12}H_{12}O$: C, 76.57; H, 6.43%.

16g: Oil; IR (neat) 3300, 2100, 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.93 (1H, t, J=2.4 Hz), 2.42—2.54 (2H, m), 2.60—2.78 (3H, m), 3.50 (3H, s), 7.02—7.20 (5H, m). Found: C, 76.94; H, 6.93%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

16i: Oil; IR (neat) 3300, 2100, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (3H, d, J=6.9 Hz), 1.99 (1H, t, J=2.82 Hz), 2.11 (2H, q, J=6.9 Hz), 2.25 (2H, td, J=7.25, 2.82 Hz), 3.73 (1H, m), 7.49 (3H, m), 7.98 (2H, m). ^{13}C NMR ($CDCl_3$) δ=16.3, 17.2, 31.7, 39.1, 69.1, 76.6, 128.4, 128.7, 130.0, 136.5, 203.7. Found: C, 83.81; H, 7.51%. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58%.

16j: Oil; IR (neat) 3300, 2100, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27 (3H, d, J=7.0 Hz), 1.98 (2H, q, J=7.0 Hz), 2.02 (1H, t, J=2.4 Hz), 2.35 (2H, td, J=7.0, 2.4 Hz), 3.03 (1H, m), 7.35 (5H, m); ^{13}C NMR ($CDCl_3$) δ=14.4, 16.8, 27.8, 36.5, 69.0, 78.3, 115.3, 121.5, 125.9, 129.4, 174.8. Found: C, 77.38; H, 6.88%. Calcd for $C_{13}H_{14}O_2$: C,77.20; H, 6.98%.

17a: Oil; IR (neat) 1680, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.85 (2H, quintet, J=7.0 Hz), 2.17 (2H, q, J=7.0 Hz), 2.98 (2H, t, J=7.0 Hz), 4.94—5.13 (2H, m), 5.69—5.88 (1H, m), 7.47—7.51 (3H, m), 7.90—8.00 (2H, m); ^{13}C NMR ($CDCl_3$) δ=23.3 (t), 33.1 (t), 37.7 (t), 115.2 (t), 128.0 (d), 128.0 (d), 128.5 (d), 132.8 (s), 136.0 (d), 200.2 (s). Found: C, 82.49; H, 7.92%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

17b: Oil; IR (neat) 1680, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.83 (2H, quintet, J=7.0 Hz), 2.12 (2H, br q, J=7.0 Hz), 2.40 (3H, s), 2.95 (2H, t, J=7.0 Hz), 4.92—5.06 (2H, m), 5.68—5.79 (1H, m), 7.24 (2H, d, J=8.13 Hz), 7.85 (2H, d, J=8.13 Hz); ^{13}C NMR ($CDCl_3$) δ=23.5 (q), 24.7 (t), 33.3 (t), 35.4 (t), 115.5 (t), 126.0 (d), 126.7 (d), 131.4 (s), 134.2 (d), 138.8 (s), 200.0 (s). Found: C, 82.61; H, 8.71%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

17c: Oil; IR (neat) 1685, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.83 (2H, quintet, J=7.2 Hz), 2.12 (2H, br q, J=7.2 Hz), 2.95 (2H, t, J=7.2 Hz), 4.93—5.12 (2H, m), 5.68 (1H, m), 7.48 (2H, d, J=8.79 Hz), 7.89 (2H, d, J=8.79 Hz); ^{13}C NMR ($CDCl_3$) δ=25.2 (t), 33.4 (t), 36.4 (t), 115.8, 127.3, 127.5, 133.6, 135.2, 139.0, 200.2. Found: C,68.97; H, 6.02%. Calcd for $C_{12}H_{13}ClO$: C, 69.06; H, 6.28%.

17d: Oil; IR (neat) 1726, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (3H, t, J=7.0 Hz), 1.80 (2H, m), 2.02 (2H, q, J=7.0 Hz), 2.23 (2H, q, J=7.0 Hz), 2.30 (2H, t, J=7.0 Hz), 5.09 (2H, m), 5.70 (1H, m); ^{13}C NMR ($CDCl_3$) δ=12.4, 21.9, 31.2, 46.6, 47.1, 120.2, 129.9, 202.2. Found: C, 75.87; H, 11.21%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

17f: Oil; IR (neat) 1708, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.97 (2H, m), 2.17 (2H, q, J=7.0 Hz), 2.72 (2H, t, J=7.0 Hz), 5.04 (2H, m), 5.81 (1H, m), 7.22 (5H, m); ^{13}C NMR ($CDCl_3$) δ=17.8, 23.6, 33.0, 115.7, 121.5, 121.6, 125.7, 125.8, 150.7, 171.6. Found: C, 75.41; H, 7.02%. Calcd for $C_{12}H_{14}O$: C, 75.76; H, 7.42%.

17g: Oil; IR (neat) 1746, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.37 (2H, m), 2.89 (1H, m), 3.39 (2H, d, J=7.0 Hz), 3.81 (3H, s), 5.13 (2H, m), 5.95 (1H, m), 7.38 (5H, m); ^{13}C NMR ($CDCl_3$) δ=31.8, 48.0, 51.8, 63.5, 116.1, 127.2, 128.0, 128.8, 135.7, 140.4, 168.4. Found: C, 76.45; H, 7.81%. Calcd for $C_{13}H_{16}O_2$: C, 76.45; H 7.81%.

17i: Oil; IR (neat) 1676, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20 (3H, d, J=7.0 Hz), 1.97 (2H, q, J=7.0 Hz), 2.09 (2H, qt, J=7.0, 1.21 Hz), 3.50 (1H, m), 4.94 (2H, m), 5.85 (1H, ddt, J=15.0, 10,2, 7.0 Hz), 7.47 (3H, m), 7.93 (2H, m); ^{13}C NMR ($CDCl_3$) δ=17.3, 31.5, 32.6, 39.8, 115.2, 128.3, 128.6, 132.8, 136.7, 138.1, 204.5. Found: C, 82.56; H, 8.57%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

17j: Oil; IR (neat) 1712, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (3H, d, J=7.0 Hz), 1.96 (2H, q, J=7.0 Hz), 2.16 (2H, q, J=7.0 Hz), 2.71 (1H, m), 5.12 (2H, m), 5.83 (1H, m), 7.12 (5H, m); ^{13}C NMR ($CDCl_3$) δ=18.4, 32.8, 38.2, 43.5, 114.9, 121.5, 121.6, 125.7, 127.1, 129.4, 171.2. Found: C, 76.33; H, 7.78%. Calcd for $C_{13}H_{16}O_2$: C,76.43; H, 7.90%.

18a: Oil; IR (neat) 1686, 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.56 (3H, br d, J=7.0 Hz), 1.72—2.10 (4H, m), 2.81 (2H, t, J=7.0 Hz), 5.31 (2H, m), 7.30 (3H, m), 7.75 (2H, m); ^{13}C NMR ($CDCl_3$) δ=20.2, 24.8, 32.3, 37.6, 121.0, 121.6, 128.6, 132.8, 136.7, 138.4, 202.0. Found: C, 82.72; H, 8.61%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

19a: Oil; IR (neat) 1684, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (3H, d J=7.0 Hz), 1.70—2.15 (3H, m), 2.81 (2H, t, 7.0 Hz), 4.98 (2H, m), 5.60 (1H, m), 7.30 (3H, m), 7.75 (2H, m); ^{13}C NMR ($CDCl_3$) δ=17.9, 24.7, 30.9, 33.7, 115.7, 125.6, 128.5, 129.0, 136.0, 138.4, 203.0. Found: C, 82.69; H, 8.46%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

18g: Oil; IR (neat) 1708, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.68 (3H, d, J=7.0 Hz), 1.84 (2H, m), 2.12 (2H, q, J=7.0 Hz), 2.57 (2H, t J=7.0 Hz), 5.47 (2H, m), 7.36 (5H, m); ^{13}C NMR($CDCl_3$) δ=20.2, 31.4. 32.3, 37.6, 113.9, 121.6, 125.8, 129.4, 129.7, 143.3, 172.3. Found: C, 76.42; H, 7.79%. Calcd for $C_{13}H_{16}O_2$; C,76.43; H, 7.90%.

19g: Oil; IR (neat) 1708, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10 (3H, d J=7.0 Hz), 1.73 (2H, q, J=7.0 Hz), 2.20 (1H, m), 2.55 (2H, t, J=7.0 Hz), 5.07 (2H, m), 5.69 (1H, m), 7.25 (5H, m); ^{13}C NMR ($CDCl_3$) δ=17.9, 24.7, 30.9, 33.7, 121.6, 125.2, 125.7, 126.2, 129.2, 129.4, 172.3. Found: C, 76.21; H, 7.92%. Calcd for $C_{13}H_{16}O_2$: C, 76.43; H, 7.90%.

20a: Oil; IR (neat) 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.66 (6H, br s), 1.78—2.27 (4H, m), 2.79 (2H, t, J=7.0 Hz), 5.30 (1H, m), 7.20 (3H, m), 7.75 (2H, m); ^{13}C NMR ($CDCl_3$) δ=23.4, 26.1, 28.3, 29.8, 41.6, 119.8, 128.0, 128.3, 128.5, 128.6, 132.8, 203.7. Found: C, 83.05; H, 8.89%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

21a: Oil; IR (neat) 1682, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.12 (6H, s), 1.70 (2H, t, J=7.0 Hz), 2.80 (2H, t, J=7.0 Hz), 5.08 (2H, m), 5.70 (1H, dd, J=16.2, 10.6 Hz), 7.21 (3H, m), 7.75 (2H, m); ^{13}C NMR ($CDCl_3$) δ=17.6, 26.2, 33.2, 41.2, 115.4, 125.2, 128.0, 128.6, 132.8, 202.4. Found: C, 82.88; H, 8.78%. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

24a: Oil; 1726, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.12 (2H, quintet, J=7.0 Hz), 2.46 (2H, t, J=7.0 Hz), 3.07 (2H, t, J=7.0 Hz), 3.70 (3H, s), 7.52 (3H, m), 7.92 (2H, m); ^{13}C NMR ($CDCl_3$) δ=23.3, 32.9, 37.0, 51.6, 127, 128, 133, 141, 174, 200. Found: C, 69.67; H, 6.74%. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%.

24b: Oil; IR (neat) 1746, 1678 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.07 (2H, quintet, J=7.2 Hz), 2.41 (3H, s), 2.44 (2H, t, J=7.25 Hz), 3.03 (2H, t, J=7.25 Hz), 3.68 (3H, s), 7.27 (2H, d, J=8.02 Hz), 7.85 (2H, d, J=8.02 Hz); ^{13}C NMR ($CDCl_3$) δ=19.5, 21.6, 33.2, 37.3, 51.6, 120.1, 128.2, 129.9, 138.4, 173.8, 199.1. Found: C, 70.77; H, 7.16%. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32%.

24c: Oil; IR (neat) 1730, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.02 (2H, m), 2.46 (2H, t, J=7.0 Hz), 3.63 (2H, t, J=7.0 Hz), 3.70 (3H, s), 7.18 (2H, d, J=8.3 Hz); 8.02 (2H, d, J=8.3 Hz); ^{13}C NMR ($CDCl_3$) δ=22.6, 33.0, 37.8, 51.6, 129, 130, 138, 140, 172, 206. Found: C, 59.77, H, 5.42%. Calcd for $C_{12}H_{13}ClO_3$: C, 59.88; H, 5.44%.

Stereoselectivity in the Reaction of (η^3-Allyl)Fe(CO)$_2$NO Complexes with a Carbon Nucleophile. A mixture of *cis*-2,6-dibromo-4-*t*-butyl-1-(trimethylsiloxy)cyclohexene (**25**, 3 mmol) and TBAFe (4 mmol) in THF (10 cm^3) was stirred at room temperature for 3 h and then $NaCH(CO_2Me)_2$ (6 mmol) in THF (5 cm^3) was added. The resulting mixture was stirred at the same temperature for 15 h, hydrolyzed with 4 M hydrochloric acid, and extracted with ether. The extract was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (9/1) gave the alkylated product, **27**: Oil; IR (neat) 1746, 1724, 1280, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (9H, s), 1.30—1.50 (2H, m), 1.65 (1H, tt, J=2 84, 12.1 Hz), 2.00—2.42 (4H, m), 3.22 (1H, ddd, J=5.24, 9.26, 13.29 Hz), 3.68 (1H, d, J=9.26 Hz), 3.74 (3H, s), 3.75 (3H, s); ^{13}C NMR ($CDCl_3$) δ=27.3, 27.6, 28.5, 32.0, 32.5, 41.1, 46.8, 49.7, 52.6, 52.7, 168.8, 168.9, 210.0. Found: C, 63.35; H, 8.33%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.50%.

A mixture of *cis*-2,6-dibromo-4-*t*-butyl-1-(trimethylsiloxy)-cyclohexene (**25**, 3 mmol) and TBAFe (4 mmol) in DMF (10 cm^3) was stirred at room temperature. To the mixture, triphenyl phosphite (3 mmol) was added and then the mixture was heated at 50 °C for 1 h. To the resulting mixture, the carbon electrophile, 2-propynyl bromide (6 mmol), was added and then the mixture was heated at 75 °C for 15 h. The mixture was hydrolyzed with 4 M hydrochloric acid, and extracted with ether. The extract was washed with 4 M NaOH aqueous solution and then water, dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (97.5/2.5) gave the alkylated product, **29**: Oil; IR (neat) 3200, 2100, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$)δ=0.94 (9H, s), 1.47 (1H, m), 1.58 (1H, m), 1.65 (1H, tt, J=12.10, 2.82 Hz) 1.97 (1H,t, J=2.82 Hz), 2.10 (1H, ddd, J=16.52, 12.10, 4.42 Hz), 2.18 (1H, ddd, J=16.52, 7.66, 2.82 Hz), 2.42 (2H, dd, J=7.66, 2.82 Hz), 2.45 (1H, qd, J=7.66, 4.42 Hz), 2.50 (1H, m), 2.65 (1H, ddd, J=16.52, 4.43, 2.42 Hz); ^{13}C NMR ($CDCl_3$) δ=18.9 (t), 27.7 (q), 28.6 (t), 32.6 (s), 34.3 (d), 41.3 (t), 46.9 (t), 48.7 (d), 69.5 (d), 82.7 (s), 211.1 (s). Found: C, 81.06; H, 10.31%. Calcd for $C_{12}H_{20}O$: C, 81.20; H, 10.48%.

Isolation of Iron Complex 26. A mixture of **25** (2 mmol) and TBAFe (2 mmol) in CH_2Cl_2 (5 cm^3) was stirred at room temperature for 3 h. The resulting mixture was chromatographed on silica gel. Complex **26** was isolated from the fraction eluted with hexane; IR (neat) 2020, 1960 cm^{-1} (CO), 1725 cm^{-1} (NO), 850 cm^{-1} (OSi); ^{1}H NMR ($CDCl_3$) δ=0.12 (9H, s), 0.92 (9H, s), 1.93 (1H, m), 2.22 (1H, m), 2.52—2.80 (3H, m), 5.30 (1H, m); ^{13}C NMR ($CDCl_3$) δ=1.8, 27.2, 31.6, 34.2, 36.2, 40.8, 47.1, 52.0, 129, 214.

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