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Diversity in Modes of Reactions of (η^3-1-Trimethylsiloxyallylic)Fe(CO)$_2$NO Complexes. Nucleophilic Addition and Cyclization on the Allylic Ligands

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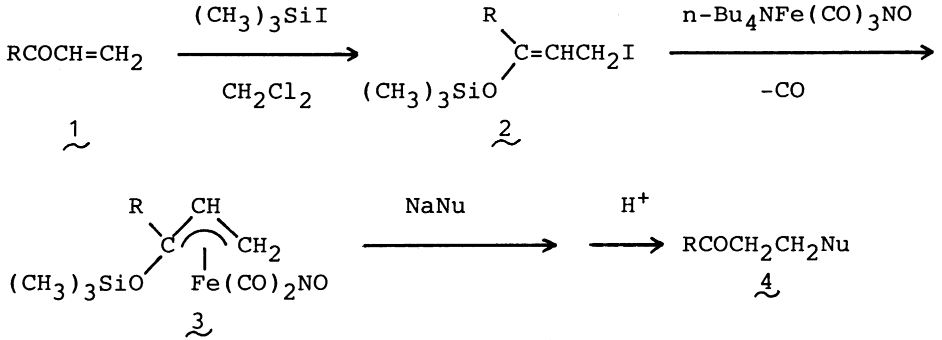
The titled iron complexes derived from 3-iodo-1-trimethylsiloxypropenes and [Bu$_4$N][Fe(CO)$_3$NO] reacted with carbon nucleophiles such as NaCH(CO$_2$Et)$_2$ to give the corresponding nucleophile addition products in high yields. The addition occurred at the 3-position of the ligands with high regioselectivity. However, the iron complexes derived from 2-alkyl-3-iodo-1-trimethylsiloxypropenes underwent cyclization reaction with the same siloxypropenes to give dihydropyran derivatives. The diversity in the modes of reactions of the iron complexes are discussed.

Recently, (η^3-allylic)Fe(CO)$_2$NO complexes have emerged as useful intermediates in organic synthesis.1,2) The allylic ligands of these complexes act as allylic anions upon treatment with electrophiles.1) They also undergo the addition reaction of carbon nucleophiles.2) In a previous paper, we have reported that (η^3-1-trimethylsiloxyallylic)Fe(CO)$_2$NO complexes can be utilized as a β-acylcarbanion equivalent.3) We now report that 1) these siloxyallylic iron complexes behave also as a β-acylcarbocation equivalent upon treatments with carbon nucleophiles, and in addition 2) these iron complexes having alkyl substituents at the 2-position of the allylic ligands undergo a [2+4] cycloaddition with their precursors, 2-alkyl-3-iodo-1-trimethylsiloxypropenes.

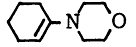
α,β-Unsaturated ketones and esters **1** were converted into (1-trimethylsiloxyallylic)Fe(CO)$_2$NO complexes **3** via 3-iodo-1-trimethylsiloxypropenes **2** (2 mmol) in essentially quantitative yields by treating successively with a small excess (2.2 mmol) of (CH$_3$)$_3$SiI and one equivalent (2 mmol) of [n-Bu$_4$N][Fe(CO)$_3$NO] (TBAF) in CH$_2$Cl$_2$ at room temperature in a similar manner as described previously.3) During these reactions, one equivalent of CO to TBAF was evolved (Scheme 1).

The iron complexes **3** reacted smoothly with a variety of carbon nucleophiles such as NaCH(CO$_2$Et)$_2$, NaCH(COMe)CO$_2$Me, NaCH(CN)$_2$, and 1-morphorinocyclohexene, giving the nucleophile addition products **4** in high yields (Scheme 1). These reactions were carried out without isolation of **3**: One equivalent of the carbon nucleophiles was added to the solutions of **3** in CH$_2$Cl$_2$, and stirred at room temperature for 5 h. The resulting mixtures were extracted with ether. The ether extracts were washed with 4 M (1 M=1 mol dm^{-3}) hydrochloric acid and water, dried over Na_2SO_4, and the solvent was removed. The products were isolated by chromatography of the residues on silica gel with hexane/ethyl acetate(9/1). The structures of the products were determined by their spectral data[4] and elemental analyses. The typical results are shown in Table 1. The regioselectivity in these reactions was extremely high, so that the single product was obtained in every case.



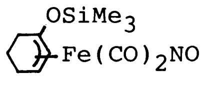
Scheme 1.

Table 1. Reaction of 3a-d with carbon nucleophiles

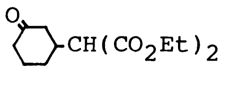
Iron complex	Nucleophile	Product		Yield/%[a]
3a: R=Ph	$NaCH(CO_2Et)_2$	4a: R=Ph,	$Nu=CH(CO_2Et)_2$	95
3a:	$NaCH(COMe)CO_2Me$	4b: R=Ph,	$Nu=CH(COMe)CO_2Me$	42
3b: R=Et	$NaCH(CO_2Et)_2$	4c: R=Et,	$Nu=CH(CO_2Et)_2$	75
3c[b]	$NaCH(CO_2Et)_2$	4d[b]		90
3d: R=MeO	$NaCH(CO_2Et)_2$	4e: R=MeO,	$Nu=CH(CO_2Et)_2$	95
3d:	$NaCH(COMe)CO_2Me$	4f: R=MeO,	$Nu=CH(COMe)CO_2Me$	60
3d:	$NaCH(CN)_2$	4g: R=MeO,	$Nu=CH(CN)_2$	92
3d:		4h[b]		89

a) Isolated yields based on iron complexes used.

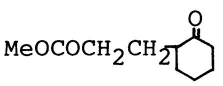
b) 3c:



4d:



4h:



These results indicate that the iron complexes 3 behave as a synthetically equivalent synthon for β-acylcarbocations. It is particularly interesting to note that these iron complexes react with both nucleophiles and electrophiles[3] at the same position of the allylic ligands with high regioselectivity; i.e., the complexes exhibit both electrophilic and nucleophilic reactivities.

However, a different mode of reaction was observed when 2-alkyl-1-aryl-2-propen-1-ones 5 were used as starting materials.

The ketone 5a was first converted into the corresponding 3-iodo-1-trimethylsiloxypropene (6a) by treating with $(CH_3)_3SiI$ in CH_2Cl_2 in a similar manner as above. The iodopropene **6a** (2 mmol) was then allowed to react with 0.5 equivalent of TBAF (1 mmol) in CH_2Cl_2 at 20 °C for 15 h and the mixture was extracted with ether. The extract was washed with 4 M hydrochloric acid and water, dried over Na_2SO_4, and then the solvent was removed. Chromatography of the residue on silica gel with hexane gave the dihydropyran derivative **7a** in 95% yield. Similar treatments of **6b**-**e** derived from **5b**-**e** with TBAF gave the corresponding dihydropyran derivatives **7b**-**e**. The results are given in Table 2. The structures of the products were assigned from their spectral data[5] and elemental analyses.

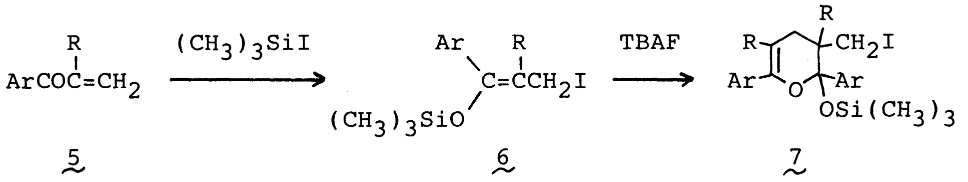
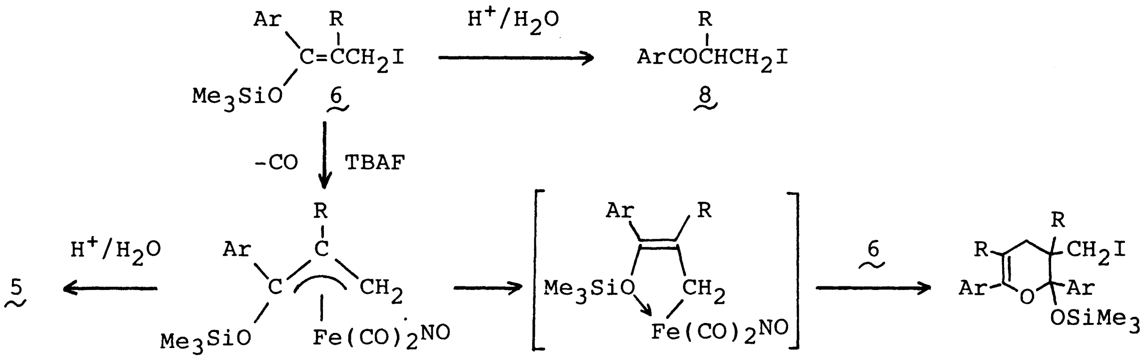


Table 2. Formation of 3,4-dihydro-2H-pyrans

Substrate	Temp/°C	Time/h	Product	Yield/%[a)]
5a: Ar=C_6H_5, R=CH_3	20	15	**7a**	95
5b: Ar=p-$CH_3C_6H_4$, R=CH_3	20	15	**7b**	82
5c: Ar=p-$CH_3OC_6H_4$, R=CH_3	40	8	**7c**	73
5d: Ar=p-ClC_6H_4, R=CH_3	40	15	**7d**	62
5e: Ar=C_6H_5, R=C_2H_5	20	15	**7e**	46

a) Isolated yields based on **5a**-**e** used.

A possible mechanism of this cyclization reaction is shown in Scheme 2. The detailed mechanism is obscure at present. However, partial support for the proposed mechanism was furnished from the following experiments: 1) Compound **6a** reacted with one equivalent of TBAF in CH_2Cl_2 at -60 °C for 3 h to form the iron complex **9a** with evolution of one equivalent of CO to TBAF. The subsequent hydrolysis of this reaction mixture with 4 M hydrochloric acid gave **5a** in 95% yield. 2) The hydrolysis of **6a** with 4 M hydrochloric acid without added TBAF gave 2-benzoyl-1-iodo-2-methylpropene (**8a**). 3) The intermediacy of **9a** was also sup-



Scheme 2.

ported by taking the IR spectrum of the reaction mixture resulting from 6a and TBAF, which showed characteristic bands for 9a: ν_{CO} 2060, 1975 cm^{-1}; ν_{NO} 1750 cm^{-1}; ν_{OSi} 870 cm^{-1}.

These results demonstrate that (1-trimethylsiloxyallylic)Fe$(CO)_2$NO complexes exhibit diverse reactivities, depending on the structures of the iron complexes and the reaction conditions.

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References

1) T. Ueda, M, Kawakita, and Y. Otsuji, Nippon Kagaku Kaishi, 1985, 271.

2) Y. Xu and B. Zhou, J. Org. Chem., 52, 974 (1987).

3) K. Ito, S. Nakanishi, and Y. Otsuji, Chem, Lett., 1987, 2103.

4) Data for 4a are shown as a typical example: IR (neat) ν_{CO} 1745, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09 (6H, t, 2x $CH_2\underline{CH_3}$), 2.10 (2H, q, $CH_2\underline{CH_2}CH$), 2.89 (2H, t, $CO\underline{CH_2}CH_2$), 3.30 (1H, t, $CH_2\underline{CH}CO_2$), 3.98 (4H, q, 2x $CO_2\underline{CH_2}CH_3$), 7.09-7.79 (5H, aromatic H).

5) All compounds gave satisfactory elemental analyses and spectral data.

7a: mp 128-130 °C; MS m/z 492 (M$^+$); IR (KBr) 3030, 1250, 1140, 1090, 1015, 870, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.02 (9H, s, $Si(CH_3)_3$), 0.96 (3H, s, CH_3), 1.86 (3H, s, =CCH_3), 1.96 and 2.45 (2H, ABq, J=14.6 Hz, =CCH_2C), 3.04 and 3.60 (2H, ABq, J=10.2 Hz, CH_2I), 7.28-7.44 (10H, m, aromatic H); ^{13}C NMR ($CDCl_3$) δ=1.14 (q), 19.13 (t), 20.59 (q), 21.08 (q), 40.14 (s), 40.24 (t), 100.31 (s), 106.01 (s), 127.22 (d x2), 127.51 (d x2), 127.80 (d x2), 127.90 (d x2), 128.62 (d x2), 135.85 (s), 140.92 (s), 142.49 (s).

7b: mp 119-121 °C; MS m/z 520 (M$^+$); IR (KBr) 3030, 1250, 1100, 1020, 880, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.02 (9H, s, $Si(CH_3)_3$), 0.90 (3H, s, CH_3), 1.89 (3H, s, CH_3), 1.96 and 2.46 (2H, ABq, J=12.6 Hz, =CCH_2C), 2.32 (6H, s, 2x CH_3), 3.08 and 3.64 (2H, ABq, J=10.8 Hz, CH_2I), 7.08-7.50 (8H, m, aromatic H).

7c: mp 140-142 °C; MS m/z 552 (M$^+$); IR (KBr) 3030, 1250, 1150, 1095, 1020, 890, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.02 (9H, s, $Si(CH_3)_3$), 0.92 (3H, s, CH_3), 1.92 (3H, s, CH_3), 2.06 and 2.37 (2H, ABq, J=12.6 Hz, =CCH_2C), 3.06 and 3.82 (2H, ABq, J=10.2 Hz, CH_2I), 3.84 (6H, s, 2x OCH_3), 6.68-6.92 (4H, m, aromatic H), 7.23-7.48 (4H, m, aromatic H).

7d: mp 139-140 °C; MS m/z 560 (M$^+$); IR (KBr) 3030, 1250, 1145, 1080, 1015, 870, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.02 (9H, s, $Si(CH_3)_3$), 0.90 (3H, s, CH_3), 1.89 (3H, s, CH_3), 1.98 and 2.32 (2H, ABq, J=13.2 Hz, =CCH_2C), 2.95 and 3.56 (2H, ABq, J=10.8 Hz, CH_2I), 7.36 (8H, s, aromatic H).

7e: mp 118-119 °C; MS m/z 520 (M$^+$); IR (KBr) 3030, 1250, 1150, 1095, 1060, 1020, 885, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.02 (9H, s, $Si(CH_3)_3$), 0.83-1.32 (8H, m, CH_2 and 2x CH_3), 1.98 and 2.38 (2H, ABq, J=13.8 Hz, =CCH_2C), 2.16 (2H, q, J=6.8 Hz, =$C\underline{CH_2}CH_3$), 2.88 and 3.66 (2H, ABq, J=10.2 Hz, CH_2I), 7.25-7.60 (10H, m, aromatic H).

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