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by 2.2 eq. of NBS. From this investigation, it may be shown that the appearance of 2-halo-4-(halomethyl)-2-(phenylsulfonyl)-γ-butyrolactone (5) in NBS or NCS-induced lactonization of 3 could be generated from α-halogenation and *in situ* subsequent halolactonization.

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Mono-dehalogenation of *gem*-Dihalocyclopropanes Using Tetracarbonylhydridoferrate

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Tetracarbonylhydridoferrate, HFe(CO)₄⁻, generated by the reaction of Fe(CO)₅ with alkaline solution, is a good reducing agent for mono-dehalogenation of *gem*-dihalocyclopropanes. It also acts as a good reducing catalyst under phase transfer reaction conditions. 1,1-Dibromo-2-phenylcyclopropane and 1,1-dichloro-2-phenylcyclopropane were reduced to the corresponding mono-dehalogenated products in excellent yields. Thermodynamically stable *trans*-1-bromo-2-phenyl cyclopropane was formed as the major product over the *cis*-isomer, *trans/cis*=3/2. The 1-bromo-2-phenyl cyclopropane radical intermediate was formed by single electron transfer from HFe(CO)₄⁻. Dissociation of bromide anion, followed abstraction of hydrogen radical from alcoholic solvent would lead to the formation of the stable *trans*-isomer. The further mechanistic aspects were discussed.

Introduction

The tetracarbonylhydridoferrate anion, HFe(CO)₄⁻, derived from the reaction of pentacarbonyliron and alkaline base in aqueous or alcoholic solution appears very versatile compound as the reducing reagent.[1] It has been reported that HFe(CO)₄⁻ was able to reduce alkyl halides[2] and vinylic halides.[3] Extensive study with this reagent has also been carried out on the reductive dehalogenation of aryl iodides.[4]

gem-Dihalocyclopropanes have been shown to be extremely valuable starting materials for the preparation of cyclopropane and cyclopropene derivatives.[5] The reduction of *gem*-dihalocyclopropanes to mono-halocyclo propanes has been effected by various reducing agents such as organotin hydride,[6] Grignard reagent,[7] chromium sulfate,[8] lithium aluminum hydride,[9] potassium diphenyl phosphide,[10] and sodium hydrogen telluride,[11] or by metals such as silver.[12] Pentacarbonyliron

in DMF has been also utilized for both the reduction of and the carbonylation of *gem*-dihalocyclopropanes.[13] However, these two reactions are in competition and the selective dehalogenation over the carbonylation of *gem*-dihalocyclopropanes or *vice versa* have not been achieved, especially for mono-dehalogenation.

In this paper, we wish to report that tetracarbonylhydridoferrate is a good reducing agent for mono-dehalogenation of *gem*-dihalocyclopropanes and it also acts as a good reducing catalyst under phase transfer reaction conditions.

Results and Discussion

Mono-debromination of 1,1-dibromo-2-phenylcyclopropane using HFe(CO)₄⁻ as reducing agent. This complex was utilized to the dehalogenation of organic halides.[2-4] In the present work, it was found that the reaction
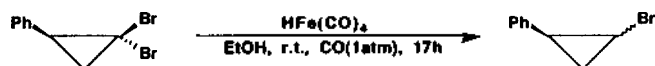
Scheme 1.

Table 1. Mono-debromination[a] of 1,1-dibromo-2-phenyl cyclopropane using HFe(CO)$_4^-$

| No. | Base | Solvent | Yield (%)[b] | | |
			Trans	cis	Total
1	MeONa	MeOH	53	34	87
2	EtONa	EtOH	59	34	93
3	"PrONa	"PrOH	47	29	76
4	"BuONa	"BuOH	47	29	76
5	LiOH	EtOH	40	20	60
6	NaOH	EtOH	50	24	74
7	KOH	EtOH	59	19	78
8	K$_2$CO$_3$	EtOH	10	5	15
9	Na$_2$CO$_3$	EtOH	tr	tr	tr

[a] 1,1-Dibromo-2-phenylcyclopropane (0.53 g, 2.0 mmol), base (10 mmol), solvent (10 m*l*), and Fe(CO)$_5$ (0.39 g, 2.0 mmol) were stirred at r.t. for 17 h under CO. [b] Isolated yield.

of HFe(CO)$_4^-$ with 1,1-dibromo-2-phenylcyclopropane led to a mixture of *trans*- and *cis*-1-bromo-2-phenylcyclopropane in excellent yield (Scheme 1).

The stereo isomeric products, *trans*- and *cis*-1-bromo-2-phenylcyclopropane were obtained in ratio of trans over *cis* isomer, 3 : 2. The thermodynamically more stable *trans*-isomer was the major product, but the preference was marginal. And the ratio was dependent on the reaction condition, although the difference was not significant. The results of mono-debromination of 1,1-dibromo-2-phenylcyclopropane using HFe(CO)$_4^-$ as reducing agent are listed in Table 1.

The better yields were obtained in this reaction using the HFe(CO)$_4^-$ generated by sodium alkoxides in the corresponding alcohols than alkali metal hydroxides. Methoxide and ethoxide gave better yields than *n*-propoxide and *n*-butoxide. Such trends could be explained by the effective concentration of HFe(CO)$_4^-$ in reaction media. And in the case of the ethanol solution of alkali metal hydroxides as base, instead of ethoxide, the products were obtained in slightly lower yields (Nos. 5-7). The bases such as sodium carbonate and potassium carbonate (Nos. 8, 9) in ethanol were too weak to be effective, probably because the concentration of hydroxide or alkoxide generated by the weak bases was too low to generate the sufficient concentration of HFe(CO)$_4^-$ to react with the substrates.

Atmosphere, either CO or N$_2$, did not affect the chemical yield (Nos. 13, 16). Presence of bases was crucial for the reasonable (No. 10) and the chemical yields were proportional to the amount of bases (Nos. 11, 12). Because the use of 5-molar excess base in ethanol under CO atmosphere at room temperature was the best condition the results of this reaction were confirmed by reacting *gem*-dihalocyclopropane (2.0 mmol) with Fe(CO)$_5$ (2.0 mmol) in the presence of 10 mmol of base (Table 1 and Table 3).

This optimized mono-debromination condition was applied

Table 2. Mono-debromination of 1,1-dibromo-2-phenyl cyclopropane under various conditions[a]

| No. | Base (mmol) | Atmosphere | Yield (%)[b] | | |
			Trans	cis	Total
10		CO	0	0	0
11	EtONa (6)	CO	41	33	74
12	EtONa (10)	CO	59	34	93
13	EtONa (10)	N$_2$	56	34	90
14	KOH (10)	CO	59	19	78
15	KOH (10)	N$_2$	54	19	73

[a] 1,1-Dibromo-2-phenylcyclopropane (0.53 g, 2.0 mmol), EtOH (10 m*l*), and Fe(CO)$_5$ (0.39 g, 2.0 mmol) were stirred at r.t. for 17h under CO. [b] Isolated yield.

Table 3. Monodehalogenation of *gem*-dihalocyclopropanes[a]

No.	Substrate	Temperature (°C)	Product	Yield (%)[b]	trans/cis[c]
16		r.t.		10	1.6/1
17		60		65	1.6/1
18		r.t.		60	1.3/1

[a] Substrate (2.0 mmol), EtOH (10 m*l*), EtONa (10 mmol), and Fe(CO)$_5$ (0.39 g, 2.0 mmol) were stirred for 17h under CO. [b] Isolated yield. [c] Determined by GC analysis.
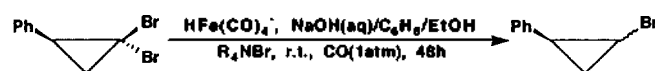
Scheme 2.

to other *gem*-dihalocyclopropanes, 7,7-dibromonorcarane (7,7-diboromobicyclo [4.1.0]heptane) and 1,1-dichloro-2-phenylcyclopropane. The conversion of 1,1-dichloro-2-phenycyclopropane to 1-chloro-2-phenylcyclopropanes was much less effective than the bromo analog at room temperature (No. 16). Mild heating (60°C) was required for the reasonable yield (No. 17). However, the concomitant formation of a by-product, atropaldehyde diethyl acetal, was another problem for this substrate.[14,15]

Mono-debromination of 1,1-dibromocyclopropanes under phase transfer condition. Encouraged by the success of mono-debromination of 1,1-dibromo-2-phenylcyclopropane by stoichiometric amount of HFe(CO)$_4^-$. We tried to pursue a catalytic reaction. The catalytic reaction was successfully realized by using a catalytic amount of Fe(CO)$_5$ in aqueous NaOH and benzene-ethanol[16] in the presence of a phase transfer catalyst, for example, quarternary ammonium salts (Scheme 2).

The results of catalytic mono-debromination under phase transfer conditions are shown in Table 4. We tried to examine several phase transfer catalysts in these reactions to find out the best one. Among various phase transfer cataly-

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Table 4. Monodebromination of 1,1-dibromo-2-phenyl cyclopropane under PTC condition[a]

No.	PTC cat.	Yield (%)[b]		
		Trans	*Cis*	Total
19	(C₁₂H₂₁)Me₃NBr	61	26	87
20	n-Bu₄NHSO₄	46	25	71
21	(C₆H₅CH₂)Et₃NCl	43	24	67
22	(C₁₂H₂₁)Me₂EtNBr	47	15	62
23	(C₁₆H₃₃)Me₃NBr	54	22	76
24	(C₁₆H₃₃)Me₂EtNBr	50	20	70
25	PEG-400	40	30	70
26	Aliqut	50	15	65
27	18-crown-6	25	17	42
28	NH₄Cl	tr	tr	tr

[a] 1,1-Dibromo-2-phenylcyclopropane (0.53 g, 2.0 mmol), benzene (10 m*l*), EtOH (5 m*l*), 8 N NaOH (10 m*l*), phase transfer catalyst (0.2 mmol), and Fe(CO)₅ (0.04 g, 0.2 mmol) were stirred for 17h at r.t. under CO. [b] Isolated yield.
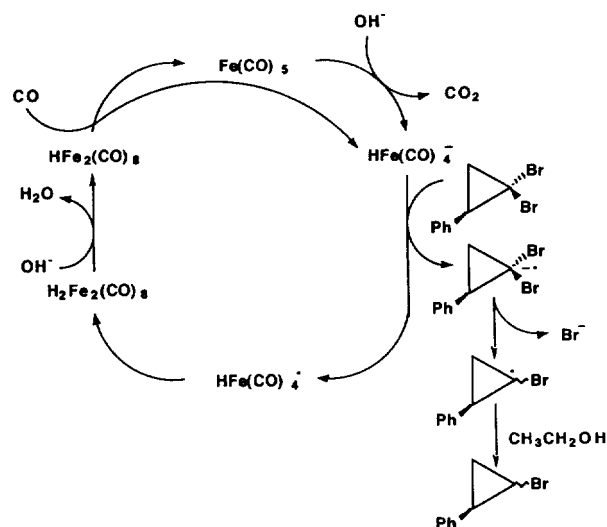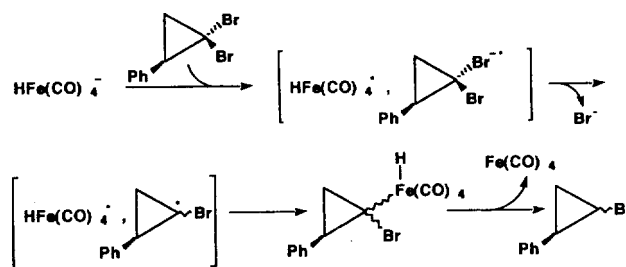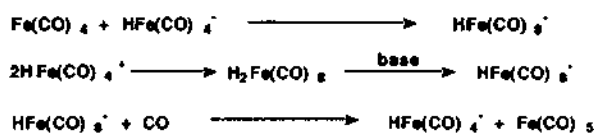

Scheme 3.

sts. (C₁₂H₂₁)Me₃NBr turned out to be the best (No. 19). Other phase transfer catalysts such as 18-crown-6 and NH₄Cl showed low activities (Nos. 27, 28).

A commonly proposed mechanism for the reaction of primary alkyl halides or secondary alkyl halides with HFe(CO)₄⁻ was the classic S_N2 oxidative addition mechanism.[17,18] This kind of S_N2 pathway is inhibited by the presence of the sterically bulky substrates such as tertiary alkyl halides.[18] For example, in a reaction of 1,1-dibromo-2-phenylcyclopropane with HFe(CO)₄⁻, it is difficult to follow S_N2 reaction fashion.

The electron transfer mechanism, in which HFe(CO)₄⁻ was a source of single electron transfer, was also proposed for the dehalogenation of aryl iodides.[19] In the electron transfer mechanism, the organic halide was coordinated by the metal, and then the electron transfer from metal to halogen gave a solvent caged or free radical pair.

Plausible reaction mechanisms for the mono-debromination under phase transfer condition are depicted in Scheme 3 and Scheme 4. At least, two reaction pathways can be propo-

Scheme 4.

Scheme 5.

sed to account for this reaction. In one pathway, probably prefered, bromine atom of 1,1-dibromo-2-phenylcyclopropane coordinates to iron metal of the HFe(CO)₄⁻. The tetracarbonylhydridoferrate anion transfers single electron to 1,1-dibromo-2-phenylcyclopropane to generate the corresponding radical anion. This radical anion is decomposed to give a bromide and a cyclopropyl radical, which can abstract a hydrogen atom from the solvent to yield the mono-debrominated product.

In other possibilities, the electron transfer occurs within a solvent cage to lead the formation of radical species. Subsequent removal of bromide ion provided free redical species, which would recombine to form the intermediate. Following reductive elimination would also give a mono-bromo compound (Scheme 4).

Considering the postulated mechanisms, the possible intermediates of iron carbonyl species are Fe(CO)₄ and HFe(CO)₄·, radical species. The recombination depicted in Scheme 5 can be proposed. Scheme 5 accounts for the generation of HFe (CO)₄⁻ in the reaction medium. It has been shown by other authors that HFe₂(CO)₈⁻ rapidly reacts with carbon monoxides (1 atm) to form HFe(CO)₄⁻ and Fe(CO)₅.[20]

The prefered formation of the major trans isomer was analyzed by the suggested mechanism. In the free radical pathway, the cyclopropyl radical intermediate can abstract hydrogen radical from the alcoholic solvent by the less hinderd face to yield thus the stable trans iosmer. On the other hand, in the solvent caged radical pair mechanism, the stereochemistry of product was determined at the stage of reductive elimination of the cyclopropyl tetracarbonylhydridoiron complex intermediate. Since the hydrotetracarbonyl iron group is bulkier than bromide, phenyl and bromide would like to sit on the same face. Thus the cis isomeric product is expected as a major product.

In summary, tetracarbonylhydridoferrate is a good reducing agent for mono-dehalogenation of gem-dihalocyclopropanes and the tetracarbonylhydridoferrate also acts a good reducing catalyst under phase transfer reaction condition. trans- and cis-1-Bromo-2-phenylcyclopropanes were obtained in excellent yields. trans-1-Bromo-2-phenyl cyclopropane, thermodynamically more stable, was major product in this reaction over the cis isomer, trans/cis = 3/2. Mono-debromi-

nation under phase transfer conditions is a good example of a catalytic reduction using $HFe(CO)_4^-$.

Experimental

Reagents and Instruments. All alcohols used in this study were wet alcohols (95%). Other commercial reagents were used as received unless otherwise mentioned. ^1H NMR spectra were recorded on a Varian Unity Plus 300 spectrometer (300 MHz) or Varian EM-360 (60 MHz). All chemical shifts were measured relative to TMS ($\delta=0.00$). GC-Mass spectra were obtained by using a Shimadzu QP-1000. Gas-liquid-chromatographic analysis was performed on a Shimadzu GC-3BT gas chromatograph using 15% GE SE 52 on 60-80 mesh smimalite W. Analytical thin layer chromatography was performed using Merck silica gel 60 F_{254}. Plates for the preparative thin layer chromatography were prepared by using Merck silica gel F_{254}, calcuim sulfate and water (weight ratio=10 : 1 : 30) on 20×20 cm² glass plate.

Preparation of gem-dihalocyclopropanes.[21]

1,1-Dibromo-2-phenylcyclopropane. A 200 m*l*, round-bottomed flask equipped with a magnetic stirring bar was charged with styrene (10.40 g, 0.1 mole) and bromoform (50. 40 g, 0.2 mole). Benzyltriethylammonium chloride (4.60 g, 0.02 mole) and 50% sodium hydroxide (50 m*l*) were added to the solution. The solution were stirred vigorously at room temperature for 20 hours. The reaction mixture was then treated with water (100 m*l*) and extracted with diethylether (3×50 m*l*). The combined organic layers were dried with anhydrous magnesium sulfate, and concentrated *in vacuo*. Distillation of the residue gave 1,1-dibromo-2-phenylcyclopropane (19.30 g, 65% yield) as yellow oil. ^1H NMR (CCl_4): δ 2.05 (q, $J=4$, 10 Hz, 2H), 2.93 (t, $J=10$ Hz, 1H), 7.31 (s, 5H, Ar).

1,1-dichloro-2-phenyl cyclopropane and 7,7-diboromonorca-rane were prepared by the same method.

Mono-debromination of gem-dihalocyclopropanes using $HFe(CO)_4^-$ as reducing agent. A 100 m*l* round-bottomed flask equipped with magnetic stirring bar was charged with gem-dihalocyclopropanes (2.0 mmol), base (10.0 mmol), alcohol (10 m*l*) and $Fe(CO)_5$ (0.39 g, 2.0 mmole). The mixture was stirred under the atmospheric pressure of carbon monoxide at room temperature for 17 hours. After removing carbon monoxide, the mixture was oxidized under air, filtered, and concentrated in vacuum. Isomeric products were separated by thin layer chromatography eluted with *n*-hexane.

***trans*-1-Bromo-2-phenylcyclopropane[22].** Yellow oil. ^1H NMR ($CDCl_3$): δ 1.51-1.59 (m, 2H), 2.47 (ddd, $J_{cis}=9.9$, $J_{trans}=6.8$, $J_{trans}=3.4$ Hz, 1H), 3.09 (ddd, $J_{cis}=7.6$, $J_{trans}=4.6$, $J_{trans}=3.4$ Hz, 1H), 7.12-7.39 (m, 5H, Ar). MS: m/e(%), 198 (M⁺ + 2, 0.5), 196 (M⁺, 0.5), 195 (0.5), 117 (100), 115 (47), 91 (23).

***cis*-1-Bromo-2-phenylcyclopropane[22].** Yellow oil. ^1H NMR ($CDCl_3$): δ 1.41 (ddd, $J_{trans}=6.8$, $J_{gem}=6.8$, $J_{trans}=4.4$ Hz, 1H), 1.63 (ddd, $J_{cis}=9.5$, $J_{cis}=7.6$, $J_{gem}=6.8$ Hz, 1H$_d$), 2.40 (ddd, $J_{cis}=9.5$, $J_{trans}=6.8$, $J_{cis}=7.6$ Hz, 1H), 3.38 (ddd, $J_{cis}=7.6$, $J_{cis}=7.6$, $J_{trans}=4.4$ Hz, 1H), 7.31-7.44 (m, 5H, Ar). MS: m/e(%), 198 (M⁺+2, 0.4), 196 (M⁺, 0.4), 117 (100), 115 (54), 91 (21).

trans-and cis-1-Chloro-2-phenyl cyclopropanes[23].

This reaction was carried out in a manner similar to that described above at 60℃. The mixture of *trans*-and *cis*-1-chloro-2-phenyl cyclopropane (65%) was obtained by thin layer chromatography eluted with *n*-haxane. The isomeric ratio was determined by GLC analysis using internal standard (*trans/cis*=1.6/1). ^1H NMR (CCl_4) δ 1.02-1.62 (m, 2H of *trans* and *cis*), 1.81-2.32 (m, 1H of *cis*), 2.02-2.52 (m, 1H of *trans*), 2.71-3.11 (m, 1H of *cis*), 3.12-3.52 (m, 1H of *trans*), 7.25 (s, 5H, Ar).

endo-and exo-7-Bromonorcarane[23]. This reaction was carried out as described above. The mixture of *endo*- and *exo*-7-boromonorcarane (60%) was obtained by thin layer chromatography eluted with *n*-hexane. The isomeric ratio was determined by GLC analysis using internal standard (*exo/endo*=1.3/1). ^1H NMR (CCl_4): δ 0.70-2.28 (m, 10H), 2.41 (t, $J=3.2$ Hz, CHBr of *exo*), 2.72 (t, $J=7.2$ Hz, CHBr of *endo*).

Mono-debromination of 1,1-dibromo-2-phenylcyclopropane under phase transfer catalysis. Aqueous 8 M NaOH (10 m*l*), benzene (10 m*l*), ethanol (5 m*l*), and benzyltriethylammonium chloride (0.04 g, 0.2 mmol) were placed in a 100 m*l* three-necked round-bottomed flask and the mixture was degassed by bubbling argon for 20 min. $Fe(CO)_5$(0.04 g, 0.2 mmol) was then added with a syringe and the mixture stirred for 30 min at room temperature. The reaction flask was then purged with carbon monoxide and connected to a gas buret filled with carbon monoxide (1 atm). 1,1-Dibromo-2-phenylcyclopropane (0.53 g, 2.0 mmol) was introduced. The mixture was stirred for 48 hours vigorously. After phase separation, organic layer was dried, and concentrated *in vacuum*. Isomeric products were separated by thin layer chromatography eluted with *n*-haxane.

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Synthesis of α,β-Enoyl-CpFe(CO)(PPh₃)

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An Efficient Synthesis of α,β-enoyl-η⁵-(C₅H₅)Fe(CO)(PPh₃) Complexes

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The α,β-enoyl chiral iron complexes, α,β-enoyl-(η⁵-C₅H₅)Fe(CO)(PPh₃) (1) were prepared from α,β-enoyl-(η⁵-C₅H₅)Fe(CO)₂ (2) and triphenylphosphine through a photochemical ligand substitution followed by carbonylation.

Introduction

Organoiron complexes have been playing an important role in the development of useful methodologies in organic synthesis.[1] Among those organoiron complexes, α,β-enoyl-(η⁵-C₅H₅)Fe(CO)(PPh₃) (1) and related complexes have been studied extensively as effective reagents for stereoselective organic transformations.[2,3]

In 1985, Michael type addition of various nucleophiles to α,β-enoyl-(η⁵-C₅H₅)Fe(CO)₂ (2) and α,β-enoyl-(η⁵-C₅H₅)Fe(CO)(PPh₃) (1) were reported, which opened new routes to β-lactams and chiral carboxylic acid derivatives.[2,3] Since the α,β-enoyl-(η⁵-C₅H₅)Fe(CO)(PPh₃) (1) complex is chiral and can act as an effective stereogenic centers for the newly forming chiral carbon in its stereoselective reactions such as Michael-type additions or Diels-Alder reactions, the efficient preparation of these complexes has significant synthetic value.[3] In addition, α,β-enoyl-(η⁵-C₅H₅)Fe(CO)(PPh₃) (1) was used as an intermediate for synthesis of an chiral iron carbene complex that is useful for cyclopropanation.[4] Therefore we decided to develop an efficient way of synthesis of α,β-enoyl-(η⁵-C₅H₅)Fe(CO)(PPh₃) (1).

Results and Discussion

Davies and Liebskind reported synthetic routes to these complexes based on Peterson's method and aldol condensation (Scheme 1), respectively, using (η⁵-C₅H₅)Fe(CO)(PPh₃)(COCH₃) (3) (CHIRAC) as the starting material.[5,6] The CHIRAC (3) can be prepared from [(η⁵-C₅H₅)Fe(CO)₂]₂ in two steps Eq. (1).[5,6] Although the yields of these reactions are reported to be good, the procedures have drawbacks since
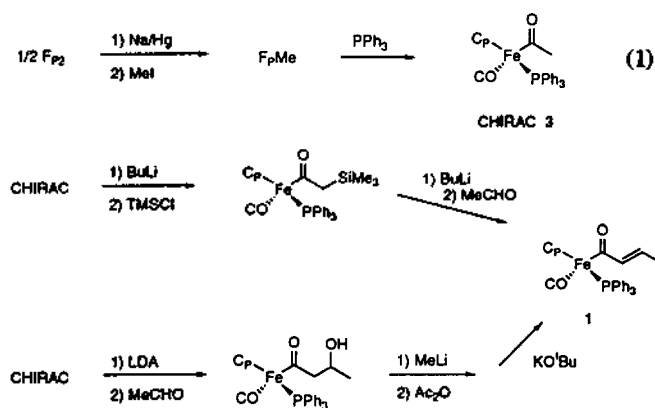
Scheme 1.

a large amount of an alkyllithium must be used for a practical scale synthesis.

Reger reported an effective route to **1** starting from cationic chiral iron-η²-alkyne complexes, {(η⁵-C₅H₅)Fe(CO)[P(OPh)₃](R₁C≡CR₂)}⁺BF₄⁻ (**4**), through the nucleophilic addition to **4** and the following oxidative carbonylation of η¹-alkenyl-(η⁵-C₅H₅)Fe(CO)[P(OPh)₃] (**5**) (Scheme 2).[7] Reger's method is general to a variety of {(η⁵-C₅H₅)Fe(CO)[P(OPh)₃](η²-R₁C≡CR₂)}⁺BF₄⁻ complexes (**4**). However, this method has limitations, *viz.*, triphenyl phosphite should be used, and the availability of alkynes is not necessarily large. In addition, synthesis of complex **4** requires three steps from [(η⁵-C₅H₅)Fe(CO)₂]₂.