A Route to Functionalized (η^3-Allyl)dicarbonylnitrosyliron Complexes: Regio- and Stereoselective Acylmetallation of Allenes

Keiji Itoh,* Saburo Nakanishi,† and Toshikazu Takata†
Department of Industrial Chemistry, Osaka Prefectural College of Technology, 26-12 Saiwai-cho, Neyagawa, Osaka 572-8572
†*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531*

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Allenes regio- and stereoselectively react with alkyl halides in the presence of tetrabutylammonium tricarbonylnitrosyl ferrate to give *anti*-(η^3-2-acylallyl)dicarbonylnitrosyliron complexes in good yields. The reaction provides a convenient method for preparation of di- and trisubstituted η^3-allyl iron complexes with acyl groups at the central carbon of the allylic ligands.

(η^3-Allyl)dicarbonylnitrosyliron complexes have been shown to be a versatile intermediate in organic synthesis. For example, the η^3-allylic ligands of the complexes react with both carbon nucleophiles and carbon electrophiles to afford addition or substitution products.[1,2] As a result, preparation of nitrosyliron complexes having various types of functionalized allylic ligands has received considerable attention. A typical method for preparation of such complexes is the reaction of tricarbonylnitrosyl ferrate $[Fe(CO)_3NO]^{-1}$ with allylic halides or tosylates.[3] The complexes having acylmethyl and acyloxymethyl substituents at the terminal position of the allylic ligands can be prepared by the reaction of 1,3-butadienes and alkenyloxiranes with (acyl)dicarbonylnitrosyliron complexes $RCOFe(CO)_2NO$ which are generated from alkyl halides and $[Fe(CO)_3NO]^{-1}$.[4,5] We now report a new method for preparation of (η^3-allyl)-dicarbonylnitrosyliron complexes having acyl groups at the central carbon of the allylic ligands. This method consists in the regio- and stereoselective acylmetallation of allenes with acyliron complexes $RCOFe(CO)_2NO$. The formation of η^3-allylic transition metal complexes has been reported for the reaction of allenes with Pd complexes[6] and $NaCo(CO)_4$,[7] and *via* the reaction of $Cp(CO)_2Fe(\eta^2\text{-allene})^+$ complexes[8] and $Cp(CO)_3Mo(\eta^2\text{-allene})^+$ complexes.[9]

The reaction of allenes **1a-g** with alkyl halides **2a-e** in the presence of tetrabutylammonium tricarbonylnitrosyl ferrate (TBAFe) in dichloromethane at room temperature gave a mixture of *anti*- and *syn*-(η^3-2-acylallyl)dicarbonylnitrosyliron complexes **3a-k** in good yields (eq 1).[10] The ratios of the *anti* and *syn* stereoisomers were determined from ^{1}H NMR spectra of the products.[11] The results are shown in Table 1.

Arylallenes **1a-d** gave predominantly the *anti*-isomers **3a-h**. Aliphatic and functionalized allenes **1e-1g** also gave the *anti*-isomers **3i-k** as the predominant products. An important feature of these acylmetallation reactions is their high regio- and stereoselectivities.

The iron complexes were obtained as sole isolated products and no other regioisomers were found in the reaction mixtures. The stereoselectivity is particularly noteworthy. In the present reaction, the *anti*-complexes were obtained with a high selectivity. It is well known that most reactions leading η^3-allyl transition metal complexes usually afford more stable *syn*-isomers than *anti*-isomers.[3-9,12] In fact, the carbopalladation of phenyallenes with Pd complex[6d] gives *syn*-isomers with a high stereoselectivity.

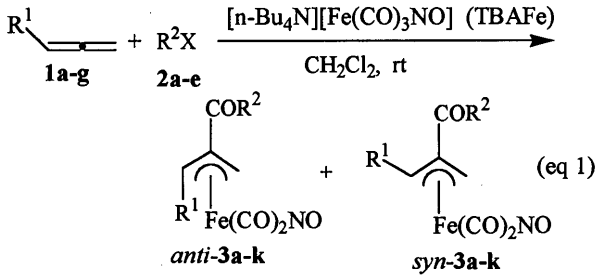
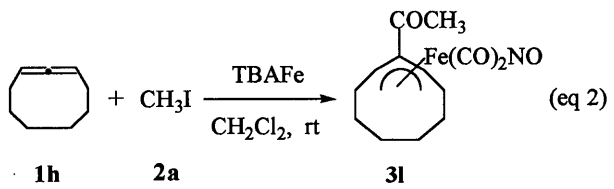


Table 1. Formation of (η^3-2-acylallyl)dicarbonylnitrosyliron complexes

Allene R^1	Alkyl halide R^2X	Product Yield/%	Ratio *anti*:*syn*	Relative rate
1a: C_6H_5	**2a**: CH_3I	**3a**: 78	95: 5	8
1a: C_6H_5	**2b**: C_2H_5I	**3b**: 60	90:10	1
1a: C_6H_5	**2c**: n-C_3H_7I	**3c**: 46	90:10	1
1a: C_6H_5	**2d**: $C_6H_5CH_2Br$	**3d**: 46	100: 0	3
1a: C_6H_5	**2e**:$C_2H_5OCOCH_2Br$	**3e**: 48	100: 0	4
1b:p-$CH_3C_6H_4$	**2a**: CH_3I	**3f**: 62	100: 0	8
1c: p-ClC_6H_4	**2a**: CH_3I	**3g**: 78	100: 0	8
1d: p-FC_6H_4	**2a**: CH_3I	**3h**: 75	90:10	8
1e: n-C_4H_9	**2a**: CH_3I	**3i**: 75	85:15	8
1f:cyclo-C_6H_{11}	**2a**: CH_3I	**3j:** 58	80:20	8
1g:C_2H_5OCO	**2a**: CH_3I	**3k**: 50	100: 0	8

Disubstituted allenes also underwent the acylmetallation. Treatment of cyclic allene **1h** with methyl iodide and TBAFe under the similar conditions gave acylated iron complex **3l** in 50% yield (eq 2). The acylmetallation of 1-phenyl-1,2-butadiene **1i** in a similar manner gave a mixture of *anti*, *anti*-**3m** and *anti*, *syn*-**3m** in a 1:1 ratio in 53% yield (eq 3).



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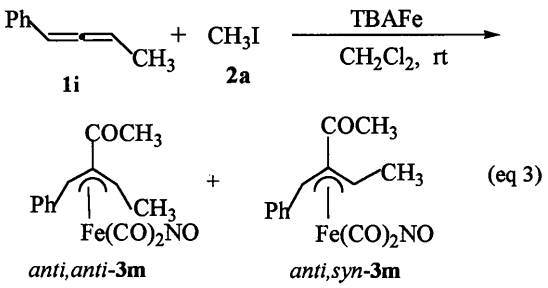
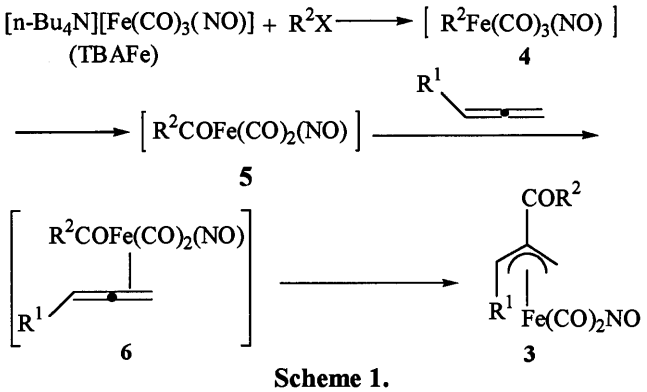


In order to gain information regarding the mechanism of the reaction, the rates of the formation of the complexes were determined by monitoring their light absorbances at about 490 nm.[13] The relative rates are shown in Table 1. The rates depended upon the structure of alkyl halides decreasing in the order: methyl iodide > ethyl bromoacetate > benzyl bromide > ethyl iodide ~ *n*-propyl iodide. On the other hand, the rates were independent of the structure of allenes. The reactivity of the alkyl halides is similar to that observed for the oxidative addition of alkyl halides toward $[Fe(CO)_4]^{2-}$ species.[14]

A possible pathway for the reaction is shown in Scheme 1. Chaudhari et al. reported that the reaction of alkyl halides with $Na[Fe(CO)_3NO]$ generates acyl iron complexes **5** *via* alkyl iron complexes **4**.[3a] Therefore, it is highly probable that the first step of the present reaction is the formation of **5**. The acylmetallation of allenes with **5** yields the acylated η^3-allylic iron complexes **3**. This reaction occurs regio- and stereoselectively *via* the coordination of allenes to the coordinatively unsaturated acyliron complexes **5**. In these steps, the allene approaches to acyliron complex **5** from the opposite side of the substituent R^1 and acylmetallation to allene is *syn* addition. The regioselectivity is similar to that of the reaction of acylcobalt complex with allenes.[7] The steric interaction between the acyliron complex and the substituents on the allenes in the step **5** → **6** → **3** is supposed to be responsible for a preferential formation of the *anti*-allylic iron complexes. The rate determining step of this reaction would be the formation of **4** or **5** because the rates of formation of **3** depend on the concentration of alkyl halides, but are independent of the concentration of allenes.



Scheme 1.

The present reaction provides a convenient method for preparation of *anti*-disubstituted and *anti*-trisubstituted η^3-allylic iron complexes having acyl groups at the central carbon of the η^3-allylic ligands.

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10 A typical procedure for the preparation of η^3-allyliron complex **3a**: Methyl iodide (4.5 mmol) and phenylallene (**1a**, 3.0 mmol) were added successively to a solution of TBAFe (3.0 mmol) in dichloromethane (10 cm^3) under argon. The mixture was stirred at room temperature for 3 h and then concentrated. Chromatography of the residue on silica gel with pentane-CH_2Cl_2 (2:1) gave (η^3-2-acetyl-1-phenylallyl)$Fe(CO)_2NO$ complex **3a** *via* regioselective acylation at the central carbon of the allene in 78% yields.

11 Spectral data of **3a** and **3i** are given as typical examples: *anti*-**3a:** ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 4.02 (d, *J* = 1.1 Hz, 1H), 4.73 (dd, *J* = 1.1, 2.0 Hz, 1H), 6.78 (d, *J* = 2.0 Hz, 1H), 7.01–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 24.0, 55.9, 78.4, 96.0, 127.2, 128.1, 128.4, 139.1, 196.5, 214.0, 215.0. *syn*-**3a:** ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 3.37 (s, 1H), 4.37 (s, 1H), 5.47 (s, 1H), 7.01–7.32 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 21.0, 57.5, 74.5, 96.0, 127.4, 128.6, 129.0, 139.0, 196.5, 214.2, 215.2. *anti*-**3i**: ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.25–1.70 (m, 6H), 2.07 (s, 3H), 3.61 (d, *J* = 1.1 Hz, 1H), 4.59 (dd, *J* = 1.1, 2.0 Hz, 1H), 5.59 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 13.8, 22.2, 22.6, 32.8, 33.5, 53.4, 85.1, 98.3, 196.3, 214.8, 215.5. *syn*-**3i:** ^{1}H NMR ($CDCl_3$) δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.25–1.70 (m, 4H), 2.07 (s, 3H), 2.25–2.45 (m, 2H), 2.64 (s, 1H), 3.31 (s, 1H), 3.88 (m, 1H), ^{13}C NMR ($CDCl_3$) δ 14.0, 20.6, 23.9, 33.6, 34.9, 57.2, 82.8, 98.2, 195.9, 214.8, 215.5.

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13 UV-VL spectral data of **3a** is shown as a typical example: 489 (ε, 940), 366 (ε, 1880), and 290 nm (ε, 7100).

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