

Unprecedented formation of η^4 -(vinylketene)iron complexes from η^4 -(diene)iron complexes and aromatic compounds in the presence of a Lewis acid

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A novel and unprecedented formation of η^4 -(vinylketene)iron complexes from η^4 -(diene)iron complexes is described herein. Treatment of η^4 -(diene)iron complexes with a Lewis acid such as GaCl_3 or AlCl_3 in the presence of aromatic compounds under a CO atmosphere affords η^4 -(vinylketene)iron complexes via electrophilic aromatic substitution.

Vinylketenes are versatile building blocks for the preparation of a variety of cyclic compounds.¹ From a synthetic standpoint, however, reactions involving vinylketenes possess certain drawbacks related to their high reactivity and instability.² Compared to vinylketenes, their iron complexed counterparts are stable and undergo interesting synthetic transformations.³⁻⁴ Although a number of η^4 -(vinylketene)iron complexes have been prepared from a variety of compounds,⁴ there are no reports on the preparation of η^4 -(vinylketene)iron complexes from η^4 -(diene)iron complexes. As part of our continuing interest in the chemistry of η^4 -(diene)iron complexes,^{5,6} we have been investigating their reaction in the presence of a Lewis acid. It is known that η^4 -(diene)iron complexes are reactive towards electrophilic reagents. For example, there are many reports of η^4 -(diene)irons undergoing Friedel–Crafts reactions⁷ and cyclocarbonylations⁸ in the presence of a Lewis acid. However, to our knowledge, these are the only studies that have reported the reaction of η^4 -(diene)iron complexes with Lewis acids. Herein, we report the unprecedented formation of η^4 -(vinylketene)iron complexes from η^4 -(diene)iron complexes and aromatic compounds in the presence of AlCl_3 or GaCl_3 .

Iron complex **1a**, which was easily prepared from a 2-siloxy-1,3-diene,⁶ was treated with AlCl_3 (5.0 equiv) in the presence of mesitylene (5.0 equiv) in CH_2Cl_2 at room temperature. After the usual workup, a yellow crystal **2a** was obtained in moderate yield.[‡] From X-ray diffraction analysis, we identified that **2a** is an unexpected η^4 -(vinylketene)iron complex. The molecular structure of complex **2a** is depicted in Figure 1.

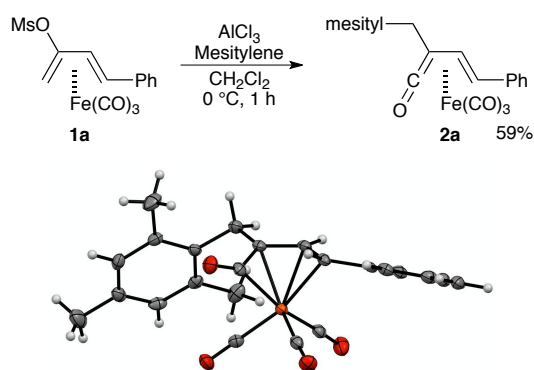
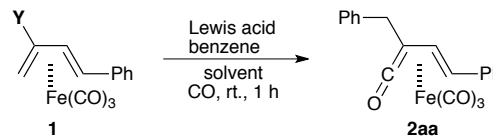


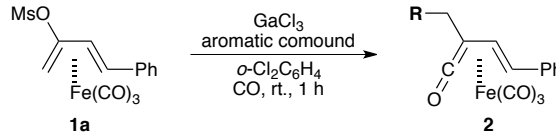
Fig. 1 Reaction of **1a** and ORTEP diagram of **2a** (50% probability).

The treatment of diene-iron complexes with an aluminum halide is known to give cyclopentenones after decomplexation.⁸ In our case, an unexpected reaction, which involved a diene-iron complex, an aromatic compound, and carbon monoxide, proceeded to afford a η^4 -(vinylketene)iron complex. This is the first example of the preparation of a η^4 -(vinylketene)iron complex from a η^4 -(diene)iron complex and an aromatic compound. With this promising result, the Lewis acid-promoted reaction between iron complex **1a** and benzene was chosen as a model reaction for optimization using different Lewis acids and solvents under a carbon monoxide atmosphere as summarized in Table 1, entries 1-11. Among the solvents tested (entries 1-5), *o*-dichlorobenzene was found to be the most appropriate. Subsequently, we examined various Lewis acids and found that GaCl_3 ⁹ was best suited for the reaction in *o*-dichlorobenzene. The yield of **2aa** decreased when the reaction was performed at lower temperature (Table 1, entry 10), and the reaction at higher temperature resulted in a complex mixture of products (Table 1, entry 11). We then examined the effect of the leaving group at the C-2 position of the diene ligand (Table 1, entries 9, 12-15). Mesylate was superior to any of the other leaving groups.

Table 1 Optimizing conditions of the reaction between diene-iron complex **1** and benzene in the presence of a Lewis acid under a CO atmosphere.^a


Entry	1	Y	Lewis acid	Solvent	Yield (%) ^b
1	1a	MsO	AlCl ₃	CH ₂ Cl ₂	34
2	1a	MsO	AlCl ₃	CH ₂ ClCH ₂ Cl	17
3	1a	MsO	AlCl ₃	Et ₂ O	— ^c
4	1a	MsO	AlCl ₃	benzene	30
5	1a	MsO	AlCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	35
6	1a	MsO	BCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	— ^c
7	1a	MsO	InCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	— ^c
8	1a	MsO	TiCl ₄	<i>o</i> -Cl ₂ C ₆ H ₄	c.m. ^d
9	1a	MsO	GaCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	51
10	1a	MsO	GaCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	36 ^e
11	1a	MsO	GaCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	c.m. ^{df}
12	1b	TsO	GaCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	25
13	1c	CH ₃ CO	GaCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	— ^c
14	1d	PhCO	GaCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	— ^c
15	1e	(EtO) ₂ P(O)	GaCl ₃	<i>o</i> -Cl ₂ C ₆ H ₄	— ^c

^a Reaction conditions: **1a** (1.0 equiv.), Lewis acid (5.0 equiv.), benzene (5.0 equiv.), solvent (5.0 mL), rt, 1 h, under CO (1 atm) ^b Isolated yield based on **1a** ^c No reaction ^d Complex mixture ^e Reaction temperature: 0 °C. ^f Reaction temperature: 40 °C

Table 2 Reaction between diene-iron complex **1a** and various aromatic compounds in the presence of GaCl₃ under a CO atmosphere.^a


Entry	Aromatic compound	R	Yield (%) ^b
1	benzene	Phenyl (2aa)	51
2	toluene	Tolyl (2ab) ^c	58
3	<i>p</i> -xylene	2,5-Me ₂ -C ₆ H ₃ (2ac)	53
4	anisole	2-MeO-C ₆ H ₄ (2ad) ^d	67
5	biphenyl	4-Ph-C ₆ H ₄ (2ae)	56
6	naphthalene	Naphthyl (2af) ^e	50
7	chlorobenzene	Cl-C ₆ H ₄ (2ag) ^f	12
8	methyl benzoate	—	— ^g
9	thiophene	—	c.m. ^h
10	furan	—	c.m. ^h

^a Reaction conditions: **1a** (1.0 equiv.), GaCl₃ (5.0 equiv.), aromatic compound (5.0 equiv.), *o*-dichlorobenzene (5.0 mL), rt, 1 h, under CO (1 atm) ^b Isolated yield based on **1a** ^c Obtained as a mixture of inseparable isomers in a ratio of ca. 1:1 determined by ¹H NMR ^d Obtained as a mixture of inseparable regioisomers in the ratio (*para* : *ortho*) of ca. 1:0.5 determined by ¹H NMR ^e Obtained as a mixture of inseparable isomers in a ratio of ca. 1:0.1 determined by ¹H NMR ^f Obtained as a mixture of inseparable isomers in a ratio of ca. 1:0.25 determined by ¹H NMR ^g No reaction ^h Complex mixture

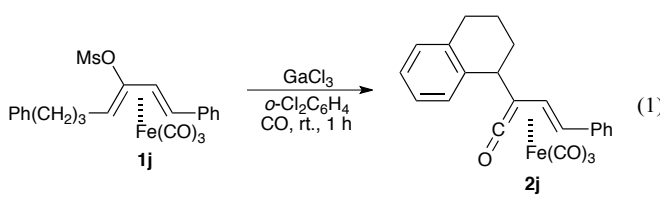
After optimization of reaction conditions, various aromatic compounds were subjected to treatment with diene-iron complexes **1a** in the presence of GaCl₃ under a CO atmosphere. The results are summarized in Table 2. Aromatic compounds with electron-donating groups underwent a reaction affording (vinylketene)iron complex **2** in moderate to good yield (entries 2-4), while electron-withdrawing substituents decreased the reactivity toward the iron complex (entries

7,8). These results show that this reaction proceeds via electrophilic aromatic substitution. In the case of five-membered heterocycles, the Lewis acid could decompose the arenes under the described reaction conditions (entries 9, 10).

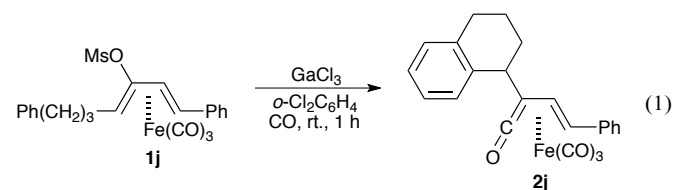
Next, various (diene)iron complexes **1** were subjected to treatment with aromatic compounds in the presence of GaCl₃ or AlCl₃. The results are summarized in Table 3. The reaction of 1,3,4-unsubstituted and 3-substituted (diene)iron complexes with mesitylene in the presence of GaCl₃ yielded the corresponding (vinylketene)iron complexes (entries 1,2). Introduction of substituents that surrounded the reaction center resulted in a lower yield (entry 3). A higher yield was obtained when a stronger Lewis acid (AlCl₃) was used in the reaction of **1h** (entry 4). The more sterically demanding 1,1-disubstituted (diene)iron complex **1i** reacted with *m*-xylene in the presence of AlCl₃, although the reaction of more hindered mesitylene did not occur (entries 5,6). To investigate the possibility of intramolecular cyclization, reaction with a (diene)iron complex bearing a phenyl ring tethered by a trimethylene was examined. The complex **1j** was cyclized after treatment with GaCl₃ under a CO atmosphere. The (vinylketene)iron complex bearing a tetralin ring was isolated in 67% yield (eq. 1).

Table 3 Reaction between various diene-iron complexes **1** and mesitylene, toluene, and benzene in the presence of a Lewis acid.^a

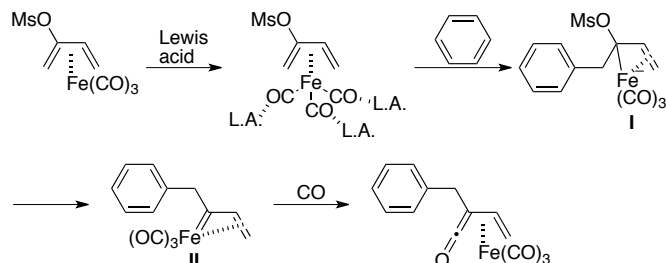
Entry	Diene-iron complex	Aromatic compound	Lewis acid	Product	Yield (%) ^b
1	1f	mesitylene	GaCl ₃	2f	61
2	1g	mesitylene	GaCl ₃	2g	69
3	1h	mesitylene	GaCl ₃	2h	25
4	1h	mesitylene	AlCl ₃	2h	51
5	1i	mesitylene	AlCl ₃	—	c.m. ^c
6	1i	<i>m</i> -xylene	AlCl ₃	2i	56



^a Reaction conditions: **1** (1.0 equiv.), Lewis acid (5.0 equiv.), aromatic compound (5.0 equiv.), *o*-dichlorobenzene (5.0 mL), rt, 1 h, under CO (1 atm) ^b Isolated yield based on **1** ^c Complex mixture



A plausible mechanism for this reaction is depicted in Scheme 1. The diene ligand is activated electrophilically by the coordination of the Lewis acid with the CO ligands.⁸ Electrophilic aromatic substitution with the activated η^4 -(diene)iron complex leads to the formation of the anionic intermediate **I**.¹⁰ Elimination of the mesylate group results in the vinylcarbene-iron complex **II**.¹¹ In the presence of carbon monoxide, CO insertion takes place in the Fe=C bond of the complex **II** to give the η^4 -(vinylketene)iron complex.¹²



Scheme 1 Proposed mechanism.

In conclusion, treatment of η^4 -(1,3-diene)iron complexes with GaCl_3 or AlCl_3 in the presence of an aromatic compound under a CO atmosphere affords η^4 -(vinylketene)iron complexes. The reaction proceeds via electrophilic aromatic substitution. This is the first reported case of the preparation of a η^4 -(vinylketene)iron complex from a η^4 -(diene)iron complex and an aromatic compound. This procedure provides a new approach to prepare η^4 -(vinylketene)iron complexes.

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Notes and references

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† Electronic supplementary information (ESI) available: Details of experimental procedures and characterization data as well as X-ray crystallographic data for **2a** in CIF format. CCDC 1043623. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXXXXX

‡ Data for **2a**: yellow solid; IR (ATR) 2917, 2051, 1976, 1766, 1608, 1450, 1373, 1029, 854 cm^{-1} ; ^1H NMR (500 MHz; CDCl_3) δ 2.30 (s, 3H), 2.35 (s, 6H), 3.18 (d, 1H, $J = 9.0$ Hz), 3.43 (d, 1H, $J = 16.5$ Hz), 3.64 (d, 1H, $J = 16.5$ Hz), 6.02 (d, 1H, $J = 9.5$ Hz), 6.92 (s, 2H), 7.29–7.21 (m, 5H); ^{13}C NMR (126 MHz; CDCl_3) δ 20.3, 20.9, 27.0, 50.1, 59.1, 96.1, 126.6, 127.5, 129.1, 129.5, 130.6, 136.8, 136.9, 138.2, 208.0, 233.7; Anal. Found: C, 66.47; H, 5.13. Calcd for $\text{C}_{23}\text{H}_{20}\text{FeO}_4$: C, 66.37; H, 4.84%.

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