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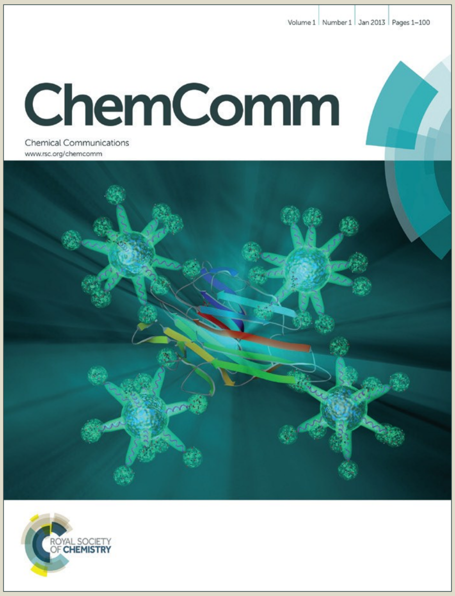

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Unprecedented formation of η^4-(vinylketene)iron complexes from η^4-(diene)iron complexes and aromatic compounds in the presence of a Lewis acid

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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 reactions[7] and cyclocarbonylations[8] 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.

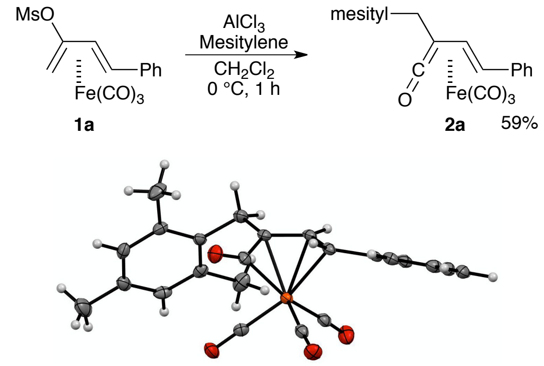
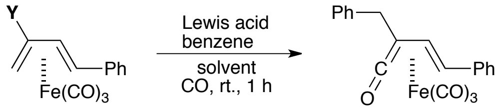


Fig. 1 Reaction of **1a** and ORTEP diagram of **2a** (50% probability).

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]

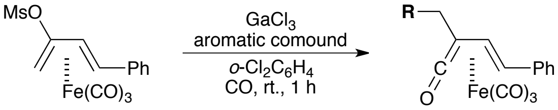


1 **2aa**

Entry	1	Y	Lewis acid	Solvent	Yield (%)[b]
1	**1a**	MsO	$AlCl_3$	CH_2Cl_2	34
2	**1a**	MsO	$AlCl_3$	CH_2ClCH_2Cl	17
3	**1a**	MsO	$AlCl_3$	Et_2O	–[c]
4	**1a**	MsO	$AlCl_3$	benzene	30
5	**1a**	MsO	$AlCl_3$	*o*-$Cl_2C_6H_4$	35
6	**1a**	MsO	BCl_3	*o*-$Cl_2C_6H_4$	–[c]
7	**1a**	MsO	$InCl_3$	*o*-$Cl_2C_6H_4$	–[c]
8	**1a**	MsO	$TiCl_4$	*o*-$Cl_2C_6H_4$	c.m.[d]
9	**1a**	MsO	$GaCl_3$	*o*-$Cl_2C_6H_4$	51
10	**1a**	MsO	$GaCl_3$	*o*-$Cl_2C_6H_4$	36[e]
11	**1a**	MsO	$GaCl_3$	*o*-$Cl_2C_6H_4$	c.m.[d,f]
12	**1b**	TsO	$GaCl_3$	*o*-$Cl_2C_6H_4$	25
13	**1c**	CH_3CO	$GaCl_3$	*o*-$Cl_2C_6H_4$	–[c]
14	**1d**	PhCO	$GaCl_3$	*o*-$Cl_2C_6H_4$	–[c]
15	**1e**	$(EtO)_2P(O)$	$GaCl_3$	*o*-$Cl_2C_6H_4$	–[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 $GaCl_3$ under a CO atmosphere.[a]



1a **2**

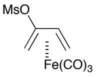
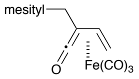
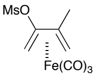
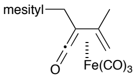
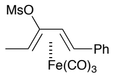
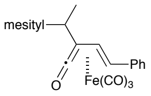
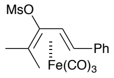
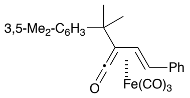
Entry	Aromatic compound	R	Yield (%)[b]
1	benzene	Phenyl (**2aa**)	51
2	toluene	Tolyl (**2ab**)[c]	58
3	*p*-xylene	2,5-Me_2-C_6H_3 (**2ac**)	53
4	anisole	2-MeO-C_6H_4 (**2ad**)[d]	67
5	biphenyl	4-Ph-C_6H_4 (**2ae**)	56
6	naphthalene	Naphthyl (**2af**)[e]	50
7	chlorobenzene	Cl-C_6H_4 (**2ag**)[f]	12
8	methyl benzoate	–	–[g]
9	thiophene	–	c.m.[h]
10	furan	–	c.m.[h]

[a] Reaction conditions: **1a** (1.0 equiv.), $GaCl_3$ (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

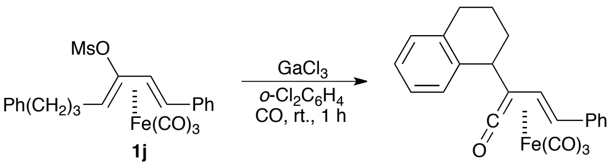
After optimization of reaction conditions, various aromatic compounds were subjected to treatment with diene-iron complexes **1a** in the presence of $GaCl_3$ under a CO atmosphere. The results are summarized in Table 2. Aromatic compounds with electron-donating groups underwent a reaction affording (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 $GaCl_3$ or $AlCl_3$. The results are summarized in Table 3. The reaction of 1,3,4-unsubstitued and 3-substituted (diene)iron complexes with mesitylene in the presence of $GaCl_3$ 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 ($AlCl_3$) 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 $AlCl_3$, 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 $GaCl_3$ 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]

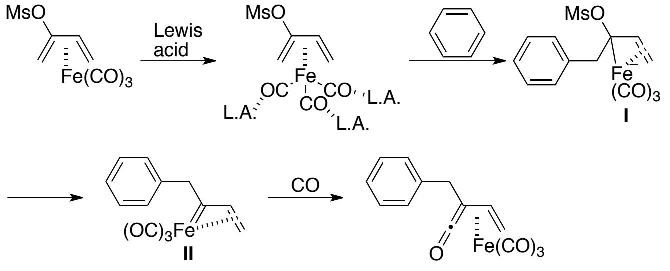
Entry	Diene-iron complex	Aromatic compound	Lewis acid	Product	Yield (%)[b]
1	 **1f**	mesitylene	$GaCl_3$	 **2f**	61
2	 **1g**	mesitylene	$GaCl_3$	 **2g**	69
3	 **1h**	mesitylene	$GaCl_3$	 **2h**	25
4	**1h**	mesitylene	$AlCl_3$	**2h**	51
5	 **1i**	mesitylene	$AlCl_3$	–	c.m.[c]
6	**1i**	*m*-xylene	$AlCl_3$	 **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



1j **2j** (1)

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: XXXXXXX

‡ Data for **2a**: yellow solid; IR (ATR) 2917, 2051, 1976, 1766, 1608, 1450, 1373, 1029, 854 cm^{-1}; ^{1}H 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 $C_{23}H_{20}FeO_4$: C, 66.37; H, 4.84%.

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