Novel Synthesis of Acyloxyferrole Complexes from Alkynes and Their Conversion to Cyclobutenediones

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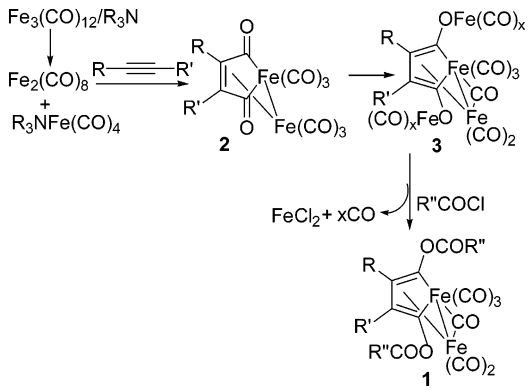
Summary: Acyloxyferrole complexes are easily prepared by the reaction of alkynes and $Fe_3(CO)_{12}/Et_3N$ in THF, which upon reaction with Br_2 in dichloromethane at −78 °C give the corresponding cyclobutenediones in 60−90% yields. The acyloxyferrole complex prepared using diphenylacetylene and acetyl chloride was characterized by single-crystal X-ray analysis.

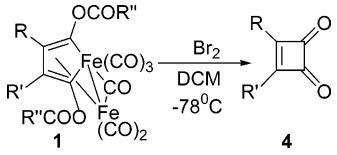
Inroduction

Since the early reports on the reaction of iron carbonyls with alkynes,[1] organometallic complexes of different structural types derived from alkynes have been prepared.[2,3] Among these complexes the hydroxyferrole complexes have good synthetic potential. The simple ferrole complex using acetylene can be readily prepared by the reactions with iron carbonyls in water.[4] Such ferrole complexes were also prepared exploiting the reaction of alkynes with an aqueous alkaline solution of $Fe(CO)_5$[5a] and by refluxing a mixture of alkynes and $Fe_3(CO)_{12}$ in hydrocarbon solvents.[5b] However, the yields reported in the above methods are around 5% and never more than 18% even after 3 weeks of reaction. Hence, such ferrole complexes are not well exploited in organic synthesis due to the lack of a practically viable method to prepare them in good amounts. In continuation of studies on the development of metal cabonyl reagents for synthetic applications,[6] we wish to report here that the Et_3N-promoted reaction of $Fe_3(CO)_{12}$ with alkynes and acid chlorides gives the corresponding acyloxyferrole complexes (65−76% yields), which upon further reaction with Br_2 in dichloromethane at −78 °C produce the corresponding cyclobutenediones.

Scheme 1

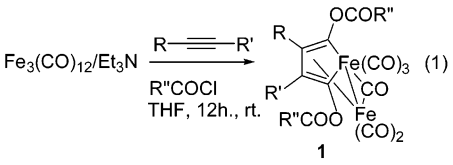


Scheme 2



Results and Discussion

We have observed that the addition of Et_3N and CH_3COCl to the iron carbonyl formed using $Fe_3(CO)_{12}$, Et_3N, and alkyne in THF gives the corresponding acyloxy ferrole complexes (Scheme 1). This transformation was found to be general for various alkynes and acid chlorides (Table 1).



(1)

The effect of other trialkylamines on the conversion of diphenylacetylene to the corresponding acyloxyferrole complex was examined. The ferrole complexes were obtained in 35% and 50% yields, respectively, using Bu_3N and pyridine (entries 2 and 3).

The structural assignment of the hydroxyferrole complex **1a** was confirmed by single-crystal X-ray analysis (Figure 1). It contains the semibridged carbonyl group between Fe(1)−Fe(2), which was considered as a stabilizing factor.[7]

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Table 1. Reaction of Alkynes with $Fe_3(CO)_{12}/R_3N$ in the Presence of R″COCl/R_3N[a]

entry	R	R′	R″	amine	complex	yield (%)
1	C_6H_5	C_6H_5	CH_3	Et_3N	**1a**	76
2	C_6H_5	C_6H_5	CH_3	Bu_3N	**1a**	35
3	C_6H_5	C_6H_5	CH_3	Py	**1a**	50
4	C_6H_5	C_6H_5	*p*-$NO_2C_6H_4$	Et_3N	**1b**	68
5	C_6H_5	H	CH_3	Et_3N	**1c**	72
6	C_5H_{11}	H	C_6H_5	Et_3N	**1d**	70
7	C_5H_{11}	H	*p*-$NO_2C_6H_4$	Et_3N	**1e**	72
8	C_6H_{13}	H	C_6H_5	Et_3N	**1f**	65
9	$C_{10}H_{21}$	H	C_6H_5	Et_3N	**1g**	68

[a] Products were identified by spectral data (IR, ^1H, ^{13}C NMR, and single-crystal X-ray analysis for **1a**). Yields are of the isolated products and based on the amount of alkynes used.

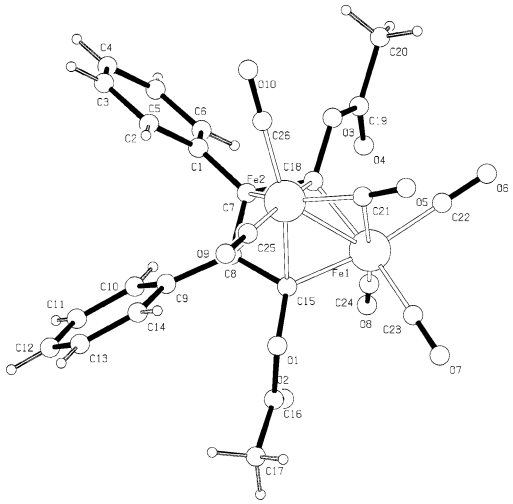


Figure 1. ORTEP diagram of acyloxyferrole complex **1a**.

The transformation of alkynes to the complexes **1** can be explained by a tentative mechanism outlined in Scheme 1. Initial decomposition of the $Fe_3(CO)_{12}$ in the presence of R_3N would give a coordinatively unsaturated reactive species.[10c] These species may further split into other coordinatively unsaturated species before reaction with alkynes. The resulting species would then react with the alkyne and CO to give the maleoyl iron complexes **2** and **3**, which could undergo acylation in the presence of R″COCl.

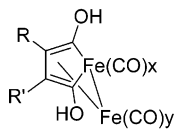
We have observed that the ferrole complexes **1** are relatively stable under nitrogen but decompose upon exposure to air. Whereas the ferrole **1a** in alcoholic solvents gave unclean reaction on ceric ammonium nitrate oxidation, it remained unaffected by $CuCl_2$ in acetone solvent at 25 °C. Interestingly, the reaction of **1** with Br_2 in dichloromethane at −78 °C produced the corresponding cyclobutenediones in moderate to good yields (Table 2).

Table 2. Formation of Cyclobutenediones upon Br_2 Oxidation[a]

	acyloxyferrole complex **1**				
entry	R	R′	R″	dione	yield (%)
1	C_6H_5	C_6H_5	CH_3	**4a**	90
2	C_6H_5	H	CH_3	**4b**	62
3	C_5H_{11}	H	*p*-$NO_2C_6H_4$	**4c**	60
4	C_6H_{13}	H	C_6H_5	**4d**	65
5	$C_{10}H_{21}$	H	C_6H_5	**4e**	63

[a] Products were identified by spectral data (IR, ^1H, ^{13}C NMR, and comparison with reported data[10]). Yields are of the isolated products and based on the amount of ferrole complexes **1** used.

The use of I_2 at 25 °C in the place of Br_2 for the oxidation of complex **1a** gave the corresponding cyclobutenedione in low yield (15%) besides a mixture of unidentified iron carbonyl complexes. In the case of the benzoyl derivative of **1** (R″ = Ph), benzoic acid (65%) was isolated besides the cyclobutenedione **4a** in the reaction with bromine. Previously, bromine and iodine have been used in the oxidative decomplexation of organometallic complexes.[8] Further, the enolic complexes of the type **5** were reported[9a] to give the corresponding cyclobutenedione upon oxidative decomplexation using $FeCl_3$. Also, the maleoyl complexes of nickel **6** were readily decomplexed to obtain the corresponding cyclobutenediones using maleic anhydride.[9b] Moreover, some Fe, Rh, and Co complexes were reported to react with benzocyclobutenedione to give phthaloyl complexes of the type **6** and **7**.[9c]



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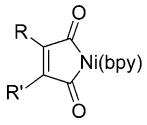

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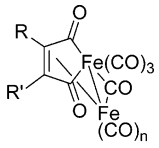

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Accordingly, it is reasonable to assume that the decomplexation of the acyl complexes **1** by bromine to the corresponding cyclobutenediones may go through intermediates similar to **5** and **7**. However, we do not have evidence in support of such intermediates in this transformation.

In conclusion, although the mechanism and the intermediates involved in the transformations reported here are not clearly understood, the simple and convenient methods for the conversion of alkynes to the acyloxy ferrole complexes and cyclobutenediones have good synthetic potential. Since certain cyclobutenedione derivatives have potential for applications as NLO materials, growth regulators, herbicides, and antitumor agents[11] and as versatile starting materials for the synthesis of several functionalzed carbocycles,[12] easy accessibility of these derivatives via the methods described here should facilitate further exploitation of such iron carbonyl complexes in organic synthesis.

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Experimental Section

General Procedures. The X-ray diffraction measurements were carried out at 293 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ cm^{-1}) radiation. Intensity data were collected by the ω-scan mode. The data were reduced using the XTAL program. No absorption correction was applied. The refinement for structure **1a** was made by full matrix least squares on F^2 (SHELX 97). ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$, and TMS was used as reference ($\delta = 0$ ppm). Melting points are uncorrected. IR spectra were recorded on a JASCO FT-5300 instrument with polystyrene as reference. Mass spectral analyses were carried out on a VG 7070H mass spectrometer using EI techniques at 70 eV. $Fe_3(CO)_{12}$ was prepared following a reported procedure using $Fe(CO)_5$ supplied by Fluka.[13] THF was distilled over sodium-benzophenone ketyl. Dichloromethane (DCM) was distilled over calcium hydride and stored over molecular sieves. Chromatographic purification was conducted by column chromatography using 100−200 mesh silica gel obtained from Acme Synthetic Chemicals, India. All reactions and manipulations were carried out under nitrogen atmosphere. All the yields reported are isolated yields of materials, judged homogeneous by TLC analysis.

Preparation of Acyloxyferrole Complexes 1. A mixture of $Fe_3(CO)_{12}$ (4 mmol) and Et_3N (10 mmol) in THF (40 mL) was stirred for 5 min under dry nitrogen at 25 °C. Diphenylacetylene (3 mmol) was added and stirred for 30 min. Then Et_3N (10 mmol) and CH_3COCl (15 mmol) were added, and the contents were further stirred at the same temperature for 12 h. Ether (100 mL) was added, and the reaction mixture was washed successively with H_2O (40 mL) and brine (2 × 50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane−EtOAc). Ethyl acetate (1%) in hexane eluted the ferrole complex **1a**. Crystals suitable for single-crystal X-ray analysis were grown as follows: Complex **1a** (100 mg) was dissolved in a minimum amount of hot methanol (4 mL) and allowed to cool to room temperature under N_2 atmosphere.

1a: Yield: 76% (1.369 g); mp 152−155 °C (dec). IR (KBr): ν (cm^{-1}) 2083, 2042, 2005, 1956, 1749. ^{1}H NMR: δ 1.9 (s, 6 H), 7.18−7.25 (m, 10 H). ^{13}C NMR: δ 211.8, 207.7, 205.3, 185.5, 168.4, 130.7, 130.5, 128.5, 127.9, 125.6, 20.6.

1b: Yield: 68% (1.662 g); mp 158−160 °C (dec). IR (KBr): ν (cm^{-1}) 2081, 2044, 2027, 1988, 1726. ^{1}H NMR: δ 9.9−10 (d, $J = 8.6$ Hz, 4H), 9.6−9.7 (d, $J = 8.6$ Hz, 4H), 8.8−9.0 (m, 10H). ^{13}C NMR: δ 211.3, 208.4, 204.9, 184.7, 162.7, 150.8, 134.2, 131.5, 130.6, 130, 128.9, 128.1, 125.9, 123.7.

1c: Yield: 72% (1.132 g); mp 150−152 °C (dec). IR (neat): ν (cm^{-1}) 2083, 2007, 1953, 1759. ^{1}H NMR: δ 7.3 (m, 5H), 6.1 (s, 1H), 2.1(s, 3H), 2.0 (s, 3H). ^{13}C NMR: δ 210.6, 208.2, 206.1, 190.7, 188.1, 168.1, 168, 131.2, 129.3, 129.0, 128.6, 118.7, 99.7, 21.0, 20.8.

1d: Yield: 70% 1.348 g). IR (neat): ν (cm^{-1}) 2081, 2040, 2000, 1957, 1732. ^{1}H NMR: δ 7.5−8.0 (m, 10H), 6.1 (s, 1H), 0.7−2.5 (m, 11H). ^{13}C NMR: δ 211.3, 208.4, 205.6, 191.5, 186.5, 164.1, 133.6, 129.8, 129.1, 128.6, 122.0, 99.4, 31.6, 29.2, 27.1, 22.2, 13.7.

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1e: Yield: 72% (1.582 g); mp 122−125 °C (dec). IR (neat): ν (cm^{-1}) 2091, 2040, 1994, 1965, 1730. ^{1}H NMR: δ 8.1−8.5 (m, 8H), 6.15 (s, 1H), 0.8−2.8 (m, 11H). ^{13}C NMR: δ 210.6, 207.8, 205.5, 190.6, 185.4, 162.4, 151.0, 134.2, 130.9, 123.8, 121.8, 99.2, 31.5, 29.1, 27.1, 22.1, 13.7.

1f: Yield: 65% (1.279 g). IR (neat): ν (cm^{-1}) 2081, 2040, 2003, 1957, 1732. ^{1}H NMR: δ 8.1−8.4 (m, 4H), 7.4−7.7(mm, 6H), 6.1 (s, 1H), 0.8−2.5 (m, 13H). ^{13}C NMR: δ 211.4, 208.5, 205.7, 191.7, 186.5, 164.2, 134.4, 133.7, 130.5, 129.9, 129.8, 129.1, 128.8, 128.7, 122.0, 99.5, 31.3, 29.6, 29.1, 27.2, 22.4, 13.8.

1g: Yield: 68% (1.453 g). IR (neat): ν (cm^{-1}) 2081, 2040, 2005, 1957, 1732. ^{1}H NMR: δ 8.0−8.2, (m, 4H), 7.4−7.7 (m, 6H), 6.1 (s, 1H), 0.8−2.2 (m, 21H). ^{13}C NMR: δ 211.3, 208.4, 205.6, 191.6, 186.5, 164.1, 133.6, 129.8, 129.1, 128.6, 122.0, 99.4, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.2, 22.6, 14.0.

Preparation of Cyclobutenedione. To a solution of ferrole complex **1a** (1 mmol) in dichloromethane (10 mL) was added Br_2 (3 mmol) at −78 °C under nitrogen atmosphere, and the reaction mixture was stirred at the same temperature for 1 h. The contents were brought to 25 °C, and the excess bromine was destroyed using aqueous $NaHSO_3$. DCM (100 mL) was added, and the combined organic mixture was washed with H_2O (40 mL) and brine (2 × 50 mL), dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography (silica gel, hexane−EtOAc). Ethyl acetate (1.5%) in hexane eluted the 3,4-diphenylcyclcobutene-1,2-dione **4a**.

4a: Yield: 90% (0.212 g); mp 95−96 °C (lit.[10] mp 97 °C). IR (KBr): ν (cm^{-1}) 1780. ^{1}H NMR: δ 7.45−7.68 (m, 6 H), 8.14 (m, 4 H). ^{13}C NMR: δ 196.1, 187.4, 134.6, 131.2, 129.7, 128.7. MS (EI): 235 (M+, 12%), 179 [(M+1) − (Ph_2C_2+1), 100%].

4b: Yield: 62% (0.099 g); mp 152−153 °C (lit.[10] mp 152−153 °C). IR (KBr): ν (cm^{-1}) 1768. ^{1}H NMR: δ 9.5 (s, 1H), 7.3−8.0 (m, 5H). ^{13}C NMR: δ 197.7, 196.0, 195.5, 178.3, 134.6, 129.5, 129.4, 128.6.

4c: Yield: 60% (0.091 g). IR (neat): ν (cm^{-1}) 1778. ^{1}H NMR: δ 9.20 (s, 1H) 2.81 (t, $J = 7.3$ Hz, 2H) 1.70−1.83 (m, 2H) 1.27−1.40 (m, 4H), 0.82 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR: δ 208.3, 199.9, 196.6, 184.8, 31.2, 27.1, 25.6, 22.1, 13.7. MS (EI): m/z 152 (M^+, 13%), 81 [$M^+ - C_5H_{11}$, 20%].

4d: Yield: 65% (0.108 g). IR (neat): ν (cm^{-1}) 1786. ^{1}H NMR: δ 9.1 (s, 1H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.7−1.2 (m, 8H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR: δ 208.3, 199.9, 196.7, 184.9, 31.8, 29.6, 28.9, 26.8, 25.9, 13.9.

4e: Yield: 63% (0.139 g). IR (neat): ν (cm^{-1}) 1774. ^{1}H NMR: δ 9.21 (s, 1H), 2.75 (t, $J = 7.4$ Hz, 2H), 2.42−1.23 (m, 16H), 0.81 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR: δ 203.4, 199.4, 199.1, 198.7, 31.9, 31.8, 29.6, 29.5, 29.2, 29.1, 26.3, 25.9, 22.6, 13.9. MS (EI): m/z 222 (M^+, 25%), 81 [$M^+ - C_{10}H_{21}$, 60%].

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Supporting Information Available: ^{13}C NMR spectra of the compounds **1a**−**1g** and **4a**−**4e**, and crystal data and structure refinement details for **1a** and CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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