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Reactive Iron Carbonyl Reagents via Reaction of Metal Alkoxides with $Fe(CO)_5$ or $Fe_2(CO)_9$: Synthesis of Cyclobutenediones via Double Carbonylation of Alkynes

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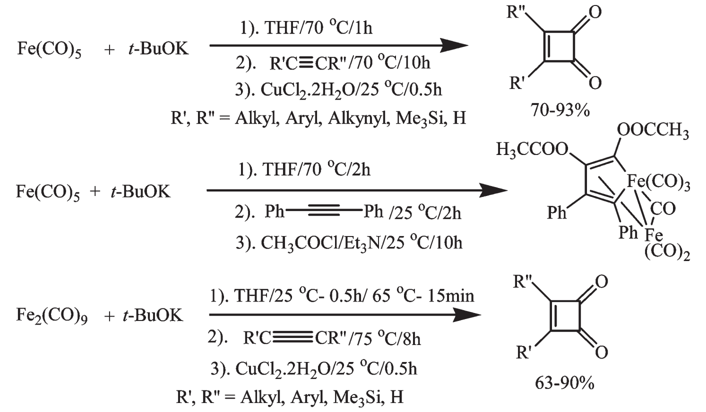

Alkoxy bases such as *t*-BuOK react with $Fe(CO)_5$ to give reactive iron carbonyl intermediates that in turn react with alkynes at 70 °C in THF to give 1,2-cyclobutenediones in 70−93% yields after $CuCl_2 \cdot 2H_2O$ oxidation. A novel 1,2-diacyloxyferrole derivative was isolated in the reaction of diphenylacetylene with $Fe(CO)_5$/*t*-BuOK in the presence of acetyl chloride in contrast to the formation of a 1,4-diacyloxyferrole complex formed in the reaction using $Fe(CO)_5/Me_3NO$. The $Fe_2(CO)_9$/*t*-BuOK reagent system also converts the alkynes to corresponding cyclobutenediones in 63−90% yields under similar reaction conditions.

Introduction

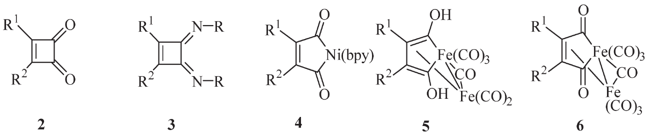

FIGURE 1. Cyclobutenediones and precursor derivatives.

The cyclobutenediones **2** (Figure 1) and squaric acid ester derivatives have been widely used in organic synthesis.[1−4] In recent years, cyclobutenedione derivatives were used not only to prepare organic molecules with biological relevance such as growth regulators, potassium channel openers, drug molecules, and sensors[5b−e] but also for applications as NLO materials,[5a] anion recognition systems,[6] and chiral ligands.[7]

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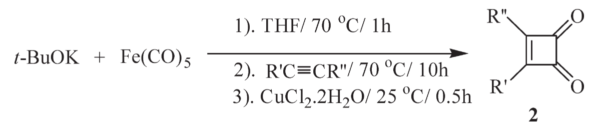
The cyclobutenediones are also versatile starting materials for the synthesis of multifunctional molecules.[8]

Synthetic methods based on transition metal mediated carbonylation reactions have enormous potential for applications in organic synthesis.[9] It was reported that tetrakis(arylisocynide)nickel (R-NC)$_4$Ni undergoes cycloaddition reaction with acetylenes to give the corresponding cyclobutenediones (30−90% yields) via the di-iminocyclobutene intermediate **3**.[10a] The nickelacyclopentenediones **4** prepared by reaction of (bpy)Ni(CO)$_2$ with alkynes afford cyclobutenediones after maleic anhydride or carbon monoxide treatment. The nickel complex **4** can be also obtained from the reaction of (bpy)-Ni(alkyne) with CO.[10b,c]

It was also reported that FeCl$_3$ oxidation of ferrole complex **5** formed in the reaction of acetylene with an alkaline solution of Fe(CO)$_5$ leads to the corresponding cyclobutenedione in 10% yield.[10d,e] Previously, we have developed several reactive iron carbonyl intermediates from the readily accessible iron carbonyls Fe(CO)$_5$ and Fe$_3$(CO)$_{12}$ in the presence of various promoters such as NaH, NaBH$_4$, Me$_3$NO, and amines, to enhance the reactivity of such iron carbonyls.[11−13] Whereas the hydride promoters would be expected to react with Fe(CO)$_5$ or Fe$_3$(CO)$_{12}$ to give the reactive iron carbonyl species such as HFe$_3$(CO)$_{11}^-$, the amine oxide or amines would give the reactive unsaturated iron carbonyls such as Fe(CO)$_4$, Fe$_2$(CO)$_8$, and Fe$_3$(CO)$_{11}$. These reactive iron carbonyl species would further undergo reaction with acetylenes to give the maleoyl complexes of the type **6** or hydroxy ferrole complexes of the type **5**, which give cyclobutenediones after CuCl$_2$·2H$_2$O oxidation in moderate to good yields (25−75%).

Previously, it was reported that Fe(CO)$_5$ reacts with metal alkoxides (*t*-BuOK or CH$_3$ONa) at 0 °C to give the corresponding [(CO)$_4$Fe(COOR)]$^-$ species.[14] We have envisaged that such species could decompose to give unsaturated iron carbonyl species as observed earlier using amine oxides and amines.[12c,13a,18] Indeed, this was observed, and the reactive iron carbonyl species obtained in this way convert the alkynes to the corresponding cyclobutenediones in higher yields through a new 1,2-diketo-iron carbonyl complex in contrast to the 1,4-dicarbonyl complex reported earlier. Herein, we report detailed synthetic studies on these transformations.

SCHEME 1. Synthesis of Cyclobutenediones with Fe(CO)$_5$/*t*-BuOK Reagent System and Alkynes



2

Results and Discussion

We have observed that the reactive iron carbonyl species generated *in situ* from *t*-BuOK and Fe(CO)$_5$ reacts with alkynes to give an intermediate that on CuCl$_2$·2H$_2$O oxidation gives the corresponding cyclobutenediones in 70−93% yields (Scheme 1). By using this method, we synthesized a variety of aryl, alkyl, silyl, and alkynyl substituted, nonsymmetrical and symmetrical cyclobutenediones. The results are summarized in Table 1. It should be pointed out that under these conditions the reactive iron carbonyl species are generated without using any electrophile (like MeI, TMSCl, and CH$_3$COOH), and the products are obtained in higher yields compared to previously reported methods (25−75%).[11−13]

The formation of silyl substituted cyclobutenediones indicates that this reagent system tolerates the silyl functional group (Table 1, entries **10−13**). The formation of alkynyl substituted cyclobutenedione **2g** (Table 1, entry 7) from 1,3-diynes reveals that this reagent system reacts with only one alkyne group without affecting the other alkyne group. This may be due to steric hindrance of the iron carbonyl intermediate for reaction at the adjacent alkyne moiety. However, the presence of an alkynyl moiety on the cyclobutenedione **2g** would give an additional handle for further synthetic exploitations. Such multifunctional derivatives have been previously used in a number of organic transformations.[15,16]

THF was found to be a good solvent for this transformation. Other solvents such as CH$_3$CN and acetone also give comparable results. However, use of solvents like CHCl$_3$ and CH$_2$Cl$_2$ gave unidentified mixtures of carbonyl products. Presumably, the coordinating solvents may form weak complexes with the coordinatively unsaturated species such as mononuclear Fe(CO)$_4$ or binuclear Fe$_2$(CO)$_9$ or Fe$_2$(CO)$_8$ or trinuclear Fe$_3$(CO)$_{11}$ that help in realizing cleaner reaction.[17] We have carried out this reaction with diphenyl acetylene **1a**

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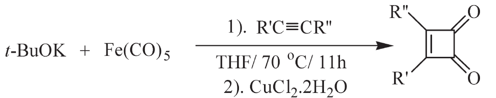
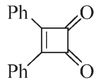
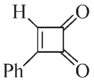
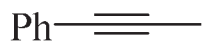
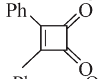
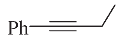
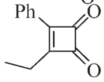
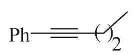
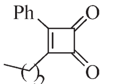
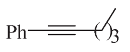
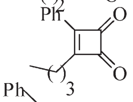
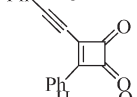
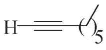
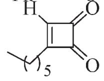
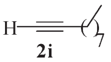
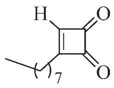
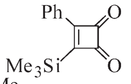
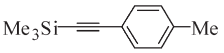
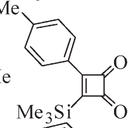
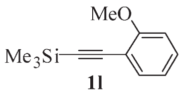
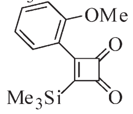
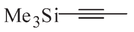
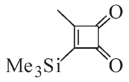
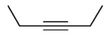
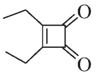
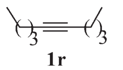
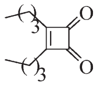
TABLE 1. Synthesis of Cyclobutenediones with the $Fe(CO)_5$/*t*-BuOK Reagent System[a]



2

Entry	Alkyne	Product[b]	Product Number	yield[c] %
1	Ph—≡—Ph **1a**		2a	90
2	Ph—≡—H **1b**		2b	78
3	 **1c**		2c	93
4	 **1d**		2d	85
5	 **1e**		2e	82
6	 **1f**		2f	84
7	Ph—≡—≡—Ph **1g**		2g	70
8	 **1h**		2h	73
9	 **2i**		2i	71
10	Me3Si—≡—Ph **1j**		2j	75
11	 **1k**		2k	80
12	 **1l**		2l	85
13	 **1p**		2p	70[d]
14	 **1q**		2q	72[d]
15	 **1r**		2r	88

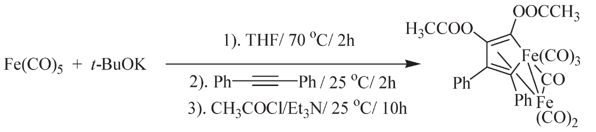
[a] All reactions were carried out using $Fe(CO)_5$ (15 mmol, 6 equiv), *t*-BuOK(15 mmol, 6 equiv), and alkyne (2.5 mmol, 1 equiv) in THF (70 mL). [b] The products were identified by spectral data (IR, ^1H NMR, ^{13}C NMR, and MS) and comparison with the reported data.[11−13] Compound **2h** has been also characterized by single crystal X-ray analysis. [c] Yields reported are based on the amount of alkynes used. [d] In entries 13 and 14, after acetylene addition the reaction temperature was maintained at 25 °C for 2 h and 60 °C for 8 h.

TABLE 2. Formation of Cyclobutenedione (2a) from $Fe(CO)_5$/ROM and Diphenyl Acetylene (1a) in Different Reaction Conditions[a]

entry	ROM	$Fe(CO)_5$:*t*-BuOK	solvent	temp (°C)	yield[b] (%)
1	*t*-BuOK	1:1	THF	70	90
2	*t*-BuOK	1:1/2	THF	70	75
3	*t*-BuOK	1:1/3	THF	70	65
4	*t*-BuOK	1:1	CH_3CN	70	81
5	*t*-BuOK	1:1	acetone	70	70
6	MeONa	1:1	THF	70	70
7	EtONa	1:1	THF	70	50
8	*t*-BuOK	1:1	THF	70 to 25	75[c]

[a] All reactions were carried out using $Fe(CO)_5$ (15 mmol, 6 equiv), ROM (R = Me, Et, *t*-BuOK; M = Na, K), and diphenyl acetylene (2.5 mmol, 1 equiv) in 70 mL of solvent. [b] Yields reported are based on the amount of alkyne used. [c] The reaction of *t*-BuOK with $Fe(CO)_5$ was carried out at 70 °C for 2 h, and the reaction of alkyne was carried out at 25 °C for 10 h.

SCHEME 2. Synthesis of 1,2-Diacyloxy Ferrole Complex 7 Using the Acetyl Chloride, $Fe(CO)_5$/*t*-BuOK Reagent System and Alkynes



7

using different ratios of $Fe(CO)_5$ and *t*-BuOK, 1:1, 1:1/2, and 1:1/3, respectively. In these cases, the cyclobutendione **2a** was obtained in 90%, 75%, and 65% yields, respectively. We also studied the effect of temperature on the reaction and found optimum results were obtained at 70 °C. Further increase of temperature had no effect on the product yields. When the reaction was carried out without heating at 70 °C, no cyclobutenedione product was obtained even after 20 h. When we carried out the first step of the reaction (i.e., reaction of *t*-BuOK with $Fe(CO)_5$) at 70 °C for 2 h and the second step of the reaction (i.e., reaction of acetylene) at 25 °C for 10 h, the cyclobutenedione **2a** was obtained in 75% yield. We also carried out experiments using NaOEt and NaOMe bases. These reagent systems also react with alkyne **1a** to give the corresponding cyclobutenedione **2a** in 50% and 70% yields, respectively, after $CuCl_2\cdot 2H_2O$ oxidation. The results are summarized in Table 2.

We also made efforts to identify the intermediate species involved in the above transformation using Et_3N and CH_3COCl to trap the intermediate species and observed that the corresponding 1,2-diacyloxyferrole complex **7** (Scheme 2) is formed in 75% yield in this reaction.

The structural assignment of the acyloxyferrole complex **7** was confirmed by single crystal X-ray analysis. It contains the semibridged carbonyl group between Fe(1) and Fe(2), which was previously considered a stabilizing factor in such complexes.[19]

Interestingly, the acyloxyferrole complex **8** was isolated when the reaction of $Fe(CO)_5/Me_3NO$ with diphenylacetylene was run in the presence of Et_3N and CH_3COCl (Scheme 3).[12d,13a]

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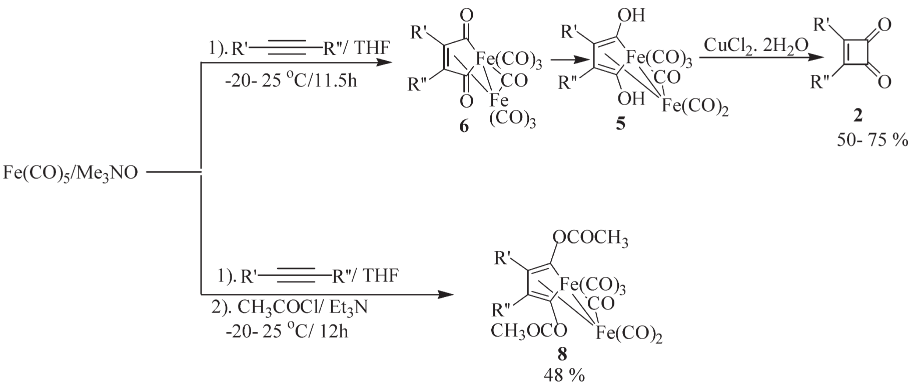
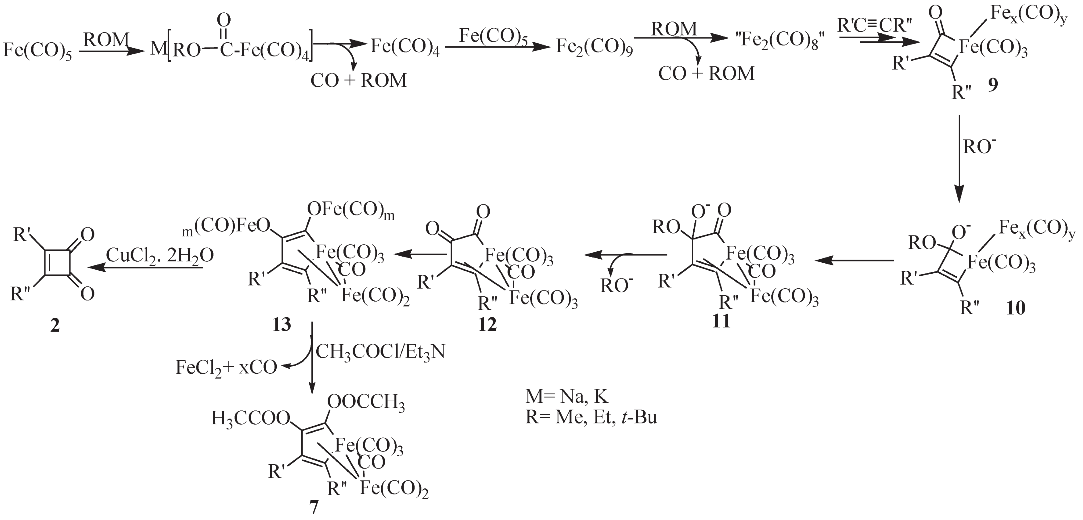
SCHEME 3



SCHEME 4. **Formation of Cyclobutenediones from the Fe(CO)$_5$/ROM Reagent System and Alkynes**

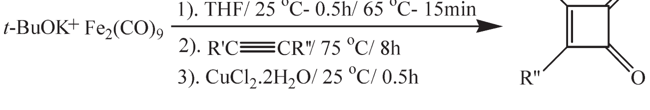


Accordingly, the formation cyclobutenediones was rationalized considering the intermediacy of maleoyl complex of the type **6** or ferrole complex of the type **5**.[11-13]

Since the 1,2-diacyloxyferrolecomplexe **7** is formed in the transformation using *t*-BuOK/Fe(CO)$_5$, the reaction would go through a different type of double carbonylation of alkynes with sequential insertion of carbon monoxide at only one end of the acetylenic carbon in contrast to erstwhile reported methods, in which the carbonylation takes place at both acetylenic carbons, giving intermediates of the type **6**. Clearly, the mechanism and the intermediate species considered in the erstwhile methods are not tenable for the present transformation. Therefore, the mechanism outlined in Scheme 4 may be considered to rationalize this difference. Previously, it was reported that certain amine bases enhance the reactivity of cobalt and iron carbonyls by assisting the decarbonylation.[12c,18] Accordingly, in the present case, addition of ROM to Fe(CO)$_5$ in THF would give the "Fe(CO)$_4$" species through such a decarbonylation (Scheme 4). These species could further undergo reaction with Fe(CO)$_5$ to give species such as Fe$_2$(CO)$_8$ via Fe$_2$(CO)$_9$. Such species would further react with alkynes followed by CO insertion to give the ferracyclopentenedione of type **12** or ferrole complex of type **13** ,which could give corresponding cyclobutenediones after CuCl$_2$·2H$_2$O oxidation. The formation 1,2-diacyloxyferrole complexes **7** in contrast to 1,4-diacyloxyferrole complexes **8** could be due to the presence of strong base leading to the nucleophilic intermediate **10** favoring another CO insertion to give the intermediate species **11** (Scheme 4).

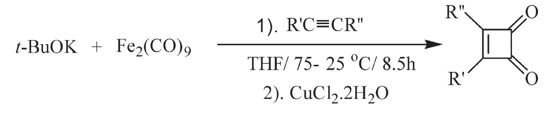
In the mechanism outlined in Scheme 4, the formation of Fe$_2$(CO)$_9$ is visualized. Accordingly, we have examined the reactivity of *t*-BuOK with Fe$_2$(CO)$_9$. Indeed, we have observed that the Fe$_2$(CO)$_9$/*t*-BuOK reagent system also converts the alkynes to corresponding cyclobutenediones in 63−90% yields under similar reaction conditions (Scheme 5).

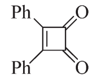
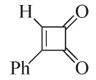
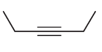
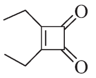
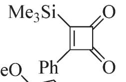
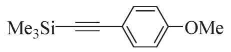
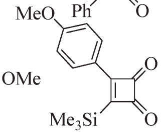
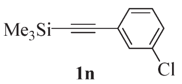
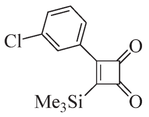
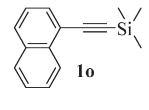
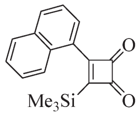
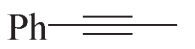
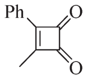
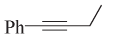
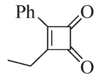
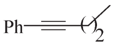
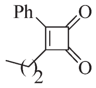
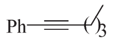
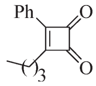
SCHEME 5. **Synthesis of Cyclobutenediones with the Fe$_2$(CO)$_9$/*t*-BuOK Reagent System and Alkynes**



By using this method, a variety of aryl, alkyl, and silyl substituted, nonsymmetrical and symmetrical alkynes are converted to the corresponding cyclobutenediones. The products were obtained here in comparable yields of 63−90% in shorter reaction times. The results are summarized in Table 3.

TABLE 3. Synthesis of Cyclobutenediones with the $Fe_2(CO)_9$/*t*-BuOK Reagent System[a]



Entry	Alkyne	Product[b]	Product Number	yield[c] %
1	Ph—≡—Ph **1a**		**2a**	88
2	Ph—≡—H **1b**		**2b**	63
3	 **1q**		**2q**	65[d]
4	Ph—≡—$SiMe_3$ **1j**		**2j**	72
5	 **1m**		**2m**	70
6	 **1n**		**2n**	71
7	 **1o**		**2o**	69
8	 **1c**		**2c**	86
9	 **1d**		**2d**	83
10	 **1e**		**2e**	85
11	 **1f**		**2f**	90

[a] All reactions were carried out using $Fe_2(CO)_9$ (6 mmol, 3 equiv), *t*-BuOK (8 mmol, 4 equiv), and alkyne (2 mmol, 1 equiv) in THF (50 mL). [b] The products were formed after $CuCl_2 \cdot 2H_2O$ oxidation, identified by spectral data (IR, ^1H NMR, ^{13}C NMR, and MS) and comparison with the reported data.[11-13] [c] Yields reported are based on the amount of alkynes used. [d] In entry 3 experiment, after alkyne addition, the reaction temperature was maintained at 25 °C for 1 h and 65 °C for 7 h.

Conclusion

In conclusion, the simple, convenient, and easily scalable synthetic routes described here for cyclobutenedione synthesis using readily accessible and inexpensive $Fe(CO)_5$, $Fe_2(CO)_9$, and *t*-BuOK, without using promoters such as NaH and Me_3NO or electrophiles such as MeI and Me_3SiCl, should make the method more useful for further synthetic exploitations. Also, the present method converts alkynes to cyclobutenediones in higher yields. Further, in the present case the cyclobutenediones were obtained via a new pathway involving a novel 1,2-dicarbonyliron intermediate **12**. Previously, formation of such complexes was reported only in some transformations using Ru and Pt complexes.[20] 1,4-Dicarbonyliron complexes of the type **6** have been used in several organic transformations, such as synthesis of cyclobutenediones, cyclic imides, quinones, and cyclic anhydrides.[11-13,21] Accordingly, the new 1,2-dicarbonyliron complexes of type **12** formed in the present transformation have potential for synthetic exploitations.

Experimental Section

Preparation of Alkynes. The alkyne **1g** was prepared from phenylacetylene **1b** following a reported procedure.[22a] The alkynes **1k**, **1m**, **1n**, and **10** were prepared from trimethylsilylacetylene and corresponding iodobenzene derivatives (4-iodotoluene, 4-iodoanisole, 3-chloroiodobenzene, and 1-iodonaphthalene) following a reported procedure.[22b]

Preparation of Cyclobutenedione 2a Using the $Fe(CO)_5$/*t*-BuOK Reagent System. $Fe(CO)_5$ (2.9 g, 15 mmol) was added dropwise to a solution of anhydrous *t*-BuOK (1.68 g, 15 mmol) in THF (70 mL) at 25 °C under dry nitrogen. The color of the reaction mixture immediately changed from yellow to dark brown. The reaction mixture was stirred for another 1 h at 70 °C and brought slowly to 25 °C. Diphenylacetylene (0.44 g, 2.5 mmol) was added and further stirred for 10 h at 70 °C. The mixture was brought slowly to 25 °C. The metal carbonyl complexes were oxidized using $CuCl_2 \cdot 2H_2O$ (5.0 g, 30 mmol) in acetone (20 mL). Saturated NaCl solution was added, and the contents were extracted with ether (2 × 75 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane/EtOAc). Ethyl acetate (2%) in hexane eluted the 3,4-diphenyl-3-cyclobutene-1,2-dione **2a**.

Preparation of Cyclobutenedione 2a Using the $Fe_2(CO)_9$/*t*-BuOK Reagent System. THF (50 mL) was added to the mixture of $Fe_2(CO)_9$ (2.0 g, 6 mmol) and *t*-BuOK (0.89 g, 8 mmol) at 25 °C under dry nitrogen. The reaction mixture was stirred for 0.5 h at 25 °C and another 15 min at 65 °C. Diphenylacetylene (0.352 g, 2.0 mmol) was added and further stirred for 8 h at 75 °C. The mixture was brought slowly to 25 °C. The metal carbonyl complexes were oxidized using $CuCl_2 \cdot 2H_2O$ (5.0 g, 30 mmol) in acetone (20 mL). Saturated NaCl solution was added, and the contents were extracted with ether (2×60 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane/EtOAc). Ethyl acetate (2%) in hexane eluted the 3, 4-diphenyl-3-cyclobutene-1,2-dione **2a**.

2a. TLC (10% EtOAc/hexanes R_f=0.45); mp 95−96 °C (lit.[11] mp 97 °C); IR (KBr) ν_{max} 1780 cm^{-1}; ^1H NMR δ 8.01−8.04 (m, 4H), 7.61−7.51 (m, 6H); ^{13}C NMR δ 195.9 (2 × C, C=O), 187.2 (2 × C), 133.3 (2 × CH), 129.2 (4 × CH), 128.1 (4 × CH), 127.9 (2 × C); MS (EI) *m*/*z* 235 (M + 1).

2b. TLC (10% EtOAc/hexanes R_f = 0.30); mp 152−153 °C (lit.[11] mp 152−153 °C); IR (KBr) ν_{max} 1768 cm^{-1}; ^1H NMR δ 9.56 (s, 1H), 8.02−7.52 (m, 5H); ^{13}C NMR δ 197.8 (C, C=O), 196.0 (C, C=O), 195.5 (C), 178.3 (CH), 134.7 (CH), 129.6 (2 × CH), 129.4 (2 × CH), 127.3 (C); MS (EI) *m*/*z* 159 (M + 1).

2c. TLC (10% EtOAc/hexanes R_f = 0.30); mp 98−100 °C (lit.[12e] mp 98−100 °C); IR (KBr) ν_{max} 1782, 1765 cm^{-1}; ^1H

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NMR δ 8.03−8.01 (m, 2H), 7.61−7.55 (m, 3H), 2.66 (s, 3H); ^{13}C NMR δ 198.4 (C, C=O), 196.9 (C, C=O), 193.7 (C), 191.3 (C), 133.5 (CH), 129.5 (2 × CH), 128.6 (2 × CH), 128.5 (C), 12.5 (CH_3); MS (EI) *m*/*z* 173 (M + 1). Anal. Calcd for $C_{11}H_8O_2$: C 76.73, H 4.68. Found: C 76.66, H 4.70.

2d. TLC (10% EtOAc/hexanes R_f = 0.40); mp 64−66 °C (lit.[12e] mp 62 °C); IR (KBr) ν_{max} 1778, 1755 cm^{-1}; ^{1}H NMR δ 8.01−7.99 (m, 2H), 7.62−7.54 (m, 3H), 3.08 (q, *J* = 7.6 Hz, 2H), 1.43 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR δ 198.7 (C, C=O), 198.3 (C, C=O), 197.5 (C), 190.3 (C), 133.5 (CH), 129.5 (2 × CH), 128.5 (2 × CH), 128.4 (C), 21.1 (CH_2), 10.3 (CH_3); MS (EI) *m*/*z* 187 (M + 1). Anal. Calcd for $C_{12}H_{10}O_2$: C 77.40, H 5.41. Found: C 77.51, H 5.42.

2e. TLC (10% EtOAc/hexanes R_f = 0.45); mp 60−62 °C; IR (KBr) ν_{max} 1766 cm^{-1}; ^{1}H NMR δ 8.03−8.01 (m, 2H), 7.61−7.55 (m, 3H), 3.05 (t, *J* = 7.2 Hz, 2H), 1.95−1.89 (m, 2H), 1.08 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR δ 198.5 (C, C=O), 197.9 (C, C=O), 197.4 (C), 190.8 (C), 133.5 (CH), 129.5 (2 × CH), 128.5 (C), 128.4 (2 × CH), 29.7 (CH_2), 19.7 (CH_2, CH_2CH_3) 14.5 (CH_3); MS (EI) *m*/*z* 201 (M + 1). Anal. Calcd for $C_{13}H_{12}O_2$:C 77.98, H 6.04. Found: C 77.96, H 6.03.

2f. TLC (10% EtOAc/hexanes R_f = 0.50); mp 49−51 °C ; IR (KBr) ν_{max} 1768 cm^{-1}; ^{1}H NMR δ 8.01−7.99(m, 2H), 7.57−7.55 (m, 3H), 3.04 (t, *J* = 7.2 Hz, 2H), 1.86−1.81 (m, 2H), 1.50−1.44 (m, 2H) 0.97 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR δ 198.5 (C, C=O), 198.1 (C, C=O), 197.4 (C), 190.6 (C), 133.5 (CH), 129.5 (2 × CH), 128.5 (C), 128.4 (2 × CH), 28.1 (CH_2), 27.5 (CH_2), 23.1 (CH_2), 13.7 (CH_3); MS (EI) *m*/*z* 215 (M + 1). Anal. Calcd for $C_{14}H_{14}O_2$:C 78.48, H 6.59. Found: C 78.48, H 6.55.

2g. TLC (10% EtOAc/hexanes R_f = 0.45); mp 116−118 °C; IR (KBr) ν_{max} 2189, 1778, 1765 cm^{-1}; ^{1}H NMR δ 8.29−7.45 (m, 10 H); ^{13}C NMR; δ 198.1 (C, C=O), 192.8 (C, C=O), 187.9 (C), 172.9 (C), 134.6 (CH), 132.4 (2 × CH),131.4 (CH), 130.9 (2 × CH), 129.4 (2 × CH), 129.1 (2 × CH), 128.8 (C), 124.7 (C), 120.7 (C), 78.3 (C); MS (EI) *m*/*z* 259 (M + 1). Anal. Calcd for $C_{18}H_{10}O_2$:C 83.71, H 3.90. Found: C 83.63, H 3.92.

2h. TLC (10% EtOAc/hexanes R_f = 0.45); IR (neat) ν_{max} 1784 cm^{-1}; ^{1}H NMR δ 9.24 (s, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 1.68−1.61 (m, 2H), 1.34−1.23 (m, 6H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 208.3 (C, C=O), 200.0 (C, C=O), 196.7 (C), 184.9 (CH), 31.1 (CH_2), 28.8 (CH_2), 27.4 (CH_2), 25.7(CH_2), 22.2 (CH_2), 13.8 (CH_3); MS (EI) *m*/*z* 167 (M + 1).

2i. TLC (10% EtOAc/hexanes R_f = 0.50); IR (neat) ν_{max} 1786 cm^{-1}; ^{1}H NMR δ 9.29 (s, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.76−1.69 (m, 2H), 1.40−1.28 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR δ 208.3 (C, C=O), 200.0 (C, C=O), 196.6 (C), 184.9 (CH), 31.6 (CH_2), 29.2 (CH_2), 29 (CH_2), 28.9 (CH_2), 27.4 (CH_2), 25.9 (CH_2), 22.5 (CH_2), 13.9 (CH_3); MS (EI) *m*/*z* 195 (M + 1).

2j. TLC (10% EtOAc/hexanes R_f = 0.55); mp 101−102 °C (lit.[11a] mp 102.8−103.2 °C); IR (KBr) ν_{max} 1774, 1766 cm^{-1}; ^{1}H NMR δ 7.96−7.94 (m, 2H), 7.60−7.55 (m, 3H), 0.46 (s, 9H); ^{13}C NMR δ 202.6 (C, C=O), 200.4 (C, C=O), 199.3 (C), 197.9 (C), 133.6 (CH), 129.5 (2 × CH), 129.3 (2 × CH), 129.1 (C), −1.83 (3 × CH_3, $SiMe_3$); MS (EI) *m*/*z* 231 (M + 1).

2k. TLC (10% EtOAc/hexanes R_f = 0.55); mp 80−82 °C (lit.[23c] mp 89−90 °C); IR (KBr) ν_{max} 1761 cm^{-1}; ^{1}H NMR δ 7.88(d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 8 Hz, 2H), 2.46 (s, 3H), 0.46 (s, 9H); ^{13}C NMR δ 201.1 (C, C=O), 200.5 (C, C=O), 199.0 (C), 198.2 (C), 144.9 (C), 130.1 (2 × CH), 129.7 (2 × CH), 126.5 (C), 22.01(CH_3, Ar−CH_3), −1.8 (3 × CH_3, $SiMe_3$); MS (EI) *m*/*z* 243 (M − 1). Anal. Calcd for $C_{14}H_{16}O_2Si$: C 68.81, H 6.60. Found: C 68.75, H 6.64.

2l. TLC (10% EtOAc/hexanes R_f = 0.40); mp 99−101 °C; IR (KBr) ν_{max} 1763 cm^{-1}; ^{1}H NMR δ 7.92−7.89 (m, 1H), 7.57−7.52 (m, 1H), 7.13−7.09 (m, 1H), 7.02(d, j = 8.4 Hz, 1H), 3.89 (s, 3H), 0.34 (s, 9H); ^{13}C NMR δ 205.4 (C, C=O), 201.4 (C, C=O), 198.3 (C), 196.8 (C), 156.4 (C), 134.7 (CH), 130.3 (CH), 120.9 (CH), 118.5 (C), 111.2 (CH), 55.2 (CH_3, Ar−OCH_3), −1.72 (3 × CH_3, $SiMe_3$); MS (EI) *m*/*z* 261 (M + 1), Anal. Calcd for $C_{14}H_{16}O_3Si$ C 64.58, H 6.19. Found: C 64.51, H 6.22.

2m. TLC (10% EtOAc/hexanes R_f = 0.40); mp 102−104 °C (lit.[23c] mp 114−115 °C); IR (KBr) ν_{max} 1768, 1751 cm^{-1}; ^{1}H NMR δ 7.97(d, *J* = 8 Hz, 2H), 7.04 (d, *J* = 8 Hz, 2H), 3.90 (s, 3H), 0.45 (s, 9H); ^{13}C NMR δ 200.2 (C, C=O), 198.9 (C, C=O), 198.4 (C), 197.7 (C), 164.1 (C), 131.9 (2 × CH), 121.9 (C), 114.8 (2 × CH), 55.6 (CH_3, Ar−OCH_3), −1.79 (3 × CH_3, $SiMe_3$); MS (EI) *m*/*z* 261 (M + 1).

2n. TLC (10% EtOAc/hexanes R_f = 0.57); mp 96−98 °C; IR (KBr) ν_{max} 1759 cm^{-1}; ^{1}H NMR δ 7.93−7.92 (m, 1H), 7.83−7.81 (m, 1H), 7.59−7.55 (m, 1H), 7.52−7.48 (m, 1H), 0.47 (s, 9H); ^{13}C NMR δ 204.1 (C, C=O), 199.9 (C, C=O), 197.8 (C), 197.1 (C), 135.4 (C), 133.2 (CH), 130.6 (CH), 130.5 (C), 129.1 (CH), 127.3 (CH), −1.84 (3 × CH_3, $SiMe_3$); MS (EI) *m*/*z* 265 (M + 1), Anal. Calcd for $C_{13}H_{13}ClO_2Si$: C 58.97, H 4.95. Found: C 58.85, H 4.91.

2o. TLC (10% EtOAc/hexanes R_f = 0.50); mp 100−102 °C; IR (KBr) ν_{max} 1768 cm^{-1}; ^{1}H NMR δ 8.05−7.80 (m, 3H), 7.62−7.53 (m, 4H), 0.34 (s, 9H); ^{13}C NMR δ 207.9 (C, C=O), 203.8 (C, C=O), 200.6 (C), 197.4 (C), 133.6 (C), 132.5 (CH), 129.6 (C), 128.7 (CH), 127.4 (CH), 127.1 (C), 127.0 (CH), 126.9 (CH), 125.4 (CH), 124.9 (CH), −2.0 (3 × CH3, $SiMe_3$); MS (EI) *m*/*z* 281 (M + 1). Anal. Calcd for $C_{17}H_{16}O_2Si$: C 72.82%, 5.75. Found: C 72.88, H 5.71.

2p. TLC (10% EtOAc/hexanes R_f = 0.50); IR (neat) ν_{max} 1779 cm^{-1}; ^{1}H NMR δ 2.42 (s, 3H), 0.33 (s, 9H); ^{13}C NMR δ 208.7 (C, C=O), 207.2 (C, C=O), 201.2 (C), 200.1 (C), 13.1 (CH_3), −2.31(3 × CH_3, $SiMe_3$); MS (EI) *m*/*z* 169 (M + 1).[23a]

2q. TLC (10% EtOAc/hexanes R_f = 0.42); IR (neat) ν_{max} 1766 cm^{-1}; ^{1}H NMR δ 2.69 (q, *J* = 7.6 Hz, 4H), 1.22 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR δ 203.1 (2 × C, C=O), 199.5 (2 × C), 19.9 (2 × CH_2), 10.3 (2 × CH_3); MS (EI) *m*/*z* 139 (M + 1).[23d]

2r. TLC (10% EtOAc/hexanes R_f = 0.50); IR (neat) ν_{max} 1768 cm^{-1}; ^{1}H NMR δ 2.67 (t, *J* = 6 Hz, 4H), 1.67−1.62 (m, 4H), 1.36−1.31 (m, 4H), 0. 89 (t, *J* = 8 Hz, 6H); ^{13}C NMR δ 202.9 (2 × C, C=O), 199.7 (2 × C), 28.0 (2 × CH_2), 26.2 (2 × CH_2), 22.7 (2 × CH_2), 13.5 (2 × CH_3); MS (EI) *m*/*z* 193 (M − 1).[23b]

Preparation of Acyloxyferrole Complex 7. $Fe(CO)_5$ (2.9 g, 15 mmol) was added dropwise to a solution of anhydrous *t*-BuOK (1.68 g, 15 mmol) in THF (70 mL) at 25 °C under dry nitrogen. Then the reaction mixture was stirred for another 2 h at 70 °C and brought slowly to room temperature. Diphenylacetylene (0.44 g, 2.5 mmol) was added and further stirred for 2 h at room temperature. Then Et_3N (2.1 mL, 15 mmol) and CH_3COCl (1 mL, 15 mmol) were added, and the contents were further stirred for 10 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 (2.5%) in hexane eluted the ferroyl complex **7**. This complex is relatively stable but long time standing or exposure to an atmosphere leads to decomposition. TLC (10% EtOAc/hexanes R_f = 0.45); mp 140−142 °C (dec); IR (KBr) ν_{max} 2077, 2038, 2000, 1780 cm^{-1}; ^{1}H NMR δ 7.21−6.83 (m, 10 H), 2.20 (s, 3 H), 2.09 (s, 3 H); ^{13}C NMR δ 212.1 (3 × C, C=O), 209.0 (C, C=O), 204.5 (C, C=O), 204.2 (C, C=O), 178.5 (C), 167.4 (C, O−C=O), 167.0 (C, O−C=O), 159.4 (C), 147.7 (C), 134.3 (C), 131.6 (C), 129.6 (CH), 128.5 (CH), 128.0 (CH), 127.7 (CH), 127.5 (CH), 126.2 (CH),

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125.1 (C), 21.0 (CH_3), 20.3 (CH_3); MS (EI) m/z 601 (M + 1), 602 (M + 2). Anal. Calcd for $C_{26}H_{16}O_{10}Fe_2$: C 52.04, H 2.69. Found: C 52.02, H 2.69.

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Supporting Information Available: Copies of ^1H and ^{13}C NMR spectra of compounds for all new compounds. Crystallographic data and CIF for compounds **2g** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.