

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

Mariappan Periasamy,\* Amere Mukkanti, and D. Shyam Raj

School of Chemistry, University of Hyderabad, Central University P.O.,  
Hyderabad-500 046, India

Received August 28, 2003

**Summary:** Acyloxyferrole complexes are easily prepared by the reaction of alkynes and  $\text{Fe}_3(\text{CO})_{12}/\text{Et}_3\text{N}$  in THF, which upon reaction with  $\text{Br}_2$  in dichloromethane at  $-78^\circ\text{C}$  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.

## Introduction

Since the early reports on the reaction of iron carbonyls with alkynes,<sup>1</sup> organometallic complexes of different structural types derived from alkynes have been prepared.<sup>2,3</sup> 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.<sup>4</sup> Such ferrole complexes were also prepared exploiting the reaction of alkynes with an aqueous alkaline solution of  $\text{Fe}(\text{CO})_5$ <sup>5a</sup> and by refluxing a mixture of alkynes and  $\text{Fe}_3(\text{CO})_{12}$  in hydrocarbon solvents.<sup>5b</sup> 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 carbonyl reagents for synthetic applications,<sup>6</sup> we wish to report here that the  $\text{Et}_3\text{N}$ -promoted reaction of  $\text{Fe}_3(\text{CO})_{12}$  with alkynes and acid chlorides gives the corresponding acyloxyferrole complexes (65–76% yields), which upon further reaction with  $\text{Br}_2$  in dichloromethane at  $-78^\circ\text{C}$  produce the corresponding cyclobutenediones.

\* Corresponding author. E-mail: mpssc@uohyd.ernet.in.

(1) Wender, I.; Friedel, R. A.; Markby, R.; Sternberg, H. W. *J. Am. Chem. Soc.* **1955**, *77*, 4946.

(2) (a) Hubel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. 1, p 273, and references therein. (b) Fehlhammer, W. R.; Stolzenberg, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1983; Vol. 4, p 545. (c) Sternberg, H. W.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1958**, *80*, 1009. (d) Clarkson, V. R.; Jones, E. R.; Wailes, P. C.; Whiting, M. C. *J. Am. Chem. Soc.* **1956**, *78*, 6206.

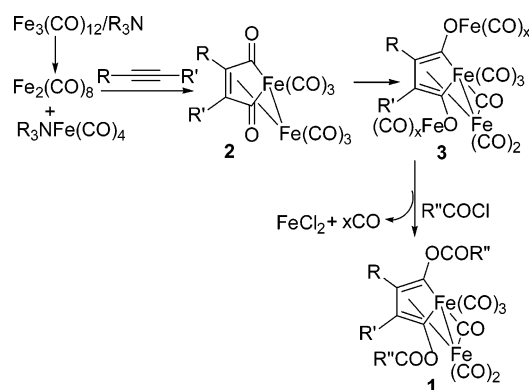
(3) (a) Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096. (b) Pearson, A. J.; Shively, R. J., Jr. *Organometallics* **1994**, *13*, 578. (c) Pearson, A. J.; Perosa, A. *Organometallics* **1995**, *14*, 5178.

(4) Hock, A. A.; Mills, O. S. *Acta Crystallogr.* **1961**, *14*, 139.

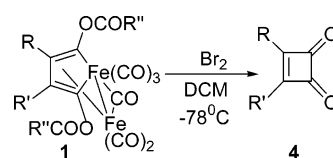
(5) (a) Sternberg, H. W.; Friedel, R. A.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 3621. (b) Aime, S.; Milone, L.; Sappa, E.; Tiripicchio, A.; Lanfredi, A. M. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1664.

(6) (a) Periasamy, M.; Radhakrishnan, U.; Brunet, J. J.; Chauvin, R.; Elzaizi, A. *Chem. Commun.* **1996**, 1499. (b) Rajesh, T.; Periasamy, M. *Organometallics* **1999**, *18*, 5709.

## Scheme 1

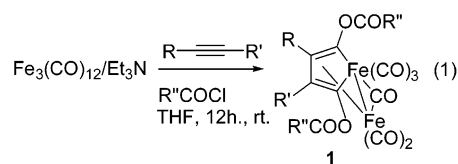


## Scheme 2



## Results and Discussion

We have observed that the addition of  $\text{Et}_3\text{N}$  and  $\text{CH}_3\text{-COCl}$  to the iron carbonyl formed using  $\text{Fe}_3(\text{CO})_{12}$ ,  $\text{Et}_3\text{N}$ , and alkyne in THF gives the corresponding acyloxyferrole complexes (Scheme 1). This transformation was found to be general for various alkynes and acid chlorides (Table 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  $\text{Bu}_3\text{N}$  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  $\text{Fe}(1)$ – $\text{Fe}(2)$ , which was considered as a stabilizing factor.<sup>7</sup>

(7) (a) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 1233. (b) Casarin, M.; Ajo, D.; Granozzi, G.; Tondello, E.; Aime, S. *Inorg. Chem.* **1985**, *24*, 1241.



## 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 K $\alpha$  ( $\lambda = 0.71073$  cm $^{-1}$ ) radiation. Intensity data were collected by the  $\omega$ -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).  $^1\text{H}$  NMR (200 MHz) and  $^{13}\text{C}$  NMR (50 MHz) spectra were recorded in  $\text{CDCl}_3$ , 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.  $\text{Fe}_3(\text{CO})_{12}$  was prepared following a reported procedure using  $\text{Fe}(\text{CO})_5$  supplied by Fluka.<sup>13</sup> 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  $\text{Fe}_3(\text{CO})_{12}$  (4 mmol) and  $\text{Et}_3\text{N}$  (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  $\text{Et}_3\text{N}$  (10 mmol) and  $\text{CH}_3\text{COCl}$  (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  $\text{H}_2\text{O}$  (40 mL) and brine ( $2 \times 50$  mL), dried over  $\text{Na}_2\text{SO}_4$ , 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  $\text{N}_2$  atmosphere.

**1a:** Yield: 76% (1.369 g); mp 152–155 °C (dec). IR (KBr):  $\nu$  (cm $^{-1}$ ) 2083, 2042, 2005, 1956, 1749.  $^1\text{H}$  NMR:  $\delta$  1.9 (s, 6 H), 7.18–7.25 (m, 10 H).  $^{13}\text{C}$  NMR:  $\delta$  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):  $\nu$  (cm $^{-1}$ ) 2081, 2044, 2027, 1988, 1726.  $^1\text{H}$  NMR:  $\delta$  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).  $^{13}\text{C}$  NMR:  $\delta$  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):  $\nu$  (cm $^{-1}$ ) 2083, 2007, 1953, 1759.  $^1\text{H}$  NMR:  $\delta$  7.3 (m, 5H), 6.1 (s, 1H), 2.1 (s, 3H), 2.0 (s, 3H).  $^{13}\text{C}$  NMR:  $\delta$  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):  $\nu$  (cm $^{-1}$ ) 2081, 2040, 2000, 1957, 1732.  $^1\text{H}$  NMR:  $\delta$  7.5–8.0 (m, 10H), 6.1 (s, 1H), 0.7–2.5 (m, 11H).  $^{13}\text{C}$  NMR:  $\delta$  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.

**1e:** Yield: 72% (1.582 g); mp 122–125 °C (dec). IR (neat):  $\nu$  (cm $^{-1}$ ) 2091, 2040, 1994, 1965, 1730.  $^1\text{H}$  NMR:  $\delta$  8.1–8.5 (m, 8H), 6.15 (s, 1H), 0.8–2.8 (m, 11H).  $^{13}\text{C}$  NMR:  $\delta$  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):  $\nu$  (cm $^{-1}$ ) 2081, 2040, 2003, 1957, 1732.  $^1\text{H}$  NMR:  $\delta$  8.1–8.4 (m, 4H), 7.4–7.7 (m, 6H), 6.1 (s, 1H), 0.8–2.5 (m, 13H).  $^{13}\text{C}$  NMR:  $\delta$  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):  $\nu$  (cm $^{-1}$ ) 2081, 2040, 2005, 1957, 1732.  $^1\text{H}$  NMR:  $\delta$  8.0–8.2 (m, 4H), 7.4–7.7 (m, 6H), 6.1 (s, 1H), 0.8–2.2 (m, 21H).  $^{13}\text{C}$  NMR:  $\delta$  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  $\text{Br}_2$  (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  $\text{NaHSO}_3$ . DCM (100 mL) was added, and the combined organic mixture was washed with  $\text{H}_2\text{O}$  (40 mL) and brine ( $2 \times 50$  mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. The residue was subjected to column chromatography (silica gel, hexane–EtOAc). Ethyl acetate (1.5%) in hexane eluted the 3,4-diphenylcyclobutene-1,2-dione **4a**.

**4a:** Yield: 90% (0.212 g); mp 95–96 °C (lit.<sup>10</sup> mp 97 °C). IR (KBr):  $\nu$  (cm $^{-1}$ ) 1780.  $^1\text{H}$  NMR:  $\delta$  7.45–7.68 (m, 6 H), 8.14 (m, 4 H).  $^{13}\text{C}$  NMR:  $\delta$  196.1, 187.4, 134.6, 131.2, 129.7, 128.7. MS (EI): 235 ( $M^+$ , 12%), 179 [ $M+1$ ] – ( $\text{Ph}_2\text{C}_2+1$ ), 100%].

**4b:** Yield: 62% (0.099 g); mp 152–153 °C (lit.<sup>10</sup> mp 152–153 °C). IR (KBr):  $\nu$  (cm $^{-1}$ ) 1768.  $^1\text{H}$  NMR:  $\delta$  9.5 (s, 1H), 7.3–8.0 (m, 5H).  $^{13}\text{C}$  NMR:  $\delta$  197.7, 196.0, 195.5, 178.3, 134.6, 129.5, 129.4, 128.6.

**4c:** Yield: 60% (0.091 g). IR (neat):  $\nu$  (cm $^{-1}$ ) 1778.  $^1\text{H}$  NMR:  $\delta$  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).  $^{13}\text{C}$  NMR:  $\delta$  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 [ $M^+ - \text{C}_5\text{H}_{11}$ , 20%].

**4d:** Yield: 65% (0.108 g). IR (neat):  $\nu$  (cm $^{-1}$ ) 1786.  $^1\text{H}$  NMR:  $\delta$  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).  $^{13}\text{C}$  NMR:  $\delta$  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):  $\nu$  (cm $^{-1}$ ) 1774.  $^1\text{H}$  NMR:  $\delta$  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).  $^{13}\text{C}$  NMR:  $\delta$  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 [ $M^+ - \text{C}_{10}\text{H}_{21}$ , 60%].

**Acknowledgment.** We are thankful to the CSIR (New Delhi) for financial support. Support of the UGC under the “University of Potential for Excellence” program is gratefully acknowledged.

**Supporting Information Available:**  $^{13}\text{C}$  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>.

OM0341395

(13) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, 7, 193.