

Synthesis and Reactivity of $\text{Fe}(\text{CO})_4(\eta^2\text{-RC}\equiv\text{CR}')$ ($\text{R}, \text{R}' = \text{CF}_3, \text{H}, \text{Me}$) Compounds: Hübél's Work Revisited and Beyond

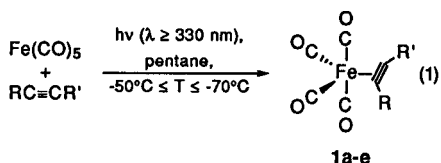
Jason Cooke and Josef Takats*

Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

Received May 30, 1997

Almost 40 years has passed since the first reports on the reaction of iron carbonyls with alkynes appeared.^{1,2} Since that time, a rich and diverse derivative chemistry developed around this theme that yielded a wealth of organometallic complexes, with a plethora of structural types,^{3,4} and practical applications to organic synthesis.^{5–7} While $\text{Fe}(\text{CO})_4(\eta^2\text{-alkyne})$ species have been postulated as intermediates in these reactions,⁴ there is only one well documented example, $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$, a compound stabilized by the bulky bistrimethylsilylacetylene ligand.^{8,9} Here we wish to disclose that, by suitable modification of our previous photochemical synthesis of $\text{M}(\text{CO})_4(\eta^2\text{-alkyne})$ ($\text{M} = \text{Ru}, \text{Os}$) compounds,^{10–13} the congeneric iron derivatives are also accessible and to report the results of a preliminary investigation into their reactivity.

As with Ru and Os, low temperature photolysis of the parent pentacarbonyl in the presence of excess alkyne is the preparative method of choice and gives species **1a–e** in moderate to good yields, eq 1.



R, R' = CF₃ (1a), 84%; R, R' = H (1b), 75%; R, R' = Me (1c), 57%; R = H, R' = CF₃ (1d), 65%; R = H, R' = Me (1e), 63%

However, adherence to the stated experimental conditions is crucial to the success of the synthesis. Thus, while the analogous ruthenium and osmium derivatives are readily formed by irradiation with $\lambda \geq 370$ nm light (GWV cut-off filter), similar treatment of $\text{Fe}(\text{CO})_5$ results in slow and incomplete conversion (**1a,b** > 6 h to 50% reaction). Use of a uranium glass filter ($\lambda \geq 330$ nm) gives satisfactory results and essentially complete consumption of $\text{Fe}(\text{CO})_5$ in 1–2 h. The thermal

(1) Sternberg, H. W.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1958**, *80*, 1009.

(2) Hübél, W.; Braye, H.; Clauss, A.; Weiss, E.; Krieterke, U.; Brown, D. A.; King, G. S. D.; Hoogzand, C. *J. Inorg. Nucl. Chem.* **1959**, *9*, 204.
(3) 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.

(4) Hübél, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. 1, p 273 and references therein.

(5) Pearson, A. J.; Shively, R. J., Jr.; Dubbert, R. A. *Organometallics* **1992**, *11*, 4096.

(6) Pearson, A. J.; Shively, R. J., Jr. *Organometallics* **1994**, *13*, 578.
(7) Pearson, A. J.; Perosa, A. *Organometallics* **1995**, *14*, 5178.
(8) Pannell, K. H.; Crawford, G. M. *J. Coord. Chem.* **1973**, *2*, 251.

(9) The isolation of $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{Bu}_2)$ was mentioned by Hübél (see ref 4) and was also obtained as a minor side product in the formation of $(\text{C}_2\text{Bu}_2)\text{Fe}_2(\text{CO})_6$ from $\text{Fe}_2(\text{CO})_9$ and C_2Bu_2 by Cotton *et al.* (Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774), but full characterization of the compound has not been published.

(10) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987**, *6*, 1918.

(11) Burn, M. J.; Kiel, G.-Y.; Seils, F.; Takats, J.; Washington, J. J. *Am. Chem. Soc.* **1989**, *111*, 6850.

(12) Gagné, M. R.; Takats, J. *Organometallics* **1988**, *7*, 561.

(13) Washington, J.; MacDonald, R.; Takats, J.; Menashe, N.; Reshef, D.; Shvo, Y. *Organometallics* **1995**, *14*, 3996.

conditions of the photolysis are quite critical, especially in the synthesis of **1b**. Photolysis at -70 °C gave isolated yields greater than 70%, whereas a rise of only 10 °C dropped the yield to below 30%. Regrettably, the scale of the reaction also appears to be a crucial parameter. Although a systematic study has not been carried out, attempts to prepare **1a** at larger scales, 750 mg instead of the optimal 140–220 mg of $\text{Fe}(\text{CO})_5$ in 120 mL pentane, resulted in overwhelming decomposition and very poor yields of the desired compound, this probably the result of secondary photoreaction of the product due to the requisite increase in the time of the photolysis.

The complexes are all volatile, off-white to pale yellow substances which are thermally sensitive to varying degrees (stability order: **1a** > **1d** \approx **1b** > **1c** \approx **1e**) and are readily separated from intractable photochemical byproducts by sublimation at low temperature. As explained in more detail previously,^{10,11,13} the characteristic spectroscopic data¹⁴ of **1a–e** conform to that expected for a trigonal-bipyramidal structure in which the alkyne occupies an in-plane equatorial position, as has been observed in the structures of $\text{Os}(\text{CO})_4(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$ ¹⁰ and $\text{M}(\text{CO})_4(\eta^2\text{-C}_2(\text{CF}_3)_2)$ ($\text{M} = \text{Ru}, \text{Os}$).¹⁵ Following the trend established by the Ru and Os derivatives,^{11,12} compounds **1** readily exchange their carbonyls with ¹³CO to give $\text{Fe}(\text{CO})_4(\eta^2\text{-RC}\equiv\text{CR}')$. However, the process occurs at much lower temperature, becoming synthetically useful at -40 °C, and exchange is observed at temperatures as low as -80 °C! A recent kinetic investigation¹⁶ to quantify the effect revealed a phenomenal 3×10^{13} -fold increase in the rate of CO dissociation from **1a** compared to $\text{Fe}(\text{CO})_5$, and a marked increase in reactivity compared to the Ru and Os analogs.

The following observations are pertinent in demonstrating the intermediacy of compounds **1** in iron carbonyl mediated coupling of alkynes and carbon monoxide, Scheme 1. When an acetylene saturated pentane solution of **1b** is allowed to warm slowly from -78 °C, the colorless solution turns yellow-orange at -60 °C with rapid formation of a brown-black precipitate by -40 °C. Extraction of the residue yielded an air-stable orange material which was identified as $(\eta^4\text{-tropone})\text{Fe}(\text{CO})_3$ (**2**) by comparison of its characteristic IR,¹⁷ ¹H NMR,¹⁸ and ¹³C NMR¹⁹ spectra with those reported in the literature. Similarly, isolated **1c** and *in situ* generated $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{Et}_2)$ ²⁰

(14) IR data (cm^{-1}) in pentane, NMR data in CD_2Cl_2 (preparative details are included in the Supporting Information). **1a**: IR: ν_{CO} 2125(w), 2058(s), 2033(m); $\nu_{\text{C}\equiv\text{C}}$ 1890(vw). ¹³C NMR (-40 °C, ¹³CO enriched): δ 205.75 (t, ²J_{CC} = 10 Hz, CO_{eq}), 199.17 (t, ²J_{CC} = 10 Hz, CO_{ax}), 121.35 (q, ¹J_{CF} = 267 Hz, CF₃), 88.51 (qq, ²J_{CF} = 50 Hz, ³J_{CF} = 6 Hz, $\equiv\text{CCF}_3$). ¹⁹F NMR (-40 °C): δ -56.10 (s). **1b**: IR: ν_{CO} 2094(w), 2018(s), 1989(m); $\nu_{\text{C}\equiv\text{C}}$ 1709(vw). ¹H NMR (-80 °C): δ 5.19 (s). ¹³C NMR (-115 °C, ¹³CO enriched): δ 213.3 (br s, CO_{eq}), 208.1 (br s, CO_{ax}); (-80 °C): δ 210.8 (br s, CO_{av}), 63.00 (s, $\equiv\text{CH}$). **1c**: IR: ν_{CO} 2079(w), 2001(s), 1975(m). ¹H NMR (-80 °C): δ 2.26 (s). ¹³C NMR (-80 °C): δ 213.21 (s, CO_{av}), 57.96 (s, $\equiv\text{CCH}_3$), 13.46 (s, CH₃). **1d**: IR: ν_{CO} 2111(w), 2040(s), 2013(m); $\nu_{\text{C}\equiv\text{C}}$ 1812(vw). ¹H NMR (-80 °C): δ 6.47 (d, ⁴J_{HF} = 2.9 Hz, CH). ¹³C NMR (-80 °C, ¹³CO enriched): δ 210.38 (t, ²J_{CeqCax} = 10 Hz, CO_{eq}), 209.23 (t, ²J_{CeqCax} = 10 Hz, CO_{eq}), 203.53 (t, ²J_{CaxCeq} = 10 Hz, CO_{ax}), 122.53 (q, ¹J_{CF} = 276 Hz, CF₃), 82.69 (q, ³J_{CF} = 6 Hz, $\equiv\text{CH}$), 74.97 (q, ²J_{CF} = 50 Hz, $\equiv\text{CCF}_3$). ¹⁹F NMR (-80 °C): δ -54.65 (d, ⁴J_{HF} = 2.9 Hz, CF₃). **1e**: IR: ν_{CO} 2086(w), 2009(s), 1981(m); $\nu_{\text{C}\equiv\text{C}}$ 1873(vw). ¹H NMR (-80 °C): δ 4.21 (q, ⁴J_{HH} = 2.6 Hz, CH), 2.47 (d, ⁴J_{HH} = 2.6 Hz, CH₃). ¹³C NMR (-80 °C, H-coupled): δ 212.06 (s, CO_{av}), 71.86 (dq, ²J_{C(CH)} = 34 Hz, ²J_{C(CH₃)} = 9 Hz, $\equiv\text{CCH}_3$), 48.75 (dq, ¹J_{CH} = 242 Hz, ³J_{C(CH₃)} = 4 Hz, $\equiv\text{CH}$), 14.09 (q, ¹J_{CH} = 132 Hz, CH₃).

(15) Marinelli, G.; Streib, W.; Huffman, J. C.; Caulton, K. G.; Gagné, M. R.; Takats, J.; Dartiguenave, M. *Polyhedron* **1990**, *9*, 1867.

(16) Pearson, J.; Cooke, J.; Takats, J.; Jordan, R. B. *J. Am. Chem. Soc.* Submitted for publication.

(17) Weiss, E.; Hübél, W. *Chem. Ber.* **1962**, *95*, 1179.

(18) Hunt, D. F.; Farrant, G. C.; Rodeheaver, G. T. *J. Organomet. Chem.* **1972**, *38*, 349.

(19) Johnson, B. F. G.; Lewis, J.; McArdle, P.; Norton, J. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1253.

(20) $\text{Fe}(\text{CO})_4(\eta^2\text{-C}_2\text{Et}_2)$ is formed quantitatively from $\text{Fe}(\text{CO})_5$ (as judged by IR spectroscopy, ν_{CO} 2080(w), 2002(s), 1975(m)) but cannot be isolated due to its low thermal stability and high boiling point of hex-3-yne (81 – 82 °C).

