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

Jason Cooke and Josef Takats*

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

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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 $Fe(CO)_4(\eta^2$ -alkyne) species have been postulated as intermediates in these reactions,⁴ there is only one well documented example, $Fe(CO)_4(\eta^2-C_2(SiMe_3)_2)$, 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 $M(CO)_4(\eta^2-alkyne)$ (M = Ru, 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%; $R = H, R' = CF_3$ (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 Fe(CO)₅ results in slow and incomplete conversion (1a, b > 6 h to 50% reaction). Use of a uranium glass filter ($\lambda \ge 330$ nm) gives satisfactory results and essentially complete consumption of $Fe(CO)_5$ in 1-2 h. The thermal

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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 Fe(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 $Os(CO)_4(\eta^2-C_2 (SiMe_3)_2)^{10}$ and M(CO)₄(η^2 -C₂(CF₃)₂) (M = Ru, Os).¹⁵ Following the trend established by the Ru and Os derivatives,^{11,12} compounds 1 readily exchange their carbonyls with 13 CO to give $Fe(^{13}CO)_4(\eta^2 - RC \equiv CR')$. However, the process occurs at much lower temperature, becoming synthetically useful at -40 $^{\circ}$ 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 Fe(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 $(\eta^4$ -tropone)Fe(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 $Fe(CO)_4(\eta^2-C_2Et_2)^{20}$

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(20) Fe(CO)₄(η^2 -C₂Et₂) is formed quantitatively from Fe(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).

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⁽¹⁴⁾ IR data (cm⁻¹) in pentane, NMR data in CD₂Cl₂ (preparative details (14) IK data (cm⁻²) in peritane, NNR data in CD₂C₁₂ (preparative details are included in the Supporting Information). **1a**: IR: v_{CO} 2125(w), 2058 (s), 203(m); $v_{C=C}$ 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 CCF₃). ¹⁹F NMR (-40 °C): δ -56.10 (s). **1b**: IR: v_{CO} 2094(w), 2018(s), 1989(m); $v_{C=C}$ 1709(vw). ¹H NMR (-80 °C): δ 5.19 (s). ¹³C NMR (-115 °C, ¹³CO enriched): δ 210.3 (br s, CO_{eq}), 208.1 (br s, CO_{ax}); (-80 °C): δ 210.8 (br s, CO_A) - δ 300 (c, \equiv CH) Le: IP: v_{CO} 2079(w) 2001(c) 1975(m) ¹H NMP s, CO_av), 63.00 (s, \equiv CH). **1c**: IR: ν_{C0} 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,
$$\begin{split} &= CCH_3', 13.46 \text{ (s, }CH_3). \text{ 1d: } IR: $v_{CO} 2111(w), 2040(s), 2013(m); $v_{C=C}$ \\ 1812(vw). ^{1}H NMR (-80 °C): δ 6.47 (d, $^{J}_{HF} = 2.9 Hz, CH). $^{13}C NMR (-80 °C, $^{13}CO enriched): δ 210.38 (t, $^{2}_{JCeqCax} = 10 Hz, COe_q), 209.23 (t, $^{2}_{JCeqCax} = 10 Hz, COe_q), 209.23 (t, $^{2}_{JCeqCax} = 10 Hz, CC_3), 82.69 (q, $^{3}_{JCF} = 6 Hz, =CH), 74.97 (q, $^{2}_{JCF} = 50 Hz, =CCF_3). $^{19}F NMR (-80 °C): δ -54.65 (d, $^{J}_{HF} = 2.9 Hz, CF_3). \text{ 1e: } \\ IR: $v_{CO} 2086(w), 2009(s), 1981(m); $v_{C=C} 1873(vw). $^{11}H NMR (-80 °C): δ 4.21 (q, $^{4}_{JHH} = 2.6 Hz, CH), 2.47 (d, $^{4}_{JHH} = 2.6 Hz, CH). $^{13}C NMR (-80 °C): δ 4.21 (q, $^{4}_{JHH} = 2.6 Hz, CH), 2.47 (d, $^{4}_{JHH} = 2.6 Hz, CH). $^{13}C NMR (-80 °C): δ 4.21 (q, $^{4}_{JHH} = 2.6 Hz, CH), 2.47 (d, $^{4}_{JHH} = 2.6 Hz, CH). $^{13}C NMR (-80 °C): δ 4.21 (q, $^{4}_{JHH} = 2.6 Hz, CH), 2.47 (d, $^{4}_{JHH} = 2.6 Hz, CH). $^{13}C NMR (-80 °C): δ 4.21 (q, $^{4}_{JHH} = 2.6 Hz, CH), 2.47 (d, $^{4}_{JHH} = 2.6 Hz, CH). $^{13}C NMR (-80 °C): δ 4.21 (q, $^{4}_{JHH} = 2.6 Hz, CH), 2.47 (d, $^{4}_{JHH} = 2.6 Hz, CH). $^{13}C NMR (-80 °C): δ 4.21 (q, $^{4}_{JHH} = 2.6 Hz, CH), 2.47 (d, $^{4}_{JHH} = 2.4 Hz, $^{3}_{JC(CH)} = 34 Hz, $^{2}_{JC(CH)} = 9 Hz, $=CCH_3, 48.75 (dq, $^{1}_{JCH} = 242 Hz, $^{3}_{JC(CH_3)} = 4 Hz, $^{2}_{CCH_3} = 132 Hz, CH_3. $^{13}_{CH} OMR (-80 °C): $^{10}_{CH} = 132 Hz, CH_3. $^{10}_{CH} = 132 Hz, $^{10}_{CH} = 130 Hz, $^{10}_{CH} = 242 Hz, $^{3}_{JC(CH_3)} = 4 Hz, $^{2}_{CCH_3} = 132 Hz, CH_3. $^{11}_{CH} = 242 Hz, $^{3}_{JC(CH_3)} = 4 Hz, $^{2}_{CH} = 132 Hz, CH_3. $^{11}_{CH} = 130 Hz, $^$$
 \equiv *C*CH₃), 13.46 (s, *C*H₃). **1d**: IR: ν_{CO} 2111(w), 2040(s), 2013(m); $\nu_{C=C}$



react cleanly with excess alkyne under a CO atmosphere at -78 °C and ambient temperature, respectively, to generate the corresponding *p*-quinone derivatives **3**. It is interesting to note that, contrary to **1b**, Os(CO)₄(η^2 -C₂H₂) does not react with free acetylene and that the reaction of Os(CO)₄(η^2 -C₂Me₂) with but-2-yne yields the cyclopentadienone species, Os(CO)₃[η^4 -C₄-Me₄C(O)], instead of a *p*-quinone derivative.¹³

As previously reported, a fascinating aspect of the M(CO)₄- $(\eta^2-RC\equiv CR')$ (M = Ru, Os) complexes is their ready reaction with other 18-electron transition metal species to afford dimetallacyclobutenes and dimetallacyclopentenones.^{11,12,21} Accordingly, the corresponding chemistry has been investigated for **1a,b**.

Contrary to $M(CO)_4(\eta^2-C_2(CF_3)_2)$ (M = Ru, Os)¹² and Os-(CO)₄($\eta^2-C_2H_2$),¹¹ **1a,b** do not form bimetallic products when reacted with $M(CO)_5$ (M = Ru, Os). Facile reactions occur with Cp*M'(CO)₂ (M' = Co, Rh, Ir; Cp* = C₅Me₅); however, the outcomes are different than those observed with the Ru, Os congeners. Thus, instead of forming dimetallacyclobutenes, as is the norm with the strongly π -acidic hexafluorobut-2-yne ligand,¹² **1a** affords CO-inserted dimetallacyclopentenones (M' = Co(**4a**), Rh(**4b**), Ir(**4c**)), eq 2.²²



Although the formation of dimetallacyclopentenones from **1b**, Scheme 2, is superficially similar to the reactivity of Os(CO)₄- $(\eta^2$ -C₂H₂),¹¹ close examination reveals several distinctive features. First, while Os(CO)₄(η^2 -C₂H₂) reacted with CpM'(CO)₂ to produce CO insertion exclusively at the group 9 metal,¹¹ with Fe the *opposite sense of CO insertion* is observed and the acyl group is attached to the iron center.²² It is noteworthy that in other families of reported heterobimetallic FeM (M = Ru,²³ Rh,²⁴ Pt²⁵) dimetallacyclopentenones, the acyl group is also Scheme 2



bonded to iron. Second, while $Os(CO)_4(\eta^2-C_2H_2)$ and CpIr-(CO)₂ react to form the stable $Os(CO)_4Ir(CO)Cp(\mu-\eta^{1}:\eta^{1}-C_2H_2C(O))$,¹¹ the corresponding compound **6** readily loses a carbonyl to form **5c**. Both outcomes are presumably due to the weaker Fe-alkyne and Fe–CO bonding in **1b** and **6** compared to the analogous $Os(CO)_4(\eta^2-C_2H_2)$ and Os–Ir compounds. Attempts to reconvert **5c** to **6** under a CO atmosphere were unsuccessful, thereby indicating that **6** is the kinetic product along the pathway to the thermodynamically favored **5c**. Compounds **4** and **5** undergo fascinating carbonyl scrambling processes, the mechanisms and energetics of which shall be reported in due course.

In conclusion, we have demonstrated that under suitable conditions the long elusive $Fe(CO)_4(\eta^2$ -alkyne) complexes can be successfully synthesized. The ready reaction of the compounds with excess alkyne vindicates Hübel's early proposal that they are intermediates in the iron carbonyl mediated coupling of alkynes with carbon monoxide. However, the remarkable acceleration toward CO substitution and the ability to form dimetallacyclic complexes clearly take the compounds beyond the realm of chemistry anticipated by Hübel and his school. Furthermore, the clear structural differences seen in the products obtained by using the iron– or osmium–alkyne complexes as starting materials should enable a more detailed evaluation of the factors which control the differing chemistry within the triad. Work along these lines is continuing.

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Supporting Information Available: Preparative details for title compounds 1a-e and spectroscopic and analytical data for compounds 3-6 (7 pages). See any current masthead page for ordering and Internet access instructions.

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