$$\text{allene} \underset{46.5\ (43.3)}{\overset{68.4\ (64.0)}{\rightleftarrows}} \text{cyclopropene} \underset{64.1\ (59.8)}{\overset{41.5\ (37.5)}{\rightleftarrows}} \text{methylacetylene} \quad (1)$$

These are in excellent agreement with the thermal experiments performed by Walsh and co-workers,[2e] and the involvement of cyclopropene in the allene to methylacetylene rearrangement is confirmed. Note that the reaction paths in Figure 2 require the vinylcarbene structure (**6**) and propenylidene (**9**). When they are not invoked the direct 1,2- or 1,3-hydrogen shifts to form cyclopropene and allene from methylacetylene, respectively, much larger barriers are calculated. The results shown in Figure 3 reveal that the transition states for the 1,3 and 1,2 shift are respectively 95.6 and 79.9 kcal/mol above methylacetylene. This latter transition state transforms to vinylmethylene and subsequently to either cyclopropene or allene.

Another viable but high-energy route for conversion of allene to cyclopropene is through cyclopropylidene, which lies 63.3 kcal/mol above methylacetylene. For the reaction to proceed two barriers must be surmounted, which collectively require 79.6 kcal/mol. The first barrier requires 74.2 kcal/mol to form cyclopropylidene *via* the bent, twisted allene transition state; the second requires 16.7 kcal/mol for the 1,2-hydrogen shift to produce cyclopropene.

Registry No. Methylacetylene, 74-99-7; allene, 463-49-0; cyclopropene, 2781-85-3; propenylidene, 70277-78-0; vinylmethylene, 19527-08-3; cyclopropylidene, 2143-70-6.

Reaction of Alkynes with (Ethoxyalkylidene)tetracarbonyliron(0) Complexes

M. F. Semmelhack,*[1] Rui Tamura,[1] Wayne Schnatter,[1] and James Springer[2]

Department of Chemistry, Princeton University
Princeton, New Jersey 08544
Merck Institute for Theraputic Research
Rahway, New Jersey 07065

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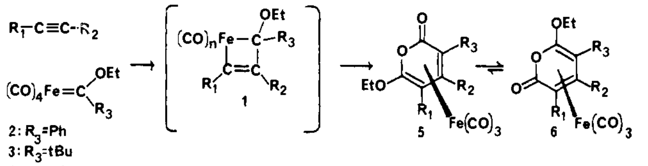
The reaction of alkynes with alkylidene–metal complexes appear in important organic processes such as alkyne polymerization[3] and naphthoquinone synthesis.[4] Initial formation of metallacyclobutenes (e.g., **1**) during these processes is suggested,[5] but has not been established. We have been interested[6] in the naphthoquinone synthesis with complexes such as $(CO)_5Cr{=}C(OMe)Ph$ and recently developed a general preparation of the analogous iron–alkylidene complexes (e.g., **2–4**).[7] Here we report the reaction of complexes **2–4** with alkynes which leads to 6-ethoxy-α-pyrone complexes (e.g., **5**). The reaction is highly regioselective with unsymmetrical alkynes, although a slow rearrangement process introduces a second isomer, of general structure **6**. Spectroscopic evidence has been obtained for a transient intermediate, for which the ferracyclobutene structure **1** is suggested.

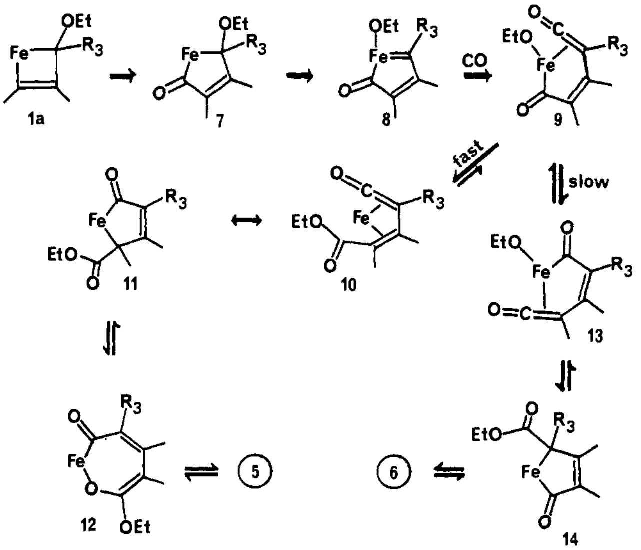
The prototype reaction is carried out as follows. A mixture of **2** and 2-butyne (10-fold molar excess) in dichloromethane at 70 °C in a simple pressure vessel[8] at 55 psi of carbon monoxide for 1 h gave as the major product a yellow crystalline, air-stable compound which was isolated by chromatography. Reproducible yields of 92–98% have been obtained.[9,10] The structure **5a** was established by X-ray crystallography[11] and reveals the incorporation of two carbon monoxide molecules with apparent migration of the ethoxy group from the carbene carbon to a carbon monoxide unit.

Scheme I



Series	Yield of 5
a: R_1,R_2=Me; R_3=Ph	89%
b: R_1,R_3=Ph; R_2=H	74%
c: R_1=Et; R_2=H; R_3=Ph	33%
d: R_1,R_2,R_3=Ph	93%
e: R_1=CO_2Me; R_2=Me; R_3=Ph	15%
f: R_1,R_2=Me; R_3=tBu	60%
g: R_1=Ph; R_2=H; R_3=tBu	39%
h: R_1,R_2=Me; R_3=nBu	33%

Scheme II



Scheme I displays a series of examples with three alkylidene complexes and five alkynes leading to eight pyrone complexes.[9] In each case, the major product was isolated by simple chromatography and only one isomer of each product was detected. The structures of the pyrone products are not easily established by spectroscopy, but X-ray crystallography verified the structures assigned to **5a** and **5c**.[11] The regioselectivity of addition of alkynes to alkylidene–chromium complexes has been defined,[5,12] and

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[1] Princeton University.

[2] Merck Institute for Theraputic Research.

[3] For examples, see: (a) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. Katz, T. J.; Savage, E. B.; Lee, S. J.; Nair, M. *Ibid.* **1980**, *102*, 7942.

[4] (a) Fischer, H.; Schubert, U.; Hofmann, P.; Kreissl, F. R.; Weiss, K.; Dötz, K. H. "Carbene Complexes"; Verlag Chemie: Weinheim, 1983. (b) Dötz, K. H.; Pruskil, I.; Muhlemeier, J. *Chem. Ber.* **1982**, *115*, 1278 and references therein.

[5] Dötz, K. H.; Fügen-Köster, B. *Chem. Ber.* **1980**, *113*, 1449–1457.

[6] (a) Semmelhack, M. F.; Bozell, J. J. *Tetrahedron Lett.* **1982**, 2931–2934. (b) Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* **1982**, *104*, 5850–5852.

[7] Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099–4100.

[8] A heavy-walled glass tube with a cap fitted with a pressure gauge and CO inlet was employed ("Griffin-Worden" vessel, Kontes No. K-767100, borosilicate). The iron-carbene complex and the alkyne were dissolved in degassed dichloromethane and transferred to the pressure vessel which was previously flushed with CO. The vessel was pressurized with CO. After the reaction period, the vessel was cooled to 25 °C and the CO was released. The volatile material was removed by rotary evaporation, and the residue was purified by column chromatography on silica gel, with mixtures of ether and hexane. The complexes **5** were obtained as yellow solids and could be recrystallized from hexane-ether at −20 °C.

[9] Satisfactory characterization data have been obtained; refer to supplementary material.

[10] A number of pyrone–$Fe(CO)_3$ complexes have been prepared by other routes. (a) Rosenblum, M.; Gatsonis, C. *J. Am. Chem. Soc.* **1967**, *89*, 5074. (b) Holland, J. M.; Jones, D. W. *Chem. Commun.* **1967**, 946. (c) Mitsudo, T.; Wantanabe, H.; Sasaki, T.; Wantanabe, Y.; Takegami, Y.; Kafuku, K.; Kinoshita, K.; Nakatzu, K. *J. Chem. Soc., Chem. Commun.* **1981**, 22. (d) Mitsudo, T.; Ogino, Y.; Komiya, Y.; Watanabe, H.; Watanabe, Y. *Organometallics* **1983**, *2*, 1202–1207.

[11] Refer to supplementary material.

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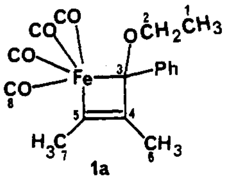
although the overall pathway is different, similar regioselectivity appears with the iron analogue. Parallel with the chromium analogues and with the reaction of **2** with alkenes,[13] the less substituted end of the alkyne is coupled with the alkylidene carbon.

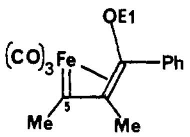
New isomers appear upon heating of the pyrone–iron complexes. For example, at 90 °C in THF, **5a** slowly rearranges into an isomer with identical melting point, similar ^1H NMR spectra, and nearly identical ^{13}C NMR spectra.[9] The new isomer was easily separated by analytical HPLC and conventional TLC and shown to have structure **6a** by X-ray diffraction.[11] Although decomposition becomes significant at long reaction times (10 h at 100 °C), the equilibrium constant can be estimated to be 3.0 at 91 ± 0.5 °C. At this temperature, the forward unimolecular rate constant is 5.4×10^{-4} min^{-1}, while the reverse rate constant is 1.8×10^{-4} min^{-1}. Heating of **6a** at 100 °C for 8.5 h also leads to a mixture from which **5a** and **6a** can be isolated, in yields of 26% and 58%, respectively. Complex **5c** shows the same behavior, producing **6c** (48% yield) and recovered **5c** (37%).

The mechanism of formation of pyrones **5** has not been established. However, a pathway can be outlined (Scheme II) which accounts for the known facts. The key ferracyclobutene intermediate **1** is suggested to undergo migratory insertion of CO (to give **7**) and α-elimination of ethoxy (to **8**). Then CO migration to the alkylidene carbon (to give **9**) and reductive elimination of EtOCO– lead to a coordinated ketene (**10**, **11**) which can assume the bonding arrangement in **12**, an obvious precursor of pyrone **5**. Intermediates related to **7** are known for iron[14] and have been postulated in the analogous alkylidene–chromium reactions,[5] although no stable example with an α-ethoxy group has been reported.

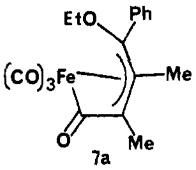
By careful monitoring of the reaction of **2** with excess 2-butyne in the absence of CO (20 °C, CH_2Cl_2, argon, 24 h), a persistent intermediate was detected. Rapid chromatography (silica gel, argon blanket) gave two products, **5a** and a brown oil, which solidified to a yellow amorphous solid at −10° C. Repeated precipitation from pentane at low temperature produced material (28% yield) which was >95% pure (^{13}C NMR) and showed spectral data compatible with structure **1a**.[15] It was unstable, decomposing to **5a** and other products at 25 °C, and proceeded to **5a** quantitatively when heated at 70 °C under CO at 55 psi. Additional data are necessary to establish the structure with certainty, but alternate bonding modes[15] such as in **15** seems unlikely, since the alkylidene carbon in **15** (C-5) would be expected at very low field (below δ 300).[16] The alternate structure **7a** is also consistent with the data, except it would be expected to show a signal in the ^{13}C NMR spectrum for the acyl carbonyl group; none is observed. Work is in progress to characterize fully a suitable derivative of **1**.



1a



15



7a

Acknowledgment. We are pleased to acknowledge support of this work through a research grant from the National Institutes of Health (GM 31352).

Supplementary Material Available: General experimental procedures, characterization data on the pyrone complexes, spectra for **1a**, and listings of atomic coordinates and details of the X-ray analyses (27 pages). Ordering information is given on any current masthead page.

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(12) For additional examples of regioselectivity involving the chromium–alkylidene complexes, see: Wulff, W. D.; Tang, T. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677–7678.

(13) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750–6752.

(14) For examples and leading references, see: Mitsudo, T.; Watanabe, H.; Watanabe, K.; Wantanabe, Y.; Takegami, Y. *J. Organomet. Chem.* **1981**, *214*, 87–92.

(15) The ^1H NMR spectrum and IR spectrum (supplementary material) were consistent but not revealing. In the ^1H NMR spectrum, the $-CH_2-$ unit in the EtO group shows diastereotopic protons, differing by 0.12 ppm, consistent with the presence nearby of a chiral center (C-3). ^{13}C NMR (63 MHz, 253 K, $CDCl_3$): δ 234.7, 234.4 (s, C=O); 138.3 (s, Ph ipso C); 128.6, 128 1 (d, Ph CH); 112.5 (s, C-4 or C-5); 106.7 (s, C-5 or C-4); 66.7 (t, C-2); 48.9 (s, C-3); 15.1, 13.8, 12.5 (q, C-1, C-6, C-7). The mass spectrum shows a peak of highest *m/e* at 328, consistent with loss of one CO from **1a** (or **7a**), or precisely the parent ion for **15**. The base peak appears at 188 [P − Fe $(CO)_4$], especially consistent with **1a**. Mass spectrum (70 eV, electron impact): *m/e* 328 (P − CO, 10%), 300 (P − 2CO, 10), 272 (P − 3CO, 42), 244 (P − 4CO, 56), 216 [P − $Fe(CO)_3$], 188 (P − $Fe(CO)_4$, 100]. The infrared spectrum was more consistent with the acyl complex **7**. In particular, the CO stretching pattern for an $Fe(CO)_3$ unit appears (2012 and 1990 cm^{-1}, strong) along with a broad asymmetric peak of moderate intensity at 1760 cm^{-1}.

(16) In 2, the alkylidene carbon signal appears at δ 326.0.

Relationship between Aromatic Character and Hydrogen Chain Systems

R. C. Haddon,* Krishnan Raghavachari, and
M. H. Whangbo[†]

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

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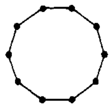
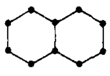
In a recent publication on the stability of polygonal H_N hydrogen chain systems (HCS),[1] Ichikawa[2] has proposed that these structures may be used as models for Hückel (HMO) aromatic character in the annulenes. We have previously examined this scheme, and the present communication points out the difficulties inherent in such an approach.

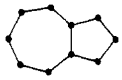
The use of hydrogen atoms to model π-electron systems is attractive for two reasons: (i) the two problems give rise to molecular orbitals of the same topological symmetry; (ii) it is possible to model the π-electron system without complications arising from the rigid stereochemistry of the σ-bonds present in organic molecules. In this way, for example, it is possible to make a straightforward comparison of the resonance energies in the [10]annulene, naphthalene, and azulene frameworks by simply replacing the C or CH groups with hydrogen atoms at an appropriate internuclear separation. Such an energy difference reflects the differing topologies of the systems without the necessity of a correction for angle strain.



R_{10}



R_{6-6}



R_{7-5}

The problem with this approach to topological resonance energies resides in a basic incompatability between HCS and HMO aromatic character which may be made transparent from a consideration of delocalization (DE) and resonance (RE) energies.[3-15] In keeping with the HMO practice of assigning a

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[†] Department of Chemistry, North Carolina State University, Raleigh, NC 27650.

(1) Seel, M.; Bagus, P. S.; Ladik, J. *J. Chem. Phys.* **1982**, *77*, 3123 and references therein.

(2) Ichikawa, H. *J. Am. Chem. Soc.* **1983**, *105*, 7467.

(3) The DE is defined in the present context as the calculated additional bonding energy that results from delocalization of electrons originally constrained to isolated double bonds (HMO)/hydrogen molecules (HCS). Streitwieser, A. "Molecular Orbital Theory for Organic Chemists"; Wiley: New York, 1961; Chapter 9.

(4) Both the DE and RE are considered on a per electron (PE) basis for comparison purposes. Positive values (in units of positive β for HMO systems) denote stabilization.

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