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Communications

Fischer-Type Iron Alkynylcarbene Complexes: Synthesis and Reactions with 1,3-Dienes

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Summary: Five (alkynylethoxymethylene)Fe(CO)$_4$ complexes (**1a–e**) are prepared through the reaction of Fe(CO)$_5$ with alkynyllithiums (R = ^{n}Pr, cyclohexyl, ^{t}Bu, trimethylsilyl, Ph) and subsequent O-ethylation of the resulting acyl anion complexes with ethyl fluorosulfonate, while (diethoxycyclopropenylidene)Fe(CO)$_4$ (**2**) is obtained in the case of (ethoxyethynyl)lithium. In the reaction of the trimethylsilyl-substituted alkynylcarbene complex **1d** with 2,3-dimethyl-1,3-butadiene, the (η^3-vinylcarbene)Fe(CO)$_3$ complex **3** is produced via [2 + 4] cycloaddition, while the reaction with cyclopentadiene leads to formation of the η^4-vinylketene complex **4** through CO insertion at the carbene carbon, promoted by chelation of another internal carbon–carbon double bond after [2 + 4] cycloaddition.

Application of Fischer-type metal carbene complexes to organic synthesis continues to attract considerable attention.[1] Not only the reactivities of the metal–carbene functionality but also those of adjacent substituents, such as alkyls,[2] cyclopropyls,[3] alkenyls,[4] alkynyls,[5] and imino groups,[6] have showed potential in a number of reactions. However, a majority of the results have come from the

Scheme I

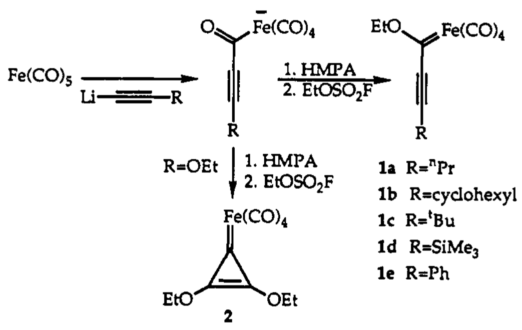

Table I. Reactions of Alkynyllithium with Iron Pentacarbonyl, Followed by O-Ethylation with Ethyl Fluorosulfonate

sustituent of alkynyllithium	product (yield,[a] %)	sustituent of alkynyllithium	product (yield,[a] %)
n-Pr	**1a** (44)	Me$_3$Si	**1d** (83)
cyclohexyl	**1b** (53)	Ph	**1e** (15)[b]
t-Bu	**1c** (90)	EtO	**2** (84)

[a] Isolated yield after flash chromatography. [b] 75% purity based on ^{1}H NMR spectroscopy.

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(1) For reviews, see: (a) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587–608. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. L.; Schubert, U.; Weiss, K. *Translation Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (c) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1.

(2) (a) Wulff, W. D.; Anderson, B. A.; Toole, A. T. *J. Am. Chem. Soc.* **1989**, *111*, 5458–5487. (b) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503–505.

(3) (a) Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854–6856. (b) Herndon, J. W.; Tumor, S. U. *Tetrahedron Lett.* **1989**, *30*, 295–296. (c) Herndon, J. W.; Tumor, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334–3335.

(4) (a) Anderson, B. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 8615–8617. (b) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659. (c) Brandvold, T. A.; Wulff, W. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 1645–1647. (d) Dötz, K. H.; Kuhn, W.; Müller, G.; Huber, B.; Alt, H. G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 812–813. (e) Wulff, W. D.; Tang, P.; Chan, K.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813–5832. (f) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726–6727.

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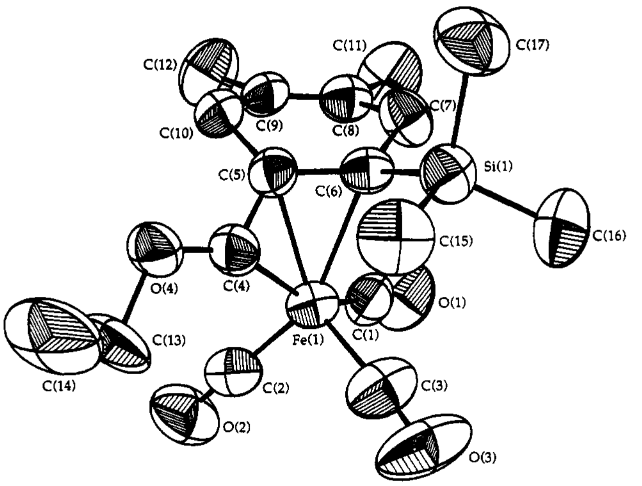
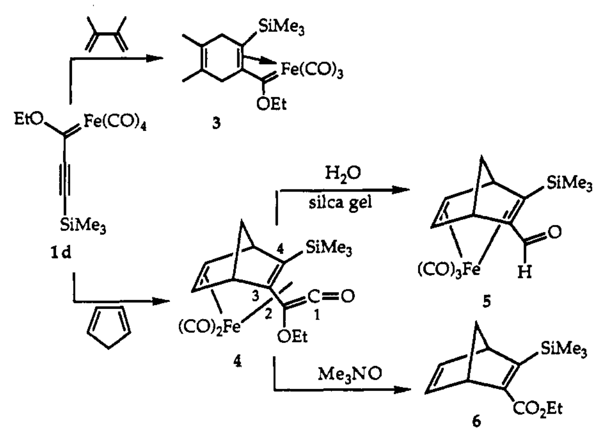


Figure 1. Structure of one of the two molecules in the crystal of **3**. Selected bond distances (Å) and angles (deg): Fe(1)–C(1), 1.807 (9); Fe(1)–C(2), 1.756 (9); Fe(1)–C(3), 1.789 (9); Fe(1)–C(4), 1.809 (8); Fe(1)–C(5), 2.118 (7); Fe(1)–C(6), 2.215 (7); C(4)–C(5), 1.42 (1); C(4)–O(4), 1.30 (1); C(5)–C(6), 1.40 (1); Fe(1)–C(4)–O(4), 150.7 (6); Fe(1)–C(4)–C(5), 81.1 (5); O(4)–C(4)–C(5), 124.1 (6); C(4)–C(5)–C(6), 113.6 (6); C(4)–C(5)–C(10), 122.6 (7).

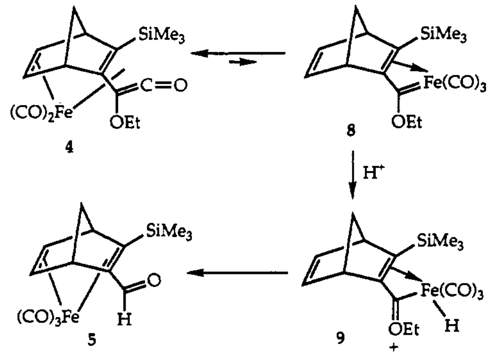
group 6 metal carbene complexes, while iron analogues have received relatively little attention.[7] In particular, it is especially rare to find studies on reactivities of conjugated substituents to the carbene carbon of iron complexes.[8] Now we describe the synthesis of iron alkynylcarbene complexes and the preliminary results from their reactions with 2,3-dimethyl-1,3-butadiene and cyclopentadiene.

By a procedure similar to that of producing simple iron carbene complexes,[7e] iron alkynylcarbene complexes **1a–e** were prepared from iron pentacarbonyl, alkynyllithium, and ethyl fluorosulfonate (Scheme I). Table I displays the results with a series of terminal alkynes:[9] The alkynylcarbene complexes are blackish purple oils with characteristic IR absorptions for the $Fe(CO)_4$ moiety and ^{13}C NMR resonances at ca. 280 ppm for the carbene carbons.[10]

Scheme II



Scheme III



For **1e** this procedure is less successful in providing a pure sample, due to partial decomposition during concentration of the resulting solution from a usual aqueous workup. Meanwhile, from the attempt to prepare an ethoxy-substituted alkynylcarbene complex, (diethoxycyclopropenylidene)$Fe(CO)_4$ (**2**) is obtained as a major product. The spectral properties of **2** are comparable to those of the known chromium analogues formed in parallel reactions.[11]

The reaction between **1d** and 2,3-dimethyl-1,3-butadiene for 5 h at 50 °C in THF led to the formation of the 1:1 adduct **3** as a major product. **3** was isolated as an orange oil in 57% yield after chromatography (silica gel/hexane) and crystallized from pentane/toluene. The molecular structure of **3** is shown in Figure 1.[12] The structure shows coordination of the conjugated C(5)–C(6) double bond and Fe–carbene carbon bond lengths considerably shorter than those in (η^1-carbene)iron complexes (1.945–2.007 Å).[13] The C(4)–C(5) bond length is also shorter than usual C(sp^2)–C(sp^2) single-bond lengths, while the C(5)–C(6) bond is much longer than those in free olefins.[14] Therefore, the

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[5] (a) Katherine, L. F.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 6419–6420. (b) Wang, S. L. B.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 4550–4552. (c) Camps, F.; Llebaria, A.; Moretó, J. M.; Ricart, S.; Viñas, J. M. *Tetrahedron Lett.* **1990**, *31*, 2479–2482. (d) Chan, K. S.; Wulff, W. D. *J. Am. Chem. Soc.* **1986**, *108*, 5229–5236. (e) Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1985**, *286*, C23. (f) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565–7567.

[6] (a) Dragisich, V.; Wulff, W. D. *Organometallics* **1990**, *9*, 2867–2870. (b) Murray, C. K.; Warner, B. P.; Dragisich, V.; Wulff, W. D.; Rogers, R. D. J. *Organometallics* **1990**, *9*, 3142–3151.

[7] (a) Semmelhack, M. F.; Park, J. *J. Am. Chem. Soc.* **1987**, *109*, 935–936. (b) Semmelhack, M. F.; Park, J. *Organometallics* **1986**, *5*, 2550–2552. (c) Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *Tetrahedron* **1984**, *106*, 5363–5364. (d) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750–6752. (e) Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 4099–4100.

[8] For reactions of (η^3-vinylcarbene)tricarbonyliron complexes, see: Mitsudo, T.; Watanabe, H.; Sasaki, T.; Yoshinobu, Y.; Takegami, Y.; Watanabe, Y. *Organometallics* **1989**, *8*, 368–378 and references therein.

[9] A typical procedure for **1d** follows: At −78 °C, to a solution of iron pentacarbonyl (2.00 mL, 15.2 mmol) in ether (50 mL) was added dropwise ((trimethylsilyl)ethynyl)lithium, generated by treatment of a solution of (trimethylsilyl)acetylene (2.20 mL, 15.6 mmol) in ether (50 mL) with *n*-BuLi (14.0 mmol in hexane) at −78 °C for 30 min. After 1 h at −78 °C, the solution was warmed to 25 °C over ca. 2 h, HMPA (30 mL) was added, and the deep brown solution was recooled to −78 °C. Ethyl fluorosulfonate (5.8 mL, 60 mmol) was added dropwise with stirring. After being stirred at −78 °C for 4 h, the reaction mixture was warmed slowly to 25 °C and partitioned between hexane and saturated aqueous sodium bicarbonate. After this solution was washed with water and saturated aqueous sodium chloride, dried over magnesium sulfate, and concentrated at 0 °C under vacuum, the residue was chromatographed (silica gel; hexane/ethyl acetate 100/1; under argon) to give 3.73 g (83%) of **1d**.

[10] Refer to the supplementary material for the spectral data of compounds **1**–**6**.

[11] Juneau, K. N.; Hegedus, L. S.; Roepke, F. R. *J. Am. Chem. Soc.* **1989**, *111*, 4762–4765.

[12] Crystal data for **3**: $C_{17}H_{24}O_4SiFe$, M_r = 376.31, triclinic, $P\bar{1}$, a = 10.455 (3) Å, b = 13.179 (3) Å, c = 15.134 (5) Å, α = 78.20 (2)°, β = 86.80 (2)°, γ = 80.07 (2)°, V = 2010 (1) Å^3, Z = 4, d_{calcd} = 1.240, monochromated Mo Kα radiation ($\lambda(K\alpha_1)$ = 0.7093 Å), μ = 8.2 cm^{-1}, $F(000)$ = 896, T = 296 K, Enraf-Nonius CAD4 diffractometer; 5571 unique reflections measured; 2751 reflections observed ($I > 3\sigma(I)$); empirical absorption correction; solved by Patterson and difference Fourier methods; full-matrix least-squares refinement; non-hydrogen atoms anisotropic; hydrogen atoms included at calculated positions; final agreement indices $R(F)$ = 0.050, $R_w(F)$ = 0.054, GOF = 0.43. The asymmetric unit contains two crystallographically independent molecules of **3**, the structures of which are nearly identical.

[13] (a) Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *Inorg. Chem.* **1982**, *21*, 1321–1328. (b) Huttner, G.; Gartzke, W. *Chem. Ber.* **1972**, *105*, 2714–2725. (c) Findley, P. F.; Mills, O. S. *J. Chem. Soc. A* **1969**, 1279–1285.

[14] *Tables of Interatomic Distances and Configuration of Molecules and Ions*; Sutton, L. E., Ed.; The Chemical Society: London, 1965.

vinylcarbene ligand in the present complex may be described as an η^3-bonded one with a strongly coordinated vinyl group.[15]

Reaction of **1d** with cyclopentadiene in THF was completed in 80 min at 40 °C, leading to another 1:1 adduct **4**, a portion of which transformed during chromatography (silica gel/hexane) into the (norbornadiene)$Fe(CO)_3$ derivative **5**, which has a formyl substituent. The isolated yields were 27% and 69%, respectively. In a separate experiment, **4** was converted to **5** quantitatively in 30 min by treatment with a small amount of water and silica gel in hexane at 25 °C. When **4** was oxidatively decomplexed with Me_3NO in acetone, the ethyl ester **6** was obtained as a major product in 48% yield (Scheme II).

The initial product **4** is formulated as an η^4-vinylketene complex by the aid of the above chemical transformations as well as on the basis of spectroscopic analysis. The IR absorption at 1733 cm^{-1} (in CH_2Cl_2) is indicative of a carbonyl group, and the ^{13}C NMR (in C_6D_6) resonance for the carbonyl carbon appears at 231.6 ppm. The other three resonances for the quaternary carbons are observed at 102.5, 86.6, and 32.3 ppm, which are assigned to C(2), C(3), and C(4), respectively, on the η^4-vinylketene moiety.[16] Meanwhile, the ^1H NMR resonances for two vinyl protons at 3.78 and 3.64 ppm indicate coordination of the corresponding carbon–carbon double bond to the iron. Considering the 18-electron rule, the coordination is also inferred from the IR absorptions in the carbonyl region at 2011 and 1957 cm^{-1} and the ^{13}C NMR resonances at 216.9 and 212.6 ppm for two carbonyl ligands.

In (η^3-vinylcarbene)iron(0) complexes analogous to **3**, carbonylation of the carbene carbon, leading to formation of the corresponding (η^4-vinylketene)iron(0) complexes, has been observed under atmospheric CO pressure.[8,17] However, carbonyl–vinylcarbene coupling did not occur in **3** under medium CO pressure (40 psi). Thus, the formation of **4** seems to be promoted by chelation of another internal carbon–carbon double bond as a donor ligand.[18]

A pathway, involving the reverse process of the carbonyl–vinylcarbene coupling, is proposed for the transformation of **4** into **5** in Scheme III: vinylcarbene **8** is generated by decarbonylation of **4** with decomplexation of the carbon–carbon double bond. Protonation on the iron of **8** leads to formation of the cationic iron hydride species **9**, which can be promoted by electron donation from the ethoxy group. Then, reductive elimination is accompanied by detachment of the ethyl group and recoordination of the carbon–carbon double bond to give **5**.

Acknowledgment. This work was supported by the Research Institute of Industrial Science & Technology and the Korean Ministry of Education.

Supplementary Material Available: Textual presentation of spectral data for **1a–e** and **2–6** and tables of atom coordinates, bond lengths, bond angles, and anisotropic temperature factors for **3** (10 pages); a listing of observed and calculated structure factors for **3** (15 pages). Ordering information is given on any current masthead page.

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(15) Nakatsu, K.; Mitsudo, T.; Nakanishi, H.; Watanabe, Y.; Takegami, Y. *Chem. Lett.* **1977**, 1447–1448.

(16) The assignment is consistent with that for the analogous (η^4-vinylketene)iron(0) complex, which appears in ref 8. For other (η^4-vinylketene)iron(0) complexes, see: Alcock, N. W.; Richards, C. J.; Thomas, S. E. *Organometallics* **1991**, *10*, 231–238 and references therein.

(17) Klimes, J.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 205; *Angew. Chem.* **1982**, *94*, 207.

(18) There is an example for carbonyl–vinylcarbene coupling by addition of chelating donor ligands: Myar, A.; Asaro, M. F.; Glines, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2215–2216.

Solid-State Organometallic Chemistry of Tripodal (Polyphosphine)metal Complexes. C–H Activation Reactions at Cobalt(I) Encapsulated into the Tetraphosphine $P(CH_2CH_2PPh_2)_3$

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Summary: The solid–vapor reactions of $[(PP_3)Co(N_2)]BPh_4$ with HC≡HC, $H_2C=CH_2$, CH_2O, MeCHO, and CO are described ($PP_3 = P(CH_2CH_2PPh_2)_3$). The organic molecules either displace N_2, forming a 1:1 complex, or undergo C–H bond cleavage at cobalt to give intermediates that may optionally eliminate H_2 or promote hydrogen transfer from metal to coordinated organic ligand.

Little attention has been given to solid-state organometallic chemistry, essentially limited to the reactions of interstitial $[(PPh_3)_2Ir(H)_2]^+$ in lattices comprised of anionic metal oxide clusters.[1]

In this communication, we describe studies designed to exploit some unique features of the tetraphenylborate salts of tripodal (polyphosphine)metal complexes in the solid–vapor reactions with small organic molecules. We report here preliminary data on the reactions of $[(PP_3)Co(N_2)]BPh_4$ (**1**)[2] with HC≡HC, $H_2C=CH_2$, CH_2O, MeCHO, and CO ($PP_3 = P(CH_2CH_2PPh_2)_3$).

Compound **1** appears as purple-red crystals, quite stable in the solid state under argon or under reduced pressure (0.1 Torr) at 100 °C. Differential scanning calorimetry (DSC) shows no phase change up to 173 °C, at which temperature the compound begins to melt with decomposition. The complex cation in **1** exhibits trigonal-bipyramidal geometry in both the solid state[3] and solution[2] with

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(1) (a) Siedle, A. R.; Newmark, R. A. *Organometallics* **1989**, *8*, 1442. (b) Siedle, A. R.; Newmark, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 2058. (c) Siedle, A. R.; Newmark, R. A.; Sahyun, M. R. V.; Lyon, P. A.; Hunt, S. L.; Skarjune, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 8346.

(2) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

(3) Crystal data: monoclinic, space group $P2_1/n$, $a = 13.049$ (2) Å, $b = 35.635$ (4) Å, $c = 13.154$ (1) Å, $\beta = 100.31$ (1)°, $d_{calcd} = 1.23$ g cm^{-3}, $Z = 4$, $n_{obsd} = 2876$, $R = 0.087$. Selected bond distances (Å) and angles (deg): $Co-P_{equatorial}$ (av) = 2.230 (5), $Co-P_{apical}$ = 2.146 (4), Co–N = 1.86 (1), N–N = 1.08 (2); $P_{apical}-Co-N$ = 176.3 (4), Co–N–N = 178.1 (1).

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