(Alkynylcyclobutadiene)tricarbonyliron: New Organometallic Alkynes

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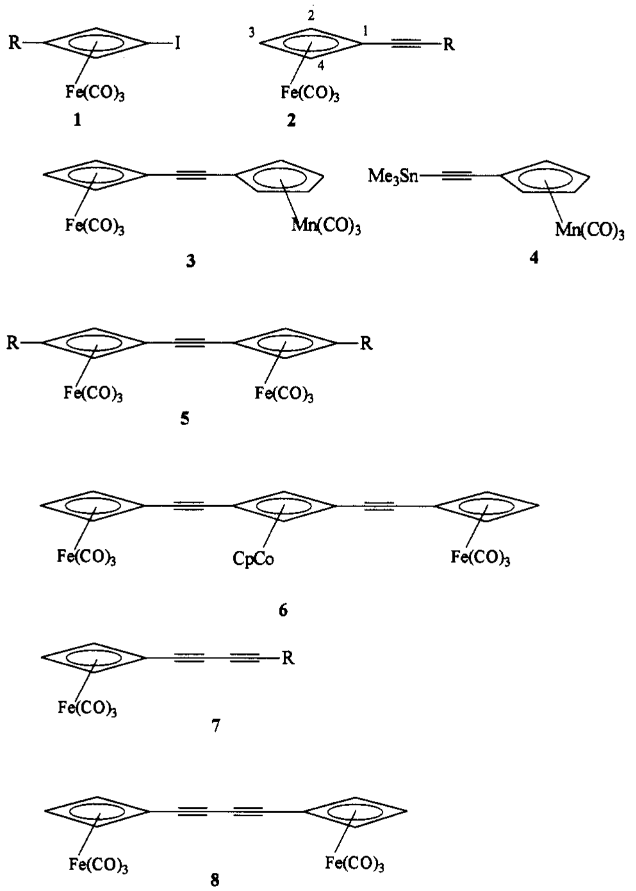
*Summary: Treatment of (iodocyclobutadiene)tricarbonyliron (**1a**) with different stannylated alkynes under the conditions of Stille coupling gives the corresponding alkynylated complexes in 35–69% yields. A dinuclear (1,2-bis[(cyclobutadiene)tricarbonyliron]ethyne) and a heterometallic trimeric complex are also obtained by this route. Stannylated butadiynes also couple readily with **1a** to the corresponding (cyclobutadiene)tricarbonyliron-substituted diynes.*

(Cyclobutadiene)metal complexes represent an intriguing class of compounds due to the properties of the cyclic π ligand.[1] One remarkable feature is the ability of (cyclobutadiene)tricarbonyliron complexes[2] to liberate free cyclobutadiene under oxidative conditions; the bound ligand is also reactive toward electrophilic reagents, leading either to substitution[1b] or ring enlargement.[3] It is also possible to exchange one of the carbon monoxide ligands with phosphines[4] or dimerize this type of compound with CO loss[5] without affecting the cyclobutadiene ring.

The alkyne unit is a versatile functional group which undergoes a large number of useful transformations.[6] Juxtaposition of the cyclobutadiene and the alkyne entity in one molecule should confer unusual features to such a compound, making it suitable not only as a model to study rearrangements[7] but also as a precursor for metal organic polymers.[8–10]

During the last few years an increasing number of publications have dealt with the synthesis of alkyne-substituted metallocenes[11] and half-sandwich complexes,[12] due to their possible applicability in materials science.

Chart I



Much less has been done in the field for alkynyl-substituted (cyclobutadiene)metal complexes.[13] The only known compounds are Vollhardt's (1,2- and (1,3-dialkynylcyclobutadiene)(cyclopentadiene)cobalt complexes,[7] which undergo an unusual rearrangement upon flash vacuum pyrolysis.

Up to now (cyclobutadiene)tricarbonyliron complexes either singly or multiply substituted with alkynyl groups have not been preparatively accessible.[13] This is probably due to the lack of appropriate starting materials. The development of a simple and efficient synthesis of monoiodides **1a** (R = H) and **1b** (R = $SiMe_3$)[14a] has changed

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[2] (a) Watts, L.; Fizpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253. (b) See also ref 1b,c and references cited therein.

[3] For example, reaction with benzoyl chloride yields the corresponding cyclopentadienyliron complex.[1c]

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[8] For example: *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K., Allcock, H. R., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1988.

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[12] (a) Lo Sterzo, C.; Miller, M. M.; Stille, J. K. *Organometallics* **1989**, *8*, 2331. Lo Sterzo, C.; Stille J. K. *Organometallics* **1990**, *9*, 687. (b) Bunel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Gonzalez, M.; Munoz, N.; Manriquez, J. M. *Organometallics* **1988**, *7*, 789.

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Table I. NMR Spectroscopic Data for the Compounds[a]

	$\delta(^1H)$			$\delta(^{13}C\{^1H\})$					
compd	H–C_3 (s)	H–$C_{2,4}$ (s)	other	C_3	$C_{2,4}$	C_1	alkyne C	CO	other
2a (R = H)	4.00	4.32	2.85	64.35	66.53	59.22	78.02, 76.70	213.04	
2b (R = $SiMe_3$)	3.93	4.30	0.16	63.63	66.70	61.21	96.27, 97.43	213.25	–0.32
3[b]	4.01	4.32	4.94, 4.65	65.28	66.76	59.86	82.44, 82.27	213.49, 224.35	81.42, 82.01, 86.53
5a (R = H)	4.01	4.30		64.78	66.35	60.28	82.83	213.01	
5b (R = $SiMe_3$)		4.31	0.07	69.59[c]	71.23	68.25[c]	82.34	213.57	
6	3.97	4.28	4.50, 4.98 (Cp)	64.18[c]	66.11	62.61	82.46, 87.06	213.32	54.41, 64.01[c]
7a (R = H)	4.05	4.36	2.43	66.13	67.17	57.19	68.15, 69.31, 71.49, 73.78	212.49	
7b (R = $SiMe_3$)	4.07	4.37	0.20	66.12	67.13	57.76	70.52, 74.59, 87.83, 91.13	212.51	–0.54
8	4.08	4.37		66.37	67.15	57.91	74.26, 75.60	212.55	

[a] At ambient temperature in $CDCl_3$. [b] ^{13}C NMR spectrum in C_6D_6. [c] Order unknown.

this situation, thereby circumventing the use of Pettit's acetoxymercuration route.[14b]

Iodides **1** should be appropriate partners in Stille[12] type couplings: Treating **1a** with (trimethylsilyl)(trimethylstannyl)acetylene, $Pd_2(dba)_3$, and triphenylarsine[15] in DMF yields a yellow crystalline (mp 62 °C) material after high-vacuum sublimation. It can be handled without problems under atmospheric conditions. The proton NMR of the compound shows three singlets in a ratio of 9:1:2 at δ 0.16, 3.93, and 4.30, representing the trimethylsilyl group and the three protons of the complexed cyclobutadiene ring, respectively. In the carbon NMR seven signals are observed at δ –0.32 (q, $SiMe_3$), 61.21 (s), 63.63 (d), 66.70 (d), 96.27 (s), 97.43 (s), and 213.25 (s); the three signals between 60 and 70 ppm are assigned to the cyclobutadiene ligand, with the most intense signal at δ 66.70 belonging to the equivalent carbons C_2 and C_4 of the ring. The resonances further downfield correspond to the two alkyne carbons and the bound carbon monoxide. The mass spectrum shows prominent peaks at 288, 260, 232, and 204 amu, which stem from the molecular ion and species formed by successive loss of one to three carbon monoxide ligands. These spectral data are in full accordance with the formation of the expected coupling product **2b**.[16,17] Deprotection with potassium carbonate in methanol affords the parent **2a** in almost quantitative yield (93%). It is a moderately air-stable yellow oil at room temperature and crystallizes at temperatures <–20 °C. In addition to the two signals for the cyclobutadiene ligand, the proton NMR of **2a** shows a resonance at δ 2.85, diagnostic for the presence of a free alkyne group.

Treatment of **1a** with the known acetylene **4**[12] under Pd conditions gives the heterobimetallic acetylene-bridged compound **3** in 55% yield. It was not possible to resolve the cyclopentadienyl coupling in the proton NMR spectrum of **3**. Instead, two slightly broadened singlets at δ 4.65 and 4.94 were observed. This is probably due to the presence of a paramagnetic trace impurity in **3**.

We also explored the Pd-catalyzed reaction of **1a** with bis(trimethylstannyl)acetylene to give the hitherto unknown **5a** (R = H) in 65% isolated yield; it represents one of the few known examples of dimeric (cyclobutadiene)tricarbonyliron complexes.[7] With **1b** (R = $SiMe_3$) as a coupling partner, the yield of product **5b** (R = $SiMe_3$) drops to 35%. Using the bisstannylated (1,3-dialkynylcyclobutadiene)(cyclopentadiene)cobalt compound (derived from Vollhardt's (1,3-dialkynylcyclobutadiene)(cyclopentadiene)cobalt[7a] by action of $(Et)_2N{-}SnMe_3$[18]) in the coupling with **1a** yields a single product (dec pt >202 °C) which could be isolated after chromatography over silica gel. Proton NMR spectroscopy of the material revealed the complete absence of signals in the region where acetylenic protons should be observed. This supports the conclusion that the reaction does not stop at the stage of singly coupled dimer under these conditions. Instead, the trimer **6** is formed quite efficiently in 55% yield.

Some diacetylenes are known to participate in a topochemical polymerization reaction.[19] Spurred by this opportunity, we also tried to couple **1a** with (trimethylsilyl)(trimethylstannyl)butadiyne. When the standard experiment was performed with THF as solvent (DMF proved to be unsuccessful for coupling of **1a** with diynes), it was possible to isolate the crystalline diyne **7b** (R = $SiMe_3$) in 44% yield after filtration over neutral aluminum oxide; deprotection of **7b** with potassium carbonate/methanol in a second step afforded the somewhat sensitive

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(16) General procedure:[15] A slight excess of **1a**, the respective stannane, 2 mol % of $Pd_2(dba)_3$, and 8 mol % of triphenylarsine are placed in a Schlenk flask under argon. Water and oxygen-free DMF (10–25 mL) are added. The mixture is stirred for 18 h at ambient temperature and then for 2 h at 35 °C. Isolation and purification of the obtained compounds: The crude reaction mixture is dissolved in ca. 80 mL of a 1:3 mixture of dichloromethane and petroleum ether and extracted several times with 100 mL of water. After removal of the organic solvents the material is chromatographed over neutral active aluminum oxide (ca. 5 cm × 1 cm). For the silylated derivatives **2b** and **7b** petroleum ether was used as eluent; for **3**, **5**, and **8** a 9:1 mixture of petroleum ether and dichloromethane was used. In this case of **6** it was necessary to chromatograph over flash-silica gel (11 cm × 2 cm) with a 8:2 mixture of petroleum ether and dichloromethane. To obtain analytically pure material, **2a** and **2b** were sublimed or distilled at reduced pressure,[17] as was the more sensitive diyne **7a**, which was still slightly contaminated by a impurity originating from petroleum ether. If desired, all solid compounds can be recrystallized from a 1:1 mixture of petroleum ether and dichloromethane.

(17) (a) Physical data for the new compounds are as follows. **2b**: 69% yield; mp 62 °C; sublimes at 80 °C/0.005 mmHg; IR (KBr) 2959, 2041, 1980, 1964, 1949 cm^{-1}; MS (EI) *m/z* 288 [M], 260, 232, 204. Anal. Calcd for $C_{12}H_{12}O_3FeSi$: C, 50.02; H, 4.20. Found: C, 49.98; H, 4.27. **2a**: 93% yield from **2b**; bp 20 °C/0.005 mmHg; IR (KBr) 3305, 3142, 3131, 3124, 2051, 1973 cm^{-1}; MS (EI) *m/z* 216 [M], 188, 160, 132. **3**: mp 126 °C; IR (KBr) 3125, 3104, 2044, 2015, 1972, 1926, 1919, 1149 cm^{-1}; MS (EI) *m/z* 418 [M], 390, 362, 334, 306, 278, 250. **5a**: 55% yield; mp 98–100 °C; IR (KBr) 3140, 3125, 3104, 2039, 1974, 1950, 1921 cm^{-1}; MS (FD) *m/z* 406 [M]. Anal. Calcd for $C_{16}H_6O_6Fe_2$: C, 47.34; H, 1.49. Found: C, 47.16; H, 1.52. **5b**: 35% yield; mp 86–87 °C; IR (KBr) 3117, 3109, 2960, 2925, 2901, 2047, 2035, 1973, 1965, 1251, 1011 cm^{-1}; MS (EI) *m/z* 550 [M], 522, 494, 466, 438, 410, 382. Anal. Calcd for $C_{22}H_{22}O_6Fe_2Si_2$: C, 48.04; H, 3.94. Found: C, 48.03; H, 3.95. **6**: 55% yield; dec pt 202 °C without melting; IR (KBr) 3130, 3111, 3102, 3090, 2059, 2054, 1963, 1953 cm^{-1}; MS (EI) *m/z* 604 [M], 576, 548, 520, 492, 464, 436. Anal. Calcd for $C_{27}H_{13}O_6Fe_2Co$: C, 53.69; H, 2.17. Found: C, 53.72; H, 2.16. **7b**: 55% yield mp 62–63 °C; IR (KBr) 3124, 3116, 3104, 2960, 2926, 2900, 2098, 2057, 2048, 1985, 1969 cm^{-1}; MS (EI) *m/z* 312 [M], 284, 256, 228. Anal. Calcd for $C_{14}H_{12}O_3FeSi$: C, 53.86; H, 3.87. Found: C, 53.92; H, 3.97. **7a**: IR (KBr) 3307, 3116, 3061, 3029, 2227, 2200, 2057, 1984 cm^{-1}; MS (EI) *m/z* 240 [M], 212, 184, 156, 130. **8**: 67% yield; mp 129 °C; IR (KBr) 3133, 3120, 3105, 2063, 2049, 1982, 1974, 1938 cm^{-1}; MS (FD) *m/z* 430 [M]. Anal. Calcd for $C_{18}H_6O_6Fe_2$: C, 50.29; H, 1.41. Found: C, 50.19; H, 1.53.

(18) (a) Reaction is performed by action of $(Et_2)N{-}SnMe_3$ on Vollhardt's dialkynylcyclobutadiene cobalt complex analog as described in ref 12. (b) Synthesis of $(Et)_2N{-}SnMe_3$: Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1944.

(19) Whole issue about poly(diacetylenes): *Adv. Polym. Sci.* **1984**, *63*.

terminal diyne **7a** (R = H) in 57% yield. Using bis(trimethylstannyl)butadiyne under the same conditions with **1a** as coupling partner gives rise to the isolation of **8** in 67% yield.

In summary, the coupling reaction of iodide **1** with several alkynes gives rise to novel structures of the type **2**–**8**, which all bear the hitherto unknown cyclobutadiene–alkyne moiety. The described coupling reaction should have a larger scope and be applicable to attach a number of different organic and organometallic alkynes to the (cyclobutadiene)tricarbonyliron moiety. The preparation of oligomeric structures consisting only of cyclobutadiene–alkyne or –butadiyne units is a challenging aspect for future developments. Additionally, reactions and rearrangements of these compounds will be reported in due course.

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