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Synthesis and Characterization of Diethynylated Tricarbonyl(cyclobutadiene)iron Complexes: The *ortho*-Lithiation Concept

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*Summary: The diethynylated complexes **6** and **7** have been synthesized by employing a deprotonation/iodination/coupling procedure. By suitable choice of the metalation conditions formation of the ortho iodide **4** as the only product was achieved, allowing the synthesis of **7** selectively.*

In an elegant study Fritch and Vollhardt[1] discovered in 1979 that the dimerization of bis(trimethylsilyl)butadiyne and the codimerization of bis(trimethylsilyl)acetylene with bis(trimethylsilyl)hexatriyne over Cp-$Co(CO)_2$ is a good method for synthesizing the diethynylcyclobutadiene complexes **1a**,**b**, constituting the only known examples of organometallics carrying an ethynylated cyclobutadiene ring.

Despite its simplicity, the Vollhardt method is only applicable to the preparation of Cp–cobalt complexes: the synthesis of derivatives carrying two differently substituted alkyne residues using this dimerization has severe limitations. One is the troublesome synthesis of unsymmetrically substituted hexatriynes,[2] and the (expected) lack of regioselectivity in the dimerization of differently substituted butadiynes (to furnish derivatives of **1b**) is a second.

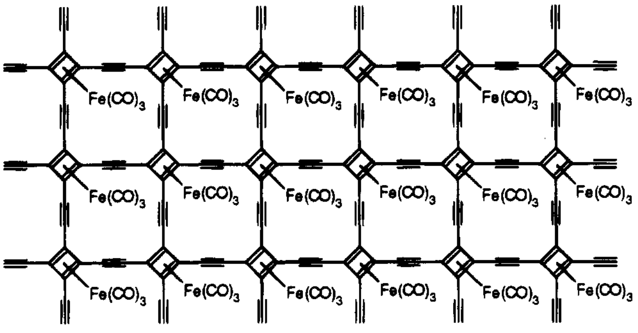

Figure 1. An organometallic all-carbon net.

We are involved in a program aimed at the synthesis of all-carbon networks[2b] supported by organometallic fragments (Figure 1) and have identified multiply ethynylated cyclobutadiene complexes of iron[3] and cobalt[4] as suitable building blocks for this purpose. One of our prime targets in this context are derivatives of diethynyl-substituted tricarbonyl(cyclobutadiene)irons. They represent useful starting materials for oligomerization and polymerization reactions leading to either linear or cyclic substructures of the desired carbon net (Figure 1).

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[1] Fritch, J. R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1978**, *100*, 3643. Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590.

[2] (a) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943 and references cited therein. Kende, A. S.; Smith, C. A. *J. Org. Chem.* **1988**, *53*, 2655 and references cited therein. (b) F. Diederich, *Nature* **1994**, *369*, 199.

[3] Wiegelmann, J. E. C.; Bunz, U. H. F. *Organometallics* **1993**, *12*, 3792. Bunz, U. H. F.; Enkelmann, V. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1653. Bunz, U. H. F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1073. Bunz, U. H. F.; Enkelman, V. *Organometallics* **1994**, *13*, 3823.

[4] Altmann, M.; Bunz, U. H. F. *Makromol. Chem. Rapid. Commun.* **1994**, *15*, 785.

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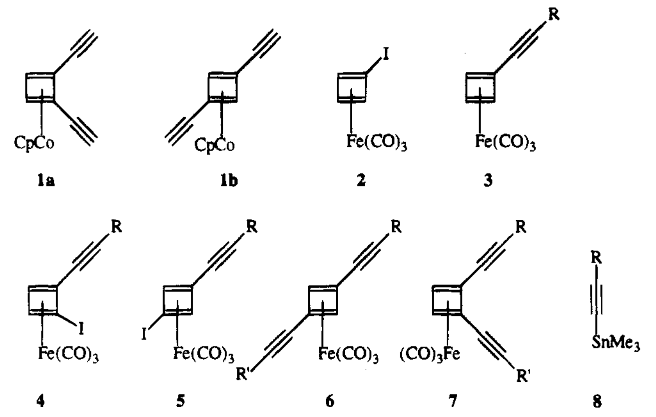
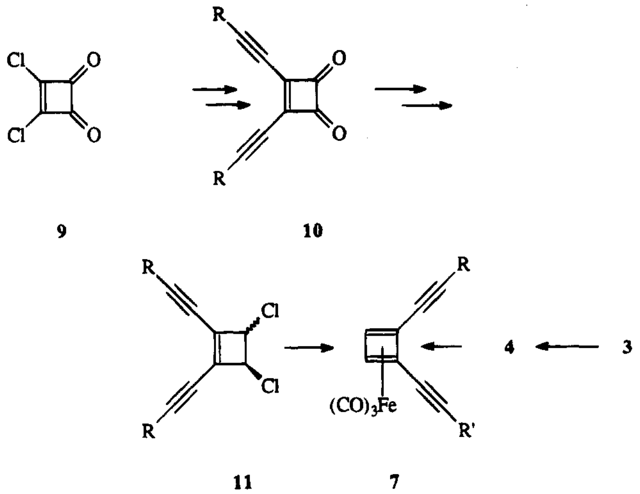
Chart 1



There should exist at least two different approaches for the preparation of the diethynyls **7**. The first approach would be to synthesize the diethynylated 3,4-dichlorocyclobutene precursor **11** (see Scheme 1) by starting out from dichlorocyclobutenedione (**9**), leading to Diederich's[5] 3,4-diethynylcyclobutenediones (**10**), which after reduction to the corresponding diols[5] should be easily converted to 3,4-dichlorocyclobutenes.[6] Reaction with diiron enneacarbonyl in turn should give rise to the formation of the desired complexes **7**. The second route is more straightforward and uses the facile deprotonation of tricarbonyl(cyclobutadiene)iron.[7] The repetitive application of a deprotonation/iodination/coupling sequence would then give access to diethynylated compounds **6** and/or **7**. Since we were able to synthesize **3a** in multigram quantities, the second retrosynthetic route became even more attractive, particularly with the presupposition that consecutive multiple functionalization of π-bound ligands has rarely been used.[7b]

Alkyne **3a** was treated with 1.2 equiv of precooled *sec*-butyllithium[8] in THF for 30 min at −78 °C. The initially light yellow reaction mixture darkened considerably during this time. A solution of 1,2-diiodoethane in THF was added: the iodination was accompanied by vigorous evolution of ethylene. After aqueous workup and sublimation a yellow crystalline material (mp 81 °C) was isolated. Its proton NMR spectrum showed three siglets at δ 0.18, 4.21, and 4.70 in the ratio 9:1:1, indicating the formation of one compound, *viz.* the *ortho* iodide **4a** in 74% yield. Support of this assignment was gathered from the ^{13}C NMR spectrum, which displayed eight lines. At −0.34 ppm the signal of the trimethylsilyl group was observed, while four lines (27.88 (s), 65.36 (d), 66.29 (s), 67.60 (d) ppm) were attributed to the ring and two singlets (95.69, 99.69 ppm) to the alkyne carbons. The singlet for the three CO groups was recorded at δ 212.52. The ^{13}C NMR spectrum of **5a**, on the other hand, would display only three signals for the cyclobutadiene ring. The interpretation of the nuclear magnetic resonance spectra thus unequivocally supports the formation of the *ortho* product **4a**.

Scheme 1. Retrosynthetic Analysis for Possible Routes to Diethynyl-Substituted Tricarbonyl(cyclobutadiene)iron Complexes 7



Reaction of **4a** with stannylated alkyne **8a** under conditions developed by Farina[9] yielded material contaminated by catalyst residues which we had never been able to remove. If the Beletskaya catalyst system ($PdCl_2(CH_3CN)_2$)[10] was used, the desired diyne **7a**[11] was formed in a clean reaction (Table 1). The proton NMR spectrum of **7a** shows one singlet for the ring (4.22 ppm) and one for the trimethylsilyl groups (0.20 ppm). The ^{13}C NMR spectrum displays six signals as expected.

Using the *ortho* iodide **4a**, a series of unsymmetrical substituted diynes **7** was obtained by coupling with stannylated alkynes **8** (Table 1; yields and substituent keys). It is worth mentioning that coupling of **4a** with the hexatriyne derivative **8d** is also successful, but a less active catalyst has to be used to prevent decomposition of the formed triyne by the Beletskaya catalyst system; this is one of the rare examples where a triyne

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[5] Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 1607.

[6] (a) Adams, C. M.; Crawford, E. S.; Salim, E. *Tetrahedron Lett.* **1992**, 3963. Adams, C. M.; Joslin, S. A.; Crawford, E. S.; Schemenaur, J. E. *Organometallics* **1993**, *12*, 656. (b) Efraty, A. *Chem. Rev.* **1977**, *77*, 691. (c) *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Frankfurt, 1981; Organoiron Compounds B7, p 25. (d) Berens, G.; Kaplan, F.; Rimerman, R.; Roberts, B. W.; Wissner, A. *J. Am. Chem. Soc.* **1975**, *97*, 7076. Grubbs, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6693.

[7] (a) Bunz, U. *Organometallics* **1993**, *12*, 3594. (b) An exception is the case of ferrocenes and ruthenocenes, where directed *ortho*-lithiation of substituted ferrocenes gives an entry to 1,2-disubstituted ferrocene derivatives: see *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Frankfurt, 1981; Organoiron Compounds.

[8] Metalation leading to the *ortho* iodide **4a**. A 1.30 g (4.51 mmol) amount of **3a**, dissolved in 150 mL of absolute THF, is placed in a flame-dried, argon-flushed Schlenk flask and cooled to −78 °C; 3.9 mL (5.41 mmol) of *sec*-BuLi, which is delivered as a 1.4 M solution in cyclohexane, is coated on the precooled walls of the reaction vessel. In this procedure the cyclohexane solution freezes. By slight shaking the *sec*-BuLi is dissolved within 10 min into the solution of **3a**. After 15 min of stirring 1,2-diiodoethane (1.62 g, 6.00 mmol in ca. 10 mL of THF) is added into the reaction mixture; after 10 min the cooling bath is removed and the deep red solution stirred for 1 h at ambient temperature, poured into a pentane/$Na_2S_2O_3$/water mixture, and partitioned. The aqueous phase is extracted several times with pentane. The combined organic phases are washed several times with water. Drying over $MgSO_4$, removal of pentane, and chromatography over flash silica gel (pentane) yields 1.28 g (74%; yellow crystals, mp 81 °C) of **4a**. This procedure leads to the isolation of exclusively (>95%) *ortho* iodinated product.

[9] Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585 and references cited therein.

[10] Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551 and references cited therein.

[11] Coupling reaction leading to diyne **7a**. A flame-dried and argon-flushed Schlenk flask with magnetic stirbar is charged with 1.00 g (2.42 mmol) of **4a**, 784 mg (3.86 mmol) of **8a**, 19 mg (72 μmol) of $PdCl_2(CH_3CN)_2$, and 20 mL of water- and oxygen-free DMF. After stirring for 18 h at ambient temperature, again 3 mol % of the catalyst is added under argon to the reaction mixture and the solution is stirred for another 18 h. The crude reaction mixture is dissolved in petroleum ether and extracted several times with a large amount of water. After drying over $MgSO_4$ and removal of petroleum ether, the residue is chromatographed over flash silica gel with pentane as eluent to yield 726 mg (78%; yellow crystals, mp 64 °C) of **7a**.

Table 1. Substituent Key for 3, 4, 7, and 8 and Yields of 4, 6, and 7

3–5	R	yield of 4, %	8	R′	6, 7	yield of 6 or 7, %
3a	SiMe$_3$	74				
	H	93				
3b	Si(*i*-Pr)$_3$	77				
3c	Ph	71				
5a	SiMe$_3$	74	**a**	SiMe$_3$	**6a**	71
4a			**a**	SiMe$_3$	**7a**	78
5a			**b**	Si(*i*-Pr)$_3$	**6b**	19
4a			**b**	Si(*i*-Pr)$_3$	**7b**	72
4a			**c**	*tert*-butyl	**7c**	57
4a			**d**	(C≡C)$_2$-*tert*-butyl	**7d**	28
4a			**e**	Ph	**7e**	65
4b	Si(*i*-Pr)$_3$	62	**a**	SiMe$_3$	**7b**	62
	H	93		H	**7f**	99
	H	93		H	**6f**	93

is coupled to an "aromatic" iodide. Table 1 shows that the *ortho* lithiation is observed not only in the case of the trimethylsilyl-carrying alkyne **3a** but also in the case of a triisopropylsilyl group being attached to the alkyne (**3b**).

When the deprotonation reaction is carried out by adding the organolithium base without prior cooling to a solution of **3a** in THF (at −78 °C), the formation of a product mixture[12] containing **4a** and **5a** is observed after quenching with diiodoethane at −78 °C. Unfortunately it is difficult to separate the mixture by column chromatography, but we were able to isolate the pure *para* iodide **5a** after repeated chromatography. After the Pd-catalyzed coupling of the mixture with **8a** was conducted, separation of **7a** from its faster eluting isomer **6a**[13] (fortunately) is achieved by flash chromatography (silica gel/pentane). The proton NMR of **6a** shows two signals (4.58 (s), 0.13 (s) ppm) in the ratio 1:9, while the ^{13}C NMR displays six signals in variance from the spectral data obtained for **7a**.

In the case of the trimethylsilyl-substituted bis(alkynes) **6a** and **7a** desilylation to obtain the parents **6f** and **7f**[14] was carried out by stirring with potassium carbonate in methanol for 20 min. Extractive workup yields the free diynes almost quantitatively. Surprisingly, they are stable under ambient conditions for a few days as for the other newly synthesized compounds. The diethynyls and the iodoethynyls **4**–**7** are all yellow crystalline solids or oils. Storage in a deep freeze renders the materials unchanged for an indefinite period (greater than several months) of time.

In conclusion, we have been able to show that the synthesis of the hitherto unknown tricarbonyl(dialkynylcyclobutadiene)iron complexes is achieved without difficulty by utilizing a repetitive deprotonation/iodination/coupling sequence. A particular advantage in the use of this route is that bis(alkynes) carrying two different protecting groups can be prepared easily. In the future we will show that this methodology is useful in synthesizing dumbbell-shaped and cyclic complexes of cyclobutadiene complexes carrying the ene–diyne motif.

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Supplementary Material Available: Text giving detailed synthetic procedures, complete characterization data, and systematic names for all new compounds (2 pages). Ordering information is given on any current masthead page.

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(12) Metalation leading to the *ortho/para* mixture **4a/5a**. A 1.30 g (4.51 mmol) amount of **3a** is placed in flame-dried and argon-flushed Schlenk tube. After addition of 150 mL of THF the reaction mixture is cooled to −78 °C. *sec*-BuLi (3.86 mL, 5.41 mmol) is injected without prior cooling into the solution of the alkyne and the protocol described in ref 8 is followed. A mixture of **4a** and **5a** (1.35 g, 72%) is isolated. Determination of the isomeric ratio **4a**:**5a** (3.1:1.0) is achieved by integrating over the ring protons of the mixture. The complete separation of the iodides **4a** and **5a** is difficult. Fractions enriched in **5a** was obtained by repeated chromatography over flash silica gel (pentane).

(13) Coupling reaction leading to the *ortho/para* mixture **6a/7a**. The **4a/5a** mixture (850 mg, 2.06 mmol), 666 mg (3.28 mmol) of **8a**, and 16 mg (61 μmol) of PdCl$_2$(CH$_3$CN)$_2$ in ca. 10 mL of DMF is treated as described in ref 11. The resulting mixture is chromatographed over flash silica gel (pentane). **6a** (174 mg, 19%; yellow crystals, mp 95 °C): IR (KBr, cm^{-1}) ν 3194, 2964, 2928, 2874, 2164, 2057, 1997, 1466, 1383; ^{1}H NMR (CDCl$_3$) δ 0.16 (s, 18 H), 4.61 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ −0.41, 61.04, 69.54, 95.35, 97.72, 212.35; MS (EI; *m/z*) 384 [M1+], 356, 328, 300, 179. Anal. Calcd for $C_{17}H_{20}O_3Si_2Fe$: C, 53.12; H, 5.24. Found: C, 53.11; H, 5.25. **7a** (445 mg, 56%; yellow crystals, mp 64 °C): IR (KBr, cm^{-1}) ν 3127, 2958, 2900, 2146, 1991, 1986, 1980, 1434; ^{1}H NMR (CDCl$_3$) δ 0.20 (s, 18 H), 4.24 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ −0.23, 64.86, 66.23, 95,98, 98.93, 212.38; MS (EI; *m/z*) 384 [M$^+$], 356, 328, 300, 178. Anal. Calcd for $C_{17}H_{20}O_3Si_2Fe$: C, 53.12; H, 5.24. Found: C, 53.13; H, 5.18.

(14) Desilylation of **6a** and **7a**. A 900 mg (2.34 mmol) amount of **7a** (**6a**; 430 mg, 1.12 mmol) and 1.30 g (9.37 mmol) of potassium carbonate are dissolved in methanol, and the mixture is stirred for 20 min; aqueous workup with subsequent chromatography over flash silica gel (pentane) yields 560 mg (99%; yellow crystals, mp 88 °C dec) of **7f**. **7f**: IR (KBr, cm^{-1}) ν 3291, 3277, 3129, 2052, 2005, 1982, 1700; ^{1}H NMR (CDCl$_3$) δ 3.04 (s, 2 H), 4.33 (s, 2 H); ^{13}C NMR (CDCl$_3$) δ 62.73, 66.75, 75.11, 76.39, 80.34, 211.79. Anal. Calcd for $C_{11}H_4O_3Fe$: C, 55.05; H, 1.68. Found: C, 54.98; H, 1.77. **6f** (250 mg, 93%; yellow crystals, mp 58 °C dec): IR (KBr, cm^{-1}) ν 3304, 3051, 2991, 2309, 2061, 1983, 1717, 1265; ^{1}H NMR (CDCl$_3$) δ 2.90 (s, 2 H), 4.63 (s, 2 H); MS (EI; *m/z*) 240 [M$^+$], 212, 184, 156, 106.