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Star-Shaped Tricarbonyl(cyclobutadiene)iron and Cymantrene Complexes: Building Blocks for Carbon Nets and Organometallic Construction Sets?

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$(C_4I_4)Fe(CO)_3$ (**2**) and $(C_5I_5)Mn(CO)_3$ (**3**) react with a variety of stannylbutadiynes (**9**) to form the corresponding $[C_4(C{\equiv}CC{\equiv}CR)_4]Fe(CO)_3$ (**10**) and $[C_5(C{\equiv}CC{\equiv}CR)_5]Mn(CO)_3$ (**11**) (R = pentyl, *tert*-butyl, isopropyl, trimethylsilyl) complexes. Iodide **2** coupled to a hexatriyne derivative to yield **13**. Pentametallic X-shaped complexes (**16**) are obtained by Pd-catalyzed coupling of organometallic stannylacetylenes with **2** in one step. X-ray crystal structure analyses have been carried out on several of the cross-shaped complexes obtained. It is likely that these molecules can also be useful in the synthesis of larger nanometer-scale objects. Crystal structures have been carried out for compounds **10a** ($P\bar{1}$; $a = 15.3172(9)$ Å, $b = 12.331(1)$ Å, $c = 11.705(2)$ Å; $\alpha = 97.585(8)°$, $\beta = 95.463(7)°$, $\gamma = 91.232(6)°$; $V = 2180.2$ Å^3; $Z = 2$; $R = 3.8\%$, $R_w = 3.8\%$ for 3194 reflections with $F > 3\sigma(F)$), **13** ($P\bar{1}$; $a = 11.7599(9)$ Å, $b = 9.186(3)$ Å, $c = 20.055(2)$ Å; $\alpha = 99.850(16)°$, $\beta = 85.556(7)°$, $\gamma = 104.040(13)°$; $V = 2069.2$ Å^3; $Z = 2$; $R = 3.9\%$, $R_w = 4.2\%$ for 3239 reflections with $F > 3\sigma(F)$), **16a** ($P\bar{1}$; $a = 13.0355(15)$ Å, $b = 13.043(3)$ Å, $c = 13.128(2)$ Å; $\alpha = 85.4678(15)°$, $\beta = 80.566(9)°$, $\gamma = 71.034(13)°$; $V = 2081.5$ Å^3; $Z = 2$; $R = 3.4\%$, $R_w = 3.6\%$ for 3095 reflections with $F > 3\sigma(F)$), and **16b** ($P\bar{1}$; $a = 12.269(3)$ Å, $b = 16.298(3)$ Å, $c = 11.560(3)$ Å; $\alpha = 99.089(9)°$, $\beta = 108.907(10)°$, $\gamma = 91.776(10)°$; $V = 2158.5$ Å^3; $Z = 2$; $R = 5.0\%$, $R_w = 5.4\%$ for 4195 reflections with $F > 3\sigma(F)$).

Introduction

A rapidly growing field in organic and organometallic chemistry is the synthesis and characterization of classes of compounds which have dimensions larger than typical "organic" molecules. Examples of these entities are dendrimers,[1] rodlike stiff molecules such as the staffanes[2] and polyphenyls,[3] and extended planar nets as Diederich's carbon nets[4] or organometallic solid-state materials.[5] A general idea is that those objects[6] are monodisperse; i.e., they possess a completely defined chemical constitution and structure on a nanometer scale; additionally, they show a certain shape as a consequence of their rigidity. This makes these entities different from typical (polydisperse) polymers. In a recent paper Michl *et al.* described some of the possible prerequisites and concepts for synthesizing such "mesoscopes".[2] His idea is to use oligo(bicyclo[1.1.1]-pentanes)[7] as building blocks for the construction of molecular "Tinkertoys" or related civil engineering sets. In our opinion the introduction of organometallic building blocks for this purpose instead of, or in combination with, oligo(bicyclo[1.1.1]pentanes) could offer an enhanced variability in the buildup of larger molecular systems and tilelike structures such as that depicted in Figure 1. Organometallics possess more structural variability, have different topologies, and exhibit multiple modes of reactivity in changing environments. For these reasons we think that the synthesis of mesoscopic organometallic structures is a long-term goal worthy of pursuit, particularly since only a very few attempts have been made in this direction.[4] In prior communications we identified ethynyl-substituted cyclobutadiene complexes of iron and cobalt as valuable aspirants for the synthesis of linear[8] and star-shaped[9] structures. The construction of multimetallic nonclustered organometallics,[10,11] the search for short pre-

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[2] Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601 and references cited therein.

[3] (a) Rehahn, M.; Schlüter, A.-D.; Wegner, G. *Polymer* **1990**, *191*, 1991. (b) Funaki, H.; Aramaki, K.; Nishihara, H. *Chem. Lett.* **1992**, 2065. (c) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.

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[5] (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698. (b) Ward, M. D.; Fagan, P. J.; Calabrese, J. C.; Johnson, D. C. *J. Am. Chem. Soc.* **1989**, *111*, 1719. (c) Abrahams, B. F.; Hoskins, B. F.; Liu, J.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3045. (d) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Williams, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 10641.

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[9] (a) Bunz, U. H. F.; Enkelmann, V. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1653. (b) Bunz, U. H. F.; Enkelmann, V.; Räder, J. *Organometallics* **1993**, *12*, 4745.

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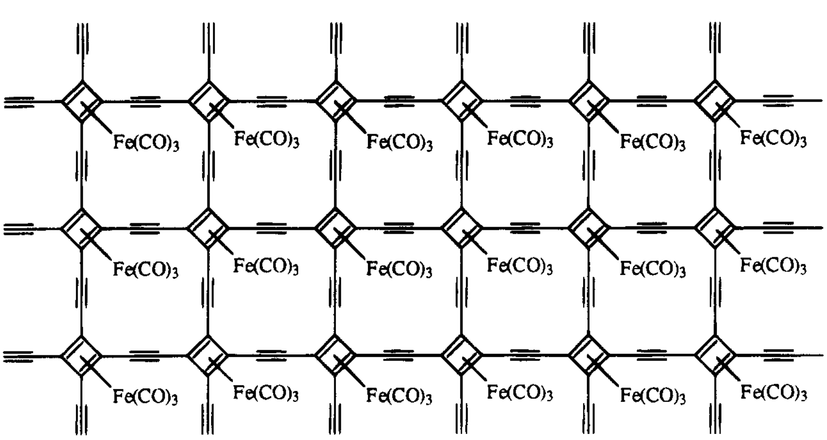
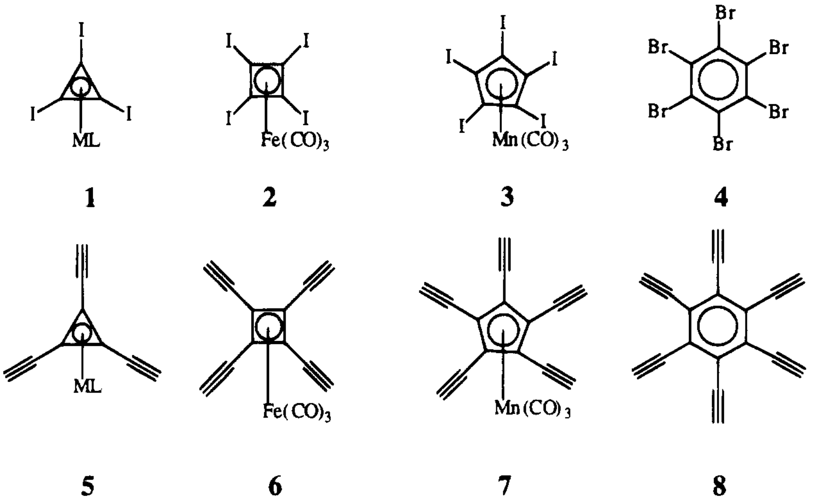


Figure 1. Organometallic carbon net comprised of 4- and 16-membered rings.

Chart 1



parative routes to highly functionalized metallocenes,[9b,10d] and the search for ruglike polymetallic complexes[10c,d] are related and interwoven into the field of hydrocarbon-bridged complexes; they represent an area of intense current research activity.[5,10,11]

While Vollhardt[12] was able to synthesize hexaethynylbenzene (**8**) by starting from **4** (Chart 1), nothing was known about the lower metal-fragment-supported polyethynyls **5**–**7**: initially we discovered that the tetraiodo complex **2**[13] and the pentaiodo cymantrene **3**[9b] were suitable partners in a Stille-type coupling that furnished compounds of the general structures **6** and **7**, respectively. Especially, the use of **6** as a connector of organometallic alkynes to structurally rigid heteropentametallic complexes offered a stimulating incentive for the synthesis of these novel organometallics.

Results and Discussion

Coupling of Butadiynes and a Hexatriyne to 2. The reaction of **2** with stannylbutadiyne **9a**[14] under the conditions described[9a] using DMF as solvent in combination with the catalyst system of Farina[15a] ($Pd_2(dba)_3/AsPh_3$) led to a mixture of products which were inseparable by column chromatography. To gain insight into the course of the reaction, we conducted a coupling experiment between **2** and **9a** in a sealed NMR tube using THF-d_8 instead of DMF as solvent. The amount of catalyst had to be increased to 12 mol %[16] (attempts to couple using only 4 mol % catalyst were unsuccessful), and the ^{13}C NMR spectrum after 4 h showed that the signals due to the starting materials had disappeared completely. In their place a set of seven new signals was observed that indicated the formation of octayne **10a**. Repetition of the experiment on a preparative scale yielded a yellow, light-sensitive but otherwise

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[10] (a) Beck, W.; Niemer, B.; Wieser, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 923 and references cited therein. (b) Bergerat, P.; Blümel, J.; Fritz, M.; Hiermeier, J.; Hudeczek, P.; Kahn, O.; Köhler, F. H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1258. (c) Janiak, C.; Schuhmann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291. (d) Okuda, J. *Top. Curr. Chem.* **1991**, *160*, 97.

[11] McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, *1*, 493.

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[13] Amiet, G.; Nicholas, R.; Pettit, R. *J. Chem. Soc. D* **1970**, 161.

[14] (a) Butadiyne **9a** was prepared from 1-(trimethylsilyl)buta-1,3-diyne[14b] by deprotonation with butyllithium in THF and reaction of the anion formed with chlorotrimethylstannane. (b) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1989; p 118. (c) Butadiynes **9b**–**d** were prepared from the corresponding (*Z*)-2-(alkylethynyl)-1-chloroethylenes[14d] by dehydrohalogenation with LDA and subsequent reaction of the intermediary lithioacetylide with chlorotrimethylstannane. (d) Kende, A. S.; Smith, C. A. *J. Org. Chem.* **1988**, *53*, 2655. (e) Hexatriyne **12** was prepared analogously after the Kendes method.[14c,d]

[15] (a) Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585 and references cited therein. (b) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551 and references cited therein.

[16] Referenced to compound **2**.

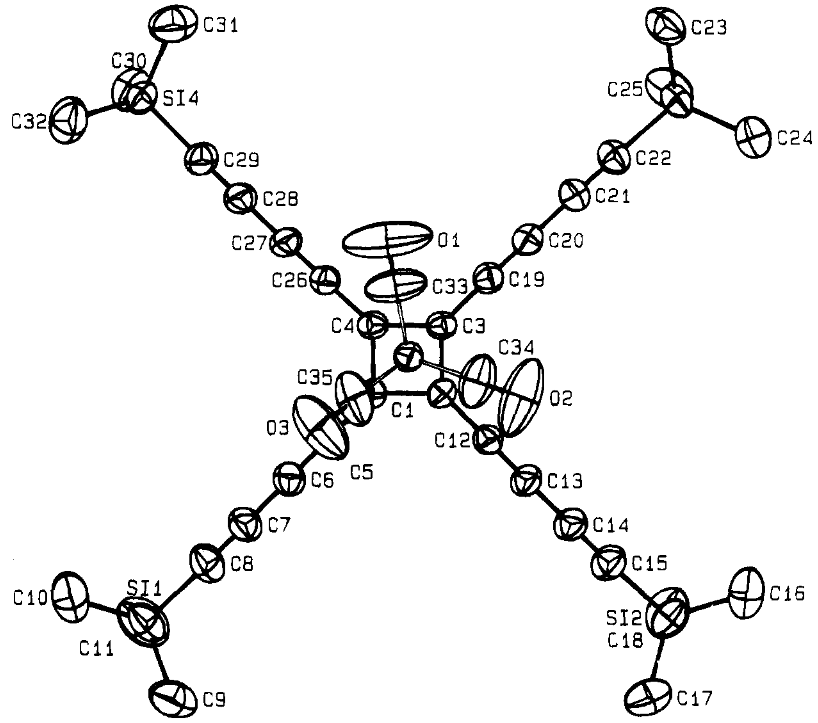


Figure 2. ORTEP drawing and numbering scheme for the octayne **10a**.

stable powder which decomposed above 220 °C with explosion. The NMR spectroscopic properties of the material isolated were in full accordance with the data obtained from the NMR-tube experiment with signals observed at 208.89 (s), 94.54 (s), 87.20 (s), 80.41 (s), 67.29 (s), 65.75 (s), and −0.64 (q) ppm. The signal at 209 ppm is assigned to the iron-bound CO groups and is diagnostic for the presence of a tetraalkynyl-substituted tricarbonyl(cyclobutadiene)iron complex.[9a] The signals between 65 and 95 ppm are attributed to the butadiyne component and the ring carbons of **10a**. The proton NMR spectrum consists of the expected singlet at 0.23 ppm. The IR spectrum shows prominent peaks at 2962 (C−H), 2099 (C≡C), and 2062, 2016, and 2009 (CO) cm^{-1} which are also in accord with the proposed structure **10a**. In the mass spectrum the molecular ion is detected at *m/z* 672. Signals at *m/z* 644 and 588 result from loss of one and three molecules of CO, respectively. Reaction of **2** with stannylbutadiynes **9b−d** gave the corresponding derivatives **10b,c** as solids and **10d** as a yellow oil; product yields are listed in Table 1. Attempts to desilylate **10a** were unsuccessful because of the extreme sensitivity of the unprotected octayne **10e**. Instead, a black and completely insoluble material was obtained.

Scheme 1

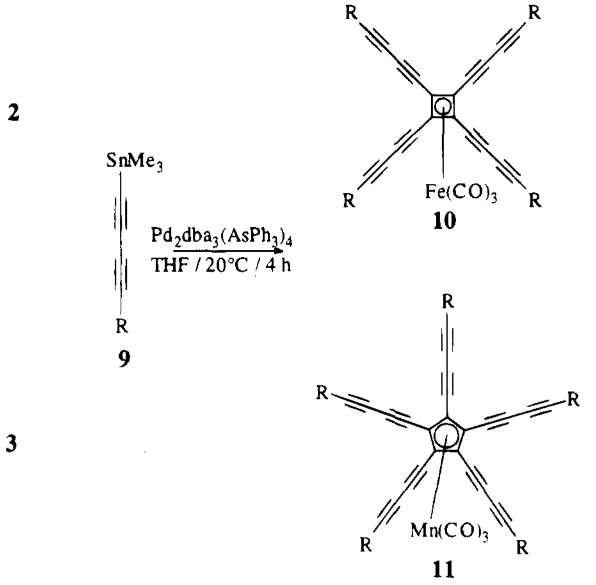


Table 1. Substituent Key for 9−11 and Yields of the Coupling Reactions of 2 and 3 with Stannylbutadiynes (9) To Give 10 and 11

9−11	R	yield of **10** (%)	yield of **11** (%)
a	SiMe$_3$	34	0
b	*t*Bu	57	10
c	*i*Pr	26	11
d	pentyl	30	5
e	H		

In order to gain access to the spatially more extended system **13**, we attempted to couple **2** with the hexatriyne derivative **12**.[14e] An experiment conducted in a sealed NMR tube indicated complete decomposition of the starting materials under the described (*vide supra*) conditions. Use of the less active catalyst system PdCl$_2$(PPh$_3$)$_2$ yielded the desired dodecayne **13** in 16% yield, but repeated flash chromatography over silica gel was necessary to effect isolation from the black viscous reaction mixture. The compound was characterized by its NMR and IR spectra. The latter shows two bands at 2209 and 2181 cm^{-1} for the triyne functionality. The split is caused by an electronic $\pi-\pi$ interaction. In the analogous butadiynyl-substituted systems **10** and **11** such splitting was not observed. Attempts to record the mass spectrum of **13** failed, due to rapid decomposition of the dodecayne under the spectroscopic conditions. The structure of **13** was established by X-ray crystallography (Figure 3).

Coupling of Butadiynes to 3. Reactions of **3** with the corresponding stannylbutadiynes **9b−d** are similar to those of **2** with the stannylbutadiynes **9**. The cor-

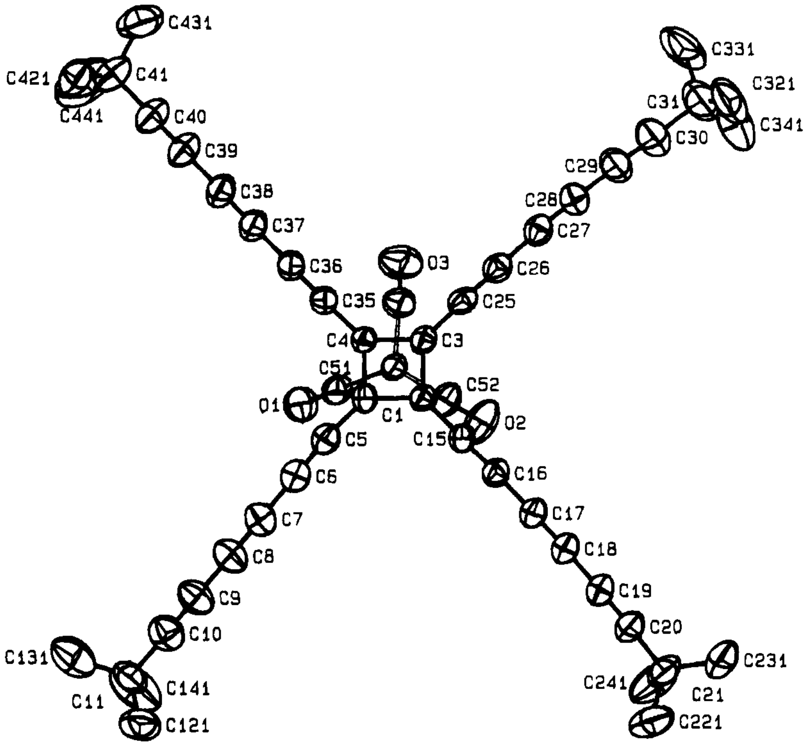
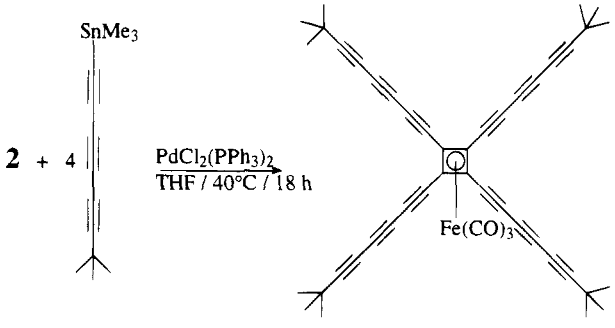


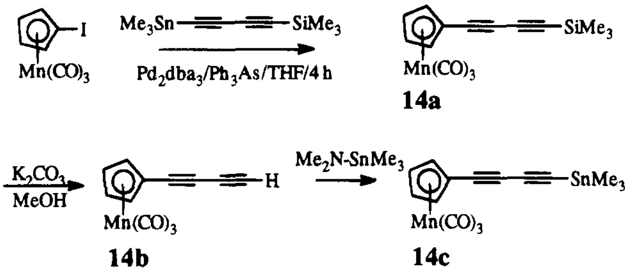
Figure 3. ORTEP drawing and numbering scheme for the dodecayne **13**.

Scheme 2



12 **13**

Scheme 3



responding derivatives **11b–d** were obtained in the yields provided by Table 1. The workup required filtration over neutral alumina and flash chromatography over silica gel employing a mixture of pentane/dichloromethane as eluent. Besides triphenylarsine and the destannylated diyne as the least polar fractions, the pentabutadiynyls **11** were the only other products detected from this reaction. The yield of **11** is decreased compared to that of the coupling products **10**, perhaps as a consequence of the enhanced steric congestion of the five iodine substituents in **3** compared to the more open tetraiodide **2**. The steric accessibility of the iodine–carbon bond to the Pd catalyst is therefore attenuated in **3**. What supports this assumption is the fact that attempts by Whitesides *et al.* to couple alkynes to hexa*iodo*benzene were largely curtailed by accompanying dehalogenation reactions; only partially alkynylated products were isolated.[12b] The comparatively low yields of coupling products **11** do not present a serious problem, because **3** is easily available in multigram quantities in a one-pot procedure.[9b] Attempts to couple **3** to the stannylbutadiyne **9a** have not met with success. We suspect that, if formed, **11a** decomposed during chromatographic workup by loss of the trimethylsilyl groups; the deprotected butadiynes would then polymerize on the silica surface. The deprotection of organometallic alkynes under such conditions has precedence in the literature.[17]

Synthesis of the Organometallic Stannylacetylenes and -butadiynes. The synthesis of alkyne **15b** has been described by Stille,[18] while the stannylacetylenes **15a,c,d** were prepared by the reaction of the corresponding known alkynes[8,18b,c] with Lappert's reagent ($Me_2N-SnMe_3$).[19] The hitherto unknown diyne **14c** was synthesized according to Scheme 3 also using the Pd-catalyzed coupling reaction. The first step proceeds in 79% yield to give **14a**. Desilylation by potassium carbonate in methanol yielded the deprotected diyne **14b**, which was remarkably unstable and polymerized during attempted distillation. Instead, reaction of the crude product **14b** with Lappert's reagent gave the desired stannane **14c** in high yield.

Coupling of Organometallic Alkynes and Butadiynes to 2. The synthesis of X-shaped or star-shaped multimetallic complexes is a synthetic endeavor, not easy to achieve. Very few hydrocarbon-bridged star-

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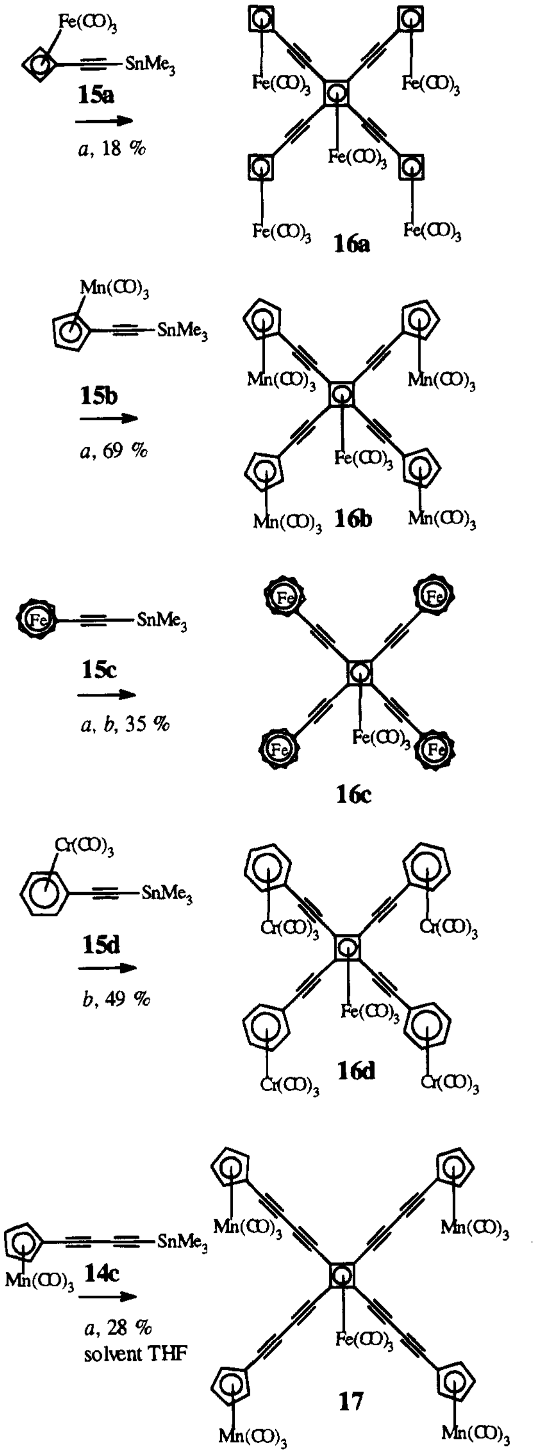
[17] Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590.

[18] (a) Lo Sterzo, C.; Stille, J. K. *Organometallics* **1990**, *9*, 687 and references cited therein. (b) Pudelski, J. K.; Callstrom, M. R. *Organometallics* **1992**, *11*, 2757.

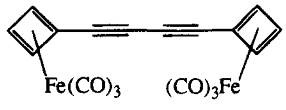
[19] Jones, K.; Lappert, M. F. *J. Chem. Soc.* **1965**, 1945.

Scheme 4[a]



[a] Legend: (*a*) $Pd_2(dba)_3$ and Ph_3As as catalyst; (*b*) $PdCl_2(CH_3CN)_2$ as catalyst in DMF solvent.

shaped organometallics have been prepared so far.[1c,5a,10b] The symmetry of **2** and its reactivity toward stannylacetylenes offered a good chance to gain an easy synthetic access to the family of novel complexes depicted in Scheme 4. Reaction of the tetraiodide **2** with **15a–d** in DMF gave the desired pentanuclear alkyne-bridged complexes **16** in yields of 18–69%. In the case of **16a,b** it was sufficient to use the Farina catalyst system[15a] ($Pd_2(dba)_3$ and triphenylarsine) for the coupling reaction, but to achieve complete conversion the reaction mixture had to be stirred for ca. 18 h at ambient temperature. While **16b** was formed in 69% yield, the analogous **16a** was obtained only in 18% yield. It was accompanied by a second product that was identified by its NMR spectra as **18**, which already had been prepared in these laboratories.[8]



18

Butadiyne **18** probably arose from symmetrical oxidative coupling of **15a** either by the presence of traces of atmospheric oxygen or, more probably through Pd-mediated oxidation by **2** and concomitant decomposition of the tetraiodide. In the case of the more bulky alkynes **15c,d** it was not sufficent to use Farina's catalyst system; instead, the more reactive, but also more sensitive, Beletskaya[15b] catalyst ($PdCl_2(CH_3CN)_2$) had to be used. It was necessary to add the palladium salt (dissolved in dry DMF) to the stirred reaction mixture every 12 h, since the stability of this catalyst was insufficient to allow for coupling with just one portion. The reaction times were typically about 48 h; four portions of catalyst were needed. Compounds **16** are all yellow-brown crystalline materials which are well (**16a,b**) or moderately (**16c,d**) soluble in dichloromethane and chloroform but almost insoluble in hexane or pentane. Tetraalkynyls **16** are only slightly sensitive to atmospheric oxygen and moisture. Tetraalkynyl **16a** can be stored for several days in an open flask without noticeable decomposition. The identification of the X-shaped pentanuclear complexes followed from their characteristic NMR, IR, and mass spectra. In particular, the ^{13}C NMR spectra showed the absorption of the iron-bound CO groups of the central ring in the region of 210 ppm and in **16a,b,d** the presence of a downfield-shifted second CO signal attributable to the CO groups attached to the peripheral complex fragments. In the case of **16a,b** suitable crystals were obtained to perform X-ray structure analyses (*vide infra*). In the cases of **16c,d** and **17** (*vide infra*) we have not been able to grow crystals of sufficient X-ray quality, despite many attempts.

We are pleased to report that it is also possible to couple the butadiyne derivative **14c** to the core **2**, thereby obtaining **17** in 28% yield under conditions identical with those used for coupling the simple butadiynes **9**; the product **17** was isolated by filtration through neutral alumina and subsequent flash chromatography over silica gel to remove traces of triphenylarsine. **17** is an air- and moisture-stable, but slightly light-sensitive, yellow powder.

Crystal Structures. Due to their heat, air, and light sensitivity in solution, **10a**, **11b**, **13**, and **16a,b** were crystallized at low temperature (−18 °C), by slow evaporation of the solvent. The coupling product, ca. 50–100 mg, was placed in a small glass vessel and dissolved in 1–2 mL of dichloromethane. The vessel was closed with a plastic lid which had a small hole (ca. 1 mm i.d.). The concentration had to be chosen such that cooling to −18 °C did not effect precipitation. Crystals developed by slow evaporation of the solvent after 1 (**13**) to 4 days (**10a**, **11b**, **16a,b**).

Common to all four structures is the centroid–metal distance at 1.76–1.79 Å. Not unexpectedly, none of the

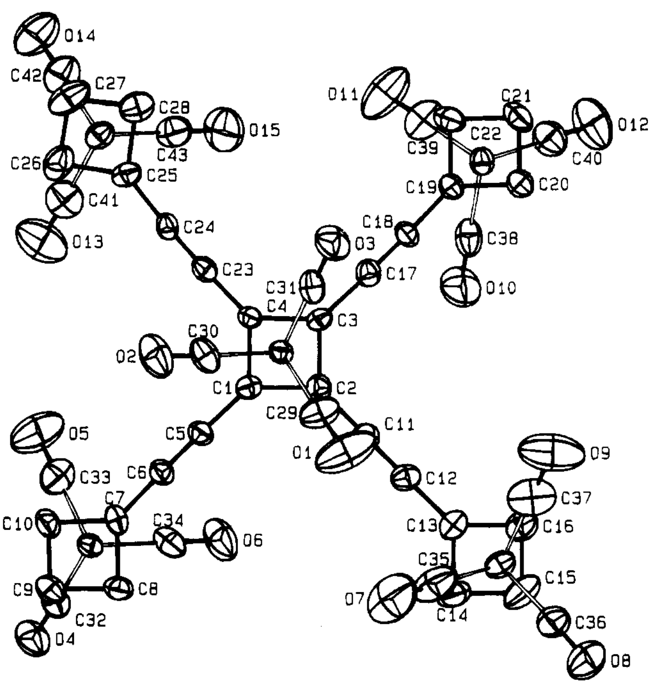


Figure 4. ORTEP drawing and numbering scheme for the tetrayne **16a**.

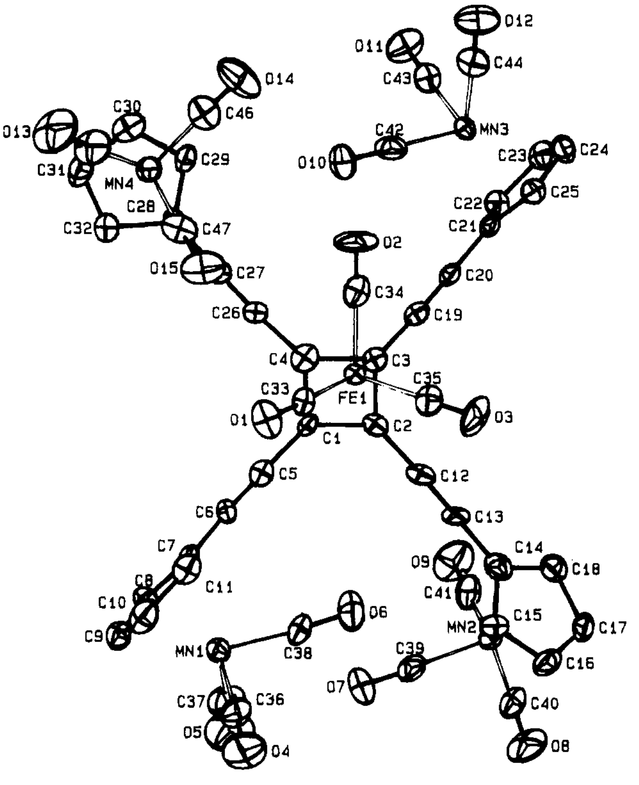


Figure 5. ORTEP drawing and numbering scheme for the tetrayne **16b**.

Table 2. Selected Bond Distances for Octayne 10a (Å)

Fe1—C1	2.074(6)	C3—C4	1.452(8)
Fe1—C2	2.064(6)	C3—C19	1.428(7)
Fe1—C3	2.024(6)	Si2—C15	1.839(7)
Fe1—C4	2.057(6)	C6—C7	1.382(9)
Fe1—C33	1.735(7)	C7—C8	1.188(9)
Fe1—C34	1.769(7)	Si3—C22	1.847(6)
Fe1—C35	1.755(7)	C13—C14	1.370(8)
C2—C12	1.407(7)	Fe—centroid	1.764(26)
C4—C26	1.407(7)	C20—C21	1.387(8)
O1—C33	1.144(9)	C28—C29	1.205(8)
O2—C34	1.117(9)	C26—C27	1.182(8)
O3—C35	1.138(8)	C21—C22	1.187(8)
C1—C2	1.432(7)	Si4—C29	1.827(6)
C1—C4	1.447(7)	C19—C20	1.194(8)
C2—C3	1.444(7)	C14—C15	1.200(9)
C12—C13	1.203(8)		

Table 3. Selected Bond Distances for Dodecayne 13 (Å)

Fe1—C51	1.793(9)	C21—C221	1.57(2)
Fe1—C52	1.782(9)	C21—C231	1.51(2)
Fe1—C53	1.749(9)	C21©241	1.48(2)
C51—O1	1.131(8)	C21—C222	1.55(3)
C52—O2	1.140(8)	C21—C232	1.45(3)
C53—O3	1.113(8)	C21—C242	1.50(4)
C1—C2	1.435(9)	C25—C26	1.19(1)
C1—C4	1.463(9)	C26—C27	1.39(1)
C1—C5	1.410(10)	C27—C28	1.19(1)
C2—C3	1.452(9)	C28—C29	1.35(1)
C2—C15	1.407(9)	C29—C30	1.17(1)
C3—C4	1.485(9)	C30—C31	1.50(1)
C3—C25	1.390(10)	C31—C321	1.53(3)
C4—C35	1.390(10)	C31—C331	1.45(2)
C5—C6	1.20(1)	C31—C341	1.53(2)
C6—C7	1.38(1)	C31—C322	1.52(3)
C7—C8	1.18(1)	C31—C332	1.47(4)
C8—C9	1.36(1)	C31—C342	1.51(5)
C9—C10	1.20(1)	C35—C36	1.19(1)
C10—C11	1.48(1)	C36—C37	1.38(1)
C11—C121	1.52(2)	C37—C38	1.19(1)
C11—C131	1.54(2)	C38—C39	1.37(1)
C11—C141	1.48(2)	C39—C40	1.17(1)
C11—C122	1.46(3)	C40—C41	1.46(1)
C11—C132	1.58(4)	C41—C421	1.53(2)
C11—C142	1.57(4)	C41—C431	1.49(2)
C15—C16	1.193(9)	C41—C441	1.48(3)
C16—C17	1.37(1)	C41—C422	1.59(4)
C17—C18	1.20(1)	C41—C432	1.50(5)
C18—C19	1.37(1)	C41—C442	1.50(5)
C19—C20	1.19(1)	Fe—centroid	1.775(3)
C20—C21	1.46(1)		

compounds investigated showed any solid-state reactivity as has been observed for diacetylenes.[20] The structures of **10a** and **13** show a certain resemblance: in both, the tricarbonyliron fragment is arranged in such a fashion that one of the Fe—CO bonds almost symmetrically intersects the angle between two of the polyyne substituents. In both, the hydrocarbon substituents are not planar. Instead, all of the four substituents are bent away from the iron fragment. This feature has been observed in unsubstituted tricarbonyl(cyclobutadiene)iron by Gray *et al.*[21] In **13** we observe an additional S-shaped deformation of the ligand. This is probably due to crystal-packing forces (see Figure 2). The stereoscopic view of the packing (Figure 7) shows that the triyne side groups interdigitate, leaving a region of less compact packing in the center of the unit cell. In **13** the *tert*-butyl groups show a rotational disorder of the three methyl substituents.

The densities of both crystals are very low (1.07 and 1.08 g cm^{-3}) as a consequence of the low space filling of an array of rigid star-shaped molecules. If the side groups are extended even more, the packing density should be so low that stable structures will exist only with the inclusion of the solvent of crystallization. Our attempts to recrystallize **11b** from dichloromethane gave crystals which rapidly lost the incorporated solvent at ambient temperature, and despite several attempts

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[20] Enkelmann, V. E. *Adv. Polym. Sci.* **1984**, *63*, 91. Wegner, G. *Z. Naturforsch.* **1969**, *24B*, 824.

[21] Harvey, P. D.; Schäfer, W. P.; Gray, H. B.; Gilson, F. R.; Butler, I. S. *Inorg. Chem.* **1988**, *27*, 57.

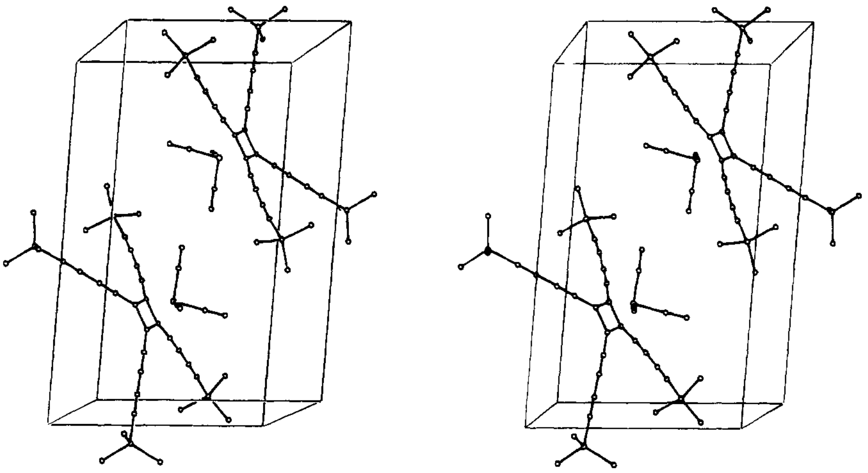

Figure 6. Stereoview and unit cell of the octayne **10a**. The *x* axis is horizontal and the *z* axis vertical in the plane of the paper.

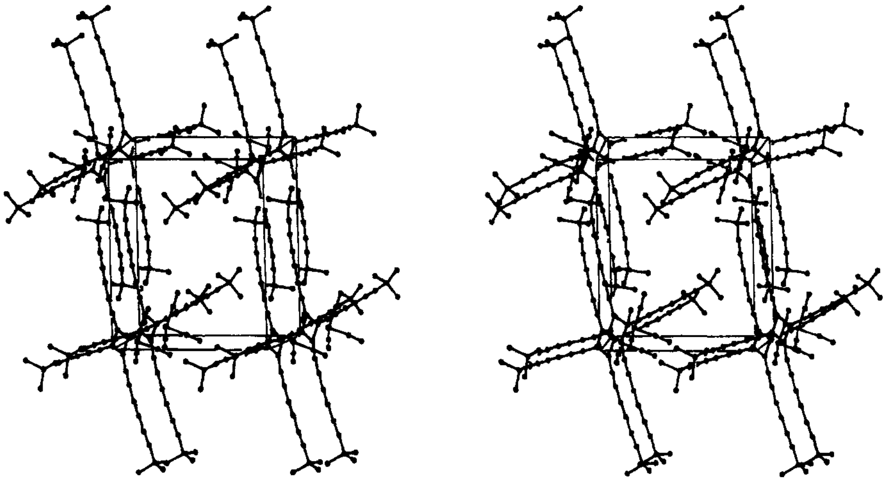

Figure 7. Stereoview and unit cell of the dodecayne **13**. The *y* axis is horizontal and the *x* axis vertical in the plane of the paper.

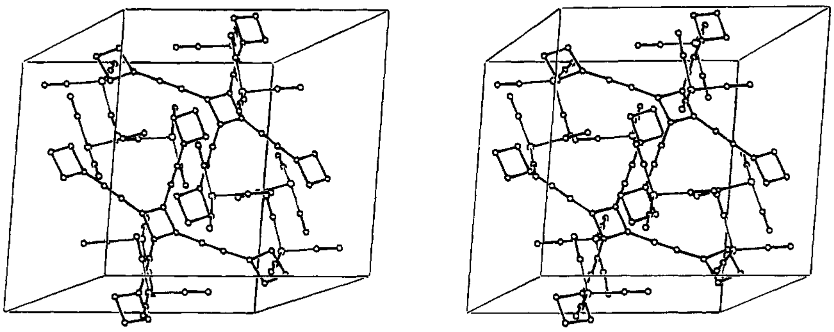

Figure 8. Stereoview and unit cell of the tetrayne **16a**. The *y* axis is horizontal and the *z* axis vertical in the plane of the paper.

we have been unable to collect data at low temperature without crystal decomposition.[22]

The structures of **16a,b** show some interesting features (see Figures 4 and 5). While in **16a** the hydrocarbon ligand is almost planar, the distribution of the iron tricarbonyl groups is unusual. By first approximation it would be expected that the central $Fe(CO)_3$ fragment is on one side of the hydrocarbon ligand and the four other fragments on the opposite side in order to minimize steric interactions. Instead, we find the central fragment and one peripheral fragment to be located on one side of the hydrocarbon ligand with the remaining three fragments located on the opposite side.

The hydrocarbon ligand in **16b**, on the other hand, shows a different arrangement. Two of the Cp rings are approximately parallel, and the remaining two are almost perpendicular with respect to the central ring. The $Mn(CO)_3$ groups are oriented in such a fashion that the central cyclobutadiene ring constitutes a center of inversion. Simple van der Waals models suggest that the 90° twist of the Cp rings compared to the central

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[22] Crystals of **11c** were monoclinic, $P2_1/c$, with $a = 13.659(9)$ Å, $b = 9.186(3)$ Å, $c = 14.664(3)$ Å, $\alpha = 90°$, $\beta = 105.598(25)°$, $\gamma = 90°$, $Z = 4$, and $V = 4008$ Å^3. If the composition **11c**·CH_2Cl_2 is assumed, a density of 1.22 g cm^{-3} can be calculated; the experimental density of the crystals obtained at 0 °C is less than the density of dichloromethane, because the crystals were floating on the solvent.

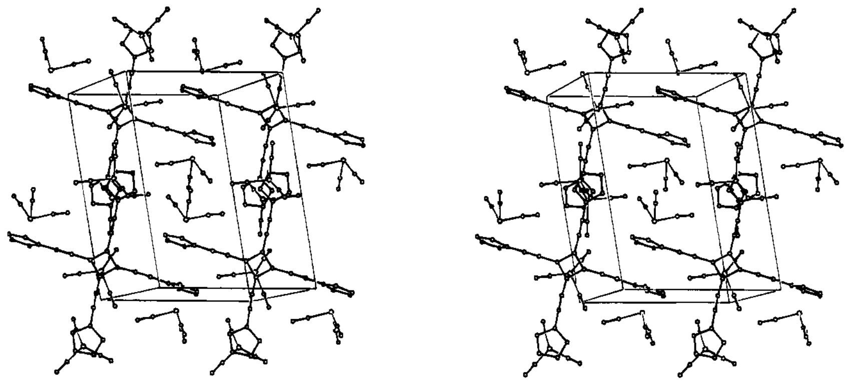

Figure 9. Stereoview and unit cell of the tetrayne **16b**. The *z* axis is horizontal and the *y* axis vertical in the plane of the paper.

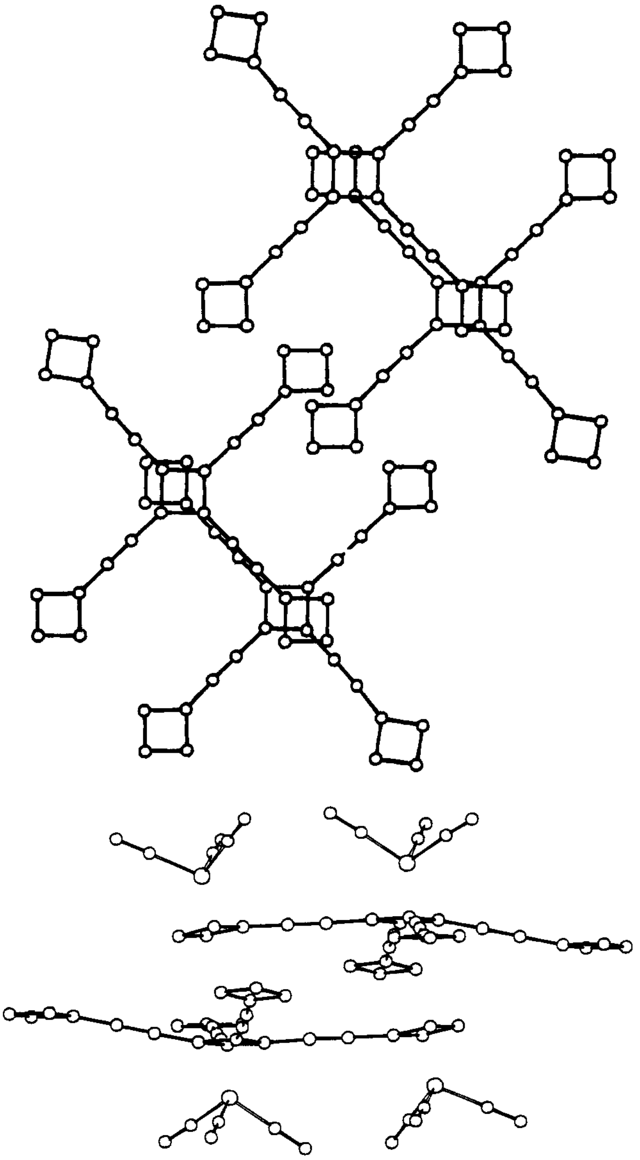

Figure 10. Detailed views of **16a**: (a, top) iron tricarbonyl fragments omitted; (b, bottom) only the iron tricarbonyl fragments of the participtating rings shown.

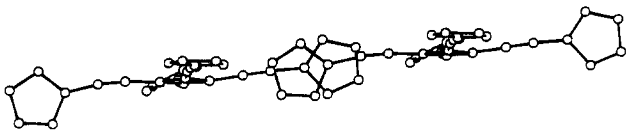

Figure 11. Detailed view of 16b. Note the five-membered-ring plane–plane distance of 3.42 Å. The overlap occurs in the crystallographic *z* axis.

Table 4. Selected Bond Distances for Tetrayne 16a (Å)

Fe1—C29	1.76(1)	O13—C41	1.14(1)
Fe1—C30	1.78(1)	O14—C42	1.16(1)
Fe1—C31	1.77(1)	O15—C43	1.15(1)
Fe2—C32	1.78(1)	C1—C2	1.46(1)
Fe2—C33	1.77(1)	C1—C4	1.47(1)
Fe2—C34	1.80(1)	C1—C5	1.42(1)
Fe3—C35	1.74(1)	C2—C3	1.43(1)
Fe3—C36	1.78(1)	C2—C11	1.42(1)
Fe3—C37	1.78(1)	C3—C4	1.45(1)
Fe4—C38	1.78(1)	C3—C17	1.43(1)
Fe4—C39	1.75(1)	C4—C23	1.40(1)
Fe4—C40	1.79(1)	C5—C6	1.18(1)
Fe5—C41	1.79(1)	C6—C7	1.42(1)
Fe5—C42	1.75(1)	C7—C8	1.44(1)
Fe5—C43	1.75(1)	C7—C10	1.44(1)
O1—C29	1.16(1)	C8—C9	1.42(1)
O2—C30	1.13(1)	C9—C10	1.39(1)
O3—C31	1.16(1)	C11—C12	1.19(1)
O4—C32	1.15(1)	C12—C13	1.41(1)
O5—C33	1.14(1)	C13—C14	1.46(1)
O6—C34	1.12(1)	C13—C16	1.44(1)
O7—C35	1.15(1)	C14—C15	1.44(1)
O8—C37	1.15(1)	C15—C16	1.39(1)
O9—C38	1.15(1)	C17—C18	1.18(1)
O10—C38	1.13(1)	C18—C19	1.40(1)
O11—C39	1.15(1)	C19—C20	1.45(1)
O12—C40	1.12(1)	C19—C22	1.43(1)

ring is *not* attributable to steric hindrance. The pairwise annihilation of the dipole moments might be responsible for the observed conformation of **16b**.

In order to understand the differences in conformational behavior in **16a,b**, an inspection of their packing plots is instructive (Figures 8 and 9). In the case of **16a** we find that the formation of a solid-state dimer accounts for the unusual distribution of the iron tricarbonyl fragments (Figures 8 and 10). Detailed plots (Figure 10) show that there must be considerable interaction between the four cyclobutadiene rings and their corresponding attendant acetylenes. The intermolecular contact of the two interacting parts of **16a** is between 3.35 and 3.65 Å. In the structure of **16b** formation of a dimer in this fashion is not observed. Instead, the search for short intermolecular contact shows that a one-dimensional "coordination polymer" is formed in the crystalline state (Figure 11). In this structural feature the two partially overlapping cyclopentadienyl moieties are 3.42 Å apart.

Conclusions

We have been able to show that the polyiodides **2** and **3** are versatile building blocks for the construction of

Table 5. Selected Bond Distances of Tetrayne 16b (Å)

Fe1—C33	1.74(1)	C7—C8	1.41(2)
C33—O1	1.19(1)	C7—C11	1.40(2)
C34—O2	1.10(2)	C8—C9	1.43(2)
C35—O3	1.11(2)	C9—C10	1.40(2)
Mn1—C38	1.78(2)	C10—C11	1.39(2)
C36—O4	1.12(2)	C12—C13	1.16(2)
C37—O5	1.15(2)	C13—C14	1.42(2)
C38—O6	1.16(2)	C14—C15	1.43(2)
Mn2—C39	1.80(2)	C14—C18	1.44(2)
Mn2—C40	1.79(1)	C15—C16	1.42(2)
C39—O7	1.14(2)	C16—C17	1.42(2)
C40—O8	1.16(2)	C17—C18	1.42(2)
C41—O9	1.13(2)	C19—C20	1.18(2)
Mn3—C42	1.78(2)	C20—C21	1.42(2)
C42—O10	1.16(2)	C21—C22	1.39(2)
C43—O11	1.14(1)	C21—C25	1.46(2)
O44—O12	1.14(2)	C22—C23	1.41(2)
Mn4—C45	1.77(2)	C23—C24	1.40(2)
Mn4—C47	1.80(2)	C24—C25	1.40(2)
C45—O13	1.17(2)	C26—C27	1.16(2)
C46—O14	1.12(2)	C27—C28	1.43(2)
C47—O15	1.15(2)	C28—C29	1.39(2)
C1—C2	1.45(2)	C28—C32	1.45(2)
C1—C4	1.46(2)	C29—C30	1.38(2)
C1—C5	1.45(2)	C30—C31	1.40(2)
C2—C3	1.43(2)	C31—C32	1.37(2)
C2—C12	1.44(2)	Fe—centroid	1.7628(21)
C3—C4	1.49(2)	Mn1—centroid	1.7660(35)
C3—C19	1.42(2)	Mn2—centroid	1.7586(24)
C4—C26	1.44(2)	Mn3—centroid	1.7903(22)
C5—C6	1.17(2)	Mn4—centroid	1.7638(26)
C6—C7	1.43(2)		

novel star-shaped perbutadiynyl-decorated complexes. The tetraiodides **2** are useful connectors for other organometallic entities that allow for the construction of novel and highly functionalized homo- and heterometallic pentanuclear complexes **16** in a one-step synthesis. Of these complexes, **16a** is a small segment of a carbon net as depicted by Figure 1. It is our intention to make larger linear and star-shaped segments and also fragments which contain cyclic components of such a metal-stabilized carbon net.

Experimental Section

Tetrahydrofuran (THF) was distilled from benzophenone/potassium under nitrogen. Dimethylformamide (DMF) was distilled from calcium hydride *in vacuo*. All reactions were conducted under an atmosphere of nitrogen in flame-dried glassware using standard inert-gas and Schlenk techniques.

Preparation of the Stannylated Alkynes 15.[8,18] In a typical experiment ca. 1.00 g of alkyne **15** was placed in a Schlenk flask equipped with a magnetic stirbar and a rubber septum. Lappert's reagent[19] ($Me_3Sn-NEt_2$, 1–2 mL, i.e. an excess) was added by syringe to the alkyne. The mixture was stirred for ca. 20 min at ambient temperature.[18] Diethylamine was distilled off *in vacuo*; the residue was dried at 35 °C/0.05 mmHg to remove excess Lappert's reagent. The stannylated alkynes so formed—brownish yellow powders—were used without further purification.

Tricarbonyl[η^5-(1-(trimethylsilyl)buta-1,3-diyn-4-yl))-cyclopentadienyl]manganese (14a). To 4.08 g (12.4 mmol) of iodocymantrene were added 3.71 g (13.0 mmol) of **9a**, 250 mg (273 μmol) of $Pd_2(dba)_3$, and 360 mg (1.18 mmol) of triphenylarsine in 20 mL of THF. After the mixture was stirred at ambient temperature for 4 h, THF was removed *in vacuo* and the residue filtered (neutral active aluminum oxide, pentane). Crystallization from pentane at −20 °C yielded 2.98 g (74%) of **14a** (yellow crystals, mp 64–66 °C). ^1H NMR ($CDCl_3$): δ 0.22 (s, 9 H), 4.69 (t, J = 2.1 Hz; 2 H), 5.08 (t, J = 2.1 Hz; 2 H). ^{13}C NMR ($CDCl_3$): δ −0.54 (q), 69.46 (s), 73.38 (s), 78.65 (s), 81.93 (d), 87.29 (s), 88.16 (d), 90.54 (s), 223.49 (s, CO). MS (EI; *m/z* (relative intensity, %)): 324 (M^+ − H, 10), 268 (25), 240 (100). Anal. Calcd: C, 55.42; H, 4.03. Found: C, 55.27; H, 4.08.

Tricarbonyl[η^5-(1-(trimethylstannyl)buta-1,3-diyn-4-yl))cyclopentadienyl]manganese (14c). A 1.72 g (5.29 mmol) amount of **14a** in 25 mL of methanol was stirred with 500 mg of potassium carbonate for 20 min. Partition between pentane and water and removal of the solvent at 10 °C *in vacuo* yield 1.21 g (91%) of **14b**, which was immediately reacted with 2.00 g of $Et_2N-SnMe_3$, and **14c** (1.98 g, 98%) was used as obtained after isolation (vide supra).

Tricarbonyl[η^4-1,2,3,4-tetrakis(1-(trimethylsilyl)-butadiyn-4-yl)-1,3-cyclobutadiene]iron (10a). In a Schlenk tube 400 mg (575 μmol) of **2**, 88.0 mg (96.1 μmol) of $Pd_2(dba)_3$, 123 mg (402 μmol) of triphenylarsine, THF (10 mL), and 688 mg (2.42 mmol) of **9a** were introduced at 0 °C. After 4 h at ambient temperature the THF was removed *in vacuo*, the residue was dissolved in the minimum amount of pentane, and this solution was filtered (neutral active aluminum oxide, pentane) to give **10a** in 34% yield (133 mg, yellow crystals, mp 220 °C explosive dec). IR (KBr, cm^{-1}): ν 2962, 2100, 2062, 2016, 2009, 1253, 1101, 846. ^1H NMR ($CDCl_3$): δ 0.20 (s, 36 H). ^{13}C NMR ($CDCl_3$): δ −0.64 (q), 65.75, 67.29, 80.41, 87.20, 94.54 (5 s), 208.89 (s, CO). MS (EI; *m/z* (relative intensity)): 672 (M^+, 1%), 644 (M − CO, 10%), 588 (M − 3CO, 53%). Anal. Calcd: C, 62.48; H, 5.39. Found: C, 62.21; H, 5.42.

Tricarbonyl[η^4-1,2,3,4-tetrakis(5,5-dimethylhexa-1,3-diyn-1-yl)-1,3-cyclobutadiene]iron (10b). A 400 mg (575 μmol) amount of **2**, 672 mg (2.50 mmol) of **9b**, 88.0 mg (96.1 μmol) of $Pd_2(dba)_3$, and 123 mg (402 μmol) of triphenylarsine were treated as described for **10a** to yield 201 mg (57%) **10b** (yellow powder, mp 245 °C dec). IR (KBr, cm^{-1}): δ 2972, 2932, 2234, 2059, 2013, 2003, 1258. ^1H NMR ($CDCl_3$): δ 1.27 (s, 36 H). ^{13}C NMR ($CDCl_3$): δ 28.47 (s), 30.25 (q), 64.03, 65.39, 67.85, 80.32, 94.90 (5 s), 209.70 (s, CO). MS (EI; *m/z* (relative intensity)): 608 (M^+, 1%), 580 (M − CO, 12%), 524 (M − 3CO, 100%).

Tricarbonyl[η^4-1,2,3,4-tetrakis(5-methylhexa-1,3-diyn-1-yl)-1,3-cyclobutadiene]iron (10c). A 200 mg (288 μmol) amount of **2**, 319 mg (1.25 mmol) of **9c**, 40.0 mg (43.7 μmol) of $Pd_2(dba)_3$, and 60.0 mg (196 μmol) of triphenylarsine in 5 mL of THF were treated as described for **10a** to yield 103 mg (26%) of **10c** (yellow powder, dec >192 °C). IR (KBr, cm^{-1}): ν 2974, 2927, 2872, 2224, 2058, 2007, 1992, 1312. ^1H NMR ($CDCl_3$): δ 1.23 (d, J = 6.92 Hz, 24 H), 2.69 (sept, J = 6.92 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ 21.51 (d), 22.12 (q), 64.56, 64.96, 67.87, 80.33, 92.44 (5 s), 209.68 (s, CO). MS (EI; *m/z* (relative intensity)): 552 (M^+, 2%), 524 (M − CO, 17%), 468 (M − 3CO, 100%).

Tricarbonyl[η^4-1,2,3,4-tetrakis(nona-1,3-diyn-1-yl)-1,3-cyclobutadiene]iron (10d). A 400 mg (575 μmol) amount of **2**, 1.00 g (3.53 mmol) of **9d**, 88.0 mg (96.1 μmol) of $Pd_2(dba)_3$, and 123 mg (402 μmol) of triphenylarsine were treated as described for **10a**. Chromatography (pentane, flash silica; 3 cm × 12 cm) yields 115 mg (30%) of a yellow oil, **10d**. IR (KBr, cm^{-1}): ν 2958, 2933, 2871, 2861, 2228, 2057, 2001, 1466, 1459. ^1H NMR ($CDCl_3$): δ 0.91 (t, J = 7.19 Hz, 12 H), 1.38, 1.57 (2 m, 24 H), 2.33 (t, J = 7.31 Hz, 8 H). ^{13}C NMR ($CDCl_3$): δ 13.83 (q), 19.70, 22.12, 27.66, 30.99 (4 t), 61.21, 65.19, 67.92, 80.50, 87.84 (5 s), 209.70 (s, C=O). Anal. Calcd: C, 77.70; H, 6.67. Found: C, 78.06; H, 6.76.

Tricarbonyl[η^4-1,2,3,4-tetrakis(7,7-dimethylocta-1,3,5-triyn-1-yl)-1,3-cyclobutadiene]iron) (13). A 200 mg (288 μmol) amount of **2**, 400 mg (1.36 mmol) of **12**, and 46.0 mg (65.5 μmol) of $Pd(PPh_3)_2Cl_2$ were placed in a NMR tube and dissolved in 1.0 mL of THF-d_8. After three freeze–pump–thaw cycles the tube was flame-sealed under high vacuum and warmed for 13 h to 38 °C. The seal was broken, THF removed *in vacuo*, and the dark residue filtered (neutral active aluminum oxide, 10 cm × 1 cm, 200 mL of pentane) and chromatographed (flash silica gel 15 cm × 2 cm, 2% dichloromethane/98% pentane) to yield 33 mg (16%) of **13** (yellow powder, dec

Table 6. Crystal and Refinement Data for 10a, 13, and 16a,b

	10a	**13**	**16a**	**16b**
mol formula	$C_{35}H_{36}Si_4FeO_3$	$C_{47}H_{36}FeO_3$	$C_{43}H_{12}Fe_5O_{15}$	$C_{47}H_{16}Mn_4FeO_{15}$
mol wt	672.86	704.65	1047.80	1096.21
color, habit	yellow block	tan coffin-shaped	dark yellow block	orange block
cryst size (mm)	0.4 × 0.3 × 0.15	0.3 × 0.3 × 0.2	0.2 × 0.2 × 0.1	0.25 × 0.15 × 0.1
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	15.3172(9)	11.7599(9)	13.0355(15)	12.269(3)
b (Å)	12.331(1)	9.186(3)	13.043(3)	16.298(3)
c (Å)	11.705(2)	20.055(2)	13.128(2)	11.560(3)
α (deg)	97.585(8)	99.850(16)	85.4678(15)	99.089(9)
β (deg)	95.463(7)	85.556(7)	80.566(9)	108.907(10)
γ (deg)	91.232(6)	104.040(13)	71.034(13)	91.776(10)
V (Å^3)	2180.2	2069.2	2081.5	2158.5
Z	2	2	2	2
μ (cm^{-1})	30.30	42.78	143.3	126.0
dens (g cm^{-3})	1.072	1.080	1.67	1.69
T (K)	295	295	295	295
diffractometer	Enraf-Nonius CAD4			
monochromator	highly oriented graphite crystal			
scan type	$2\theta-\theta$			
2θ range (deg)	0−110			
R	0.038	0.039	0.034	0.050
R_w	0.038	0.042	0.036	0.054
no. of unique rflns	5503	4988	5214	5423
no. of obsd rflns	3194 ($I > 3\sigma(I)$)	3239 ($I > 3\sigma(I)$)	3095 ($I > 3\sigma(I)$)	4195 ($I > 3\sigma(I)$)

>182 °C). Crystals for X-ray analysis were obtained by slow evaporation of a solution of **13** in dichloromethane at −18 °C. IR (KBr, cm^{-1}): ν 2971, 2954, 2927, 2209, 2181, 2063, 2006, 1738. ^{1}H NMR ($CDCL_3$): δ 1.27 (s, 36 H). ^{13}C NMR ($CDCl_3$): δ 28.43 (s), 30.18 (q), 60.28, 64.37, 65.14, 67.79, 70.25, 81.15, 92.15 (7 s), 208.70 (s, CO).

Tricarbonyl[η^5-1,2,3,4,5-pentakis(5,5-dimethylhexa-1,3-diyn-1-yl)cyclopentadienyl]manganese (11b). A 769 mg (923 μmol) amount of **3**, 1.54 g (6.00 mmol) of **9b**, 100 mg (109 μmol) of $Pd_2(dba)_3$, and 150 mg (490 μmol) of triphenylarsine were stirred in 3.0 mL of THF for 18 h at ambient temperature. The solvent was removed *in vacuo* and the residue filtered (neutral active alumina, 5% dichloromethane/95% pentane) and chromatographed (flash silica 20 × 3 cm, 5% dichloromethane/95% pentane). The yellow powder was washed with the dichloromethane/pentane mixture to remove impurities, and **11b** was obtained in 10% yield (67 mg) (dec 200 °C). IR (KBr, cm^{-1}): ν 2973, 2930, 2902, 2242, 2029, 1963, 1267. ^{1}H NMR ($CDCl_3$): δ 1.30 (s, 45 H). ^{13}C NMR ($CDCl_3$): δ 28.38 (s), 30.26 (q), 63.82, 64.90, 79.47, 86.25, 94.26 (5 s), 221.34 (s, CO). MS (EI; *m/z* (relative intensity)): 724 (M$^+$, 2%), 640 (M − 3CO, 100%).

Tricarbonyl[η^5-1,2,3,4,5-pentakis(5-methylhexa-1,3-diyn-1-yl)cyclopentadienyl]manganese (11c). An 833 mg (1.00 mmol) amount of **3**, 1.35 g (5.29 mmol) of **9c**, 88.0 mg (96.1 μmol) of $Pd_2(dba)_3$, and 123 mg (402 μmol) of triphenylarsine were treated as described for **11b**, yielding 69 mg (11%) of **11c** (dec >200 °C). IR (KBr, cm^{-1}): ν 2972, 2929, 2870, 2241, 2031, 1975, 1958, 1315. ^{1}H NMR ($CDCl_3$): δ 1.25 (d, J = 6.92 Hz, 30 H), 2.73 (sept, J = 6.92 Hz, 5 H). ^{13}C NMR ($CDCl_3$): δ 21.46 (d), 22.14 (q), 64.36, 64.47, 79.52, 86.29, 91.84 (5 s), 221.33 (s, CO). MS (EI; *m/z* (relative intensity)): 654 (M$^+$, 5%), 570 (M − 3CO, 100%). Anal. Calcd: C, 78.89; H, 5.39. Found: C, 78.41; H, 5.22.

Tricarbonyl[η^5-1,2,3,4,5-pentakis(nona-1,3-diyn-1-yl)cyclopentadienyl]manganese (11d). A 700 mg (840 μmol) amount of **3**, 1.22 g (4.30 mmol) of **9d**, 88.0 mg (96.1 μmol) of $Pd_2(dba)_3$, and 123 mg (402 μmol) of triphenylarsine were treated as described for **11b**, yielding 32 mg (4.8%) of **11d** (yellow crystals, mp 96 °C). IR (KBr, cm^{-1}): ν 2957, 2931, 2860, 2237, 2032, 1982. ^{1}H NMR ($CDCl_3$): δ 0.90 (t, J = 6.62 Hz, 15 H), 1.35, 1.57 (2 m, 30 H), 2.35 (t, J = 6.91 Hz, 10 H). ^{13}C NMR ($CDCl_3$): δ 13.86 (q), 19.66, 22.13, 27.67, 31.05 (4 t), 63.73, 64.92, 79.59, 86.26, 87.22 (5 s), 221.36 (s, CO).

Tricarbonyl{η^4-1,2,3,4-tetrakis[(tricarbonyl(η^4-1,3-cyclobutadien-1′-yl)ferrio)ethyn-1-yl]-1,3-cyclobutadiene}iron (16a). A 278 mg (400 μmol) amount of **2**, 758 mg (2.00 mmol) of **15a**, 10.0 mg (10.9 μmol) of $Pd_2(dba)_3$, and 21.0 mg (68.6 μmol) of triphenylarsine in 20 mL of DMF are stirred for 24 h. After removal of the DMF at 25 °C/0.1 mmHg the residue was filtered (neutral active aluminum oxide) and chromatographed (flash silica, 5% dichloromethane/95% pentane) to furnish 177 mg (21%) of **1,4-Bis[tricarbonyl(η^4-1,3-cyclobutadien-1-yl)ferrio]buta-1,3-diyne**[8] (yellow powder, mp 129 °C). Elution with 20% dichloromethane/80% pentane yields 75 mg (18%) of **16a** (mp 157 °C). Slow evaporation of a dichloromethane solution of **16a** gave crystals suitable for X-ray measurement. IR (KBr, cm^{-1}): ν 3125, 2202, 2050, 1977. ^{1}H NMR ($CDCl_3$): δ 4.06 (s, 4 H), 4.38 (s, 8 H). ^{13}C NMR ($CDCl_3$): δ 58.71 (s), 65.62 (d), 66.85 (d), 66.86 (s), 79.04, 88.73 (2 s), 209.96 (s, CO), 212.75 (s, 4 CO). MS (FD; *m/z*): 1048.8 (M$^+$). Anal. Calcd: C, 49.29; H, 1.15. Found: C, 49.98; H, 1.28.

Tricarbonyl{η^4-1,2,3,4-tetrakis[2-(tricarbonyl(η^5-cyclopentadienyl)manganesio)ethyn-1-yl]-1,3-cyclobutadiene}iron (16b). A 390 mg (560 μmol) amount of **2**, 921 mg (2.35 mmol) of **15b**, 21.0 mg (22.9 μmol) of $Pd_2(dba)_3$, and 10.0 mg (32.7 μmol) of triphenylarsine were treated as described for **16a**. The residue was filtered (neutral active alumina, 20% dichloromethane/80% pentane) and triturated several times with small amounts of pentane, furnishing 423 mg of **16b** (69%, mp 187 °C dec). IR (KBr, cm^{-1}): ν 3124, 2224, 2059, 2023, 1997, 1934, 1497. ^{1}H NMR ($CDCl_3$): δ 4.72 (t, J = 2.1 Hz; 8 H), 5.09 (t, J = 2.1 Hz; 8 H). ^{13}C NMR ($CDCl_3$): δ 66.65 (s), 78.07 (s), 79.84 (s), 82.21 (d), 87.17 (d), 87.98 (s), 210.05 (s, CO), 223.68 (s, 4 CO). MS (FD; *m/z*): 1096 (M$^+$). Anal. Calcd: C, 51.50; H, 1.47. Found: C, 51.49; H, 1.54.

Tricarbonyl{η^4-1,2,3,4-tetrakis[2-(tricarbonyl(η^6-benzene)chromio)ethyn-1-yl]-1,3-cyclobutadiene}iron (16d). To 240 mg (345 μmol) of **2** and 606 mg (1.51 mmol) of **15d** in 15 mL of DMF was added 4.5 mg (17 μmol) of $Pd(CH_3CN)_2Cl_2$ in 0.5 mL of DMF. The solution was stirred for 12 h. After this time again 4.5 mg (17 μmol) of the catalyst was added. This was repeated four times (48 h) until 18 mg of catalyst had been added. The workup was identical to that described for **16b**. Elution with 33% dichloromethane/66% pentane yields unreacted and deprotected alkyne **15d**; elution with dichloromethane furnishes 192 mg (49%) of **16d** (dec 192 °C). IR (KBr, cm^{-1}): ν 3103, 3085, 2212, 2063, 2022, 1974, 1901, 1867, 1464, 1459; ^{1}H NMR ($CDCl_3$): δ 5.26 (m, 12 H), 5.44 (m, 8 H); ^{13}C NMR ($CDCl_3$): δ 66.52 (s), 78.82 (s), 87.44 (s), 90.93 (d), 91.14 (d), 91.85 (s) 95.16 (d), 209.84 (s, CO), 231.64 (s, 4CO); MS (FD *m/s*): 1136 (M$^+$).

Tricarbonyl[η^4-1,2,3,4-tetrakis(2-(ferrocenyl)ethyn-1-

yl)-1,3-cyclobutadiene]iron (16c). A 25.8 mg (37.2 μmol) amount of **2** and 69.2 mg (186 μmol) of **15c** were treated as described for **16d** (1.8 mg, 6.8 μmol of $Pd(CH_3CN)_2Cl_2$). Chromatography of the residue (neutral active alumina, dichloromethane) yields 13.2 mg (35%) of **16c** (brownish powder, dec >200 °C). IR (KBr, cm^{-1}): ν 3097, 2210, 2046, 1985, 1106, 820. ^1H NMR ($CDCl_3$): δ 4.28 (m, 28 H), 4.55 (t, $J = 1.8$ Hz; 8 H). MS (FD; m/z): 1024 (M^+).

Tricarbonyl{η^4-1,2,3,4-tetrakis[4-(tricarbonyl(η^5-cyclopentadienyl)manganesio)-1,3-butadiyn-1-yl]-1,3-cyclobutadiene}iron (17). A 424 mg (610 μmol) amount of **2**, 1.19 g (2.86 mmol) of **14c**, 50 mg (54.5 μmol) of $Pd_2(dba)_3$, and 75 mg (245 μmol) of triphenylarsine were reacted as described for **10a**. Filtration (neutral active alumina, 3 cm × 8 cm, 20% dichloromethane/80% pentane) and repeated chromatography (flash silica, 3 cm × 15 cm; 33% dichloromethane/66% pentane) yielded 202 mg (28%) of **17** (dec 192 °C). IR (KBr, cm^{-1}): ν 3124, 2213, 2066, 2025, 1935, 1871, 910, 668. ^1H NMR ($CDCl_3$): δ 4.70 (t, $J = 2.1$ Hz; 8 H), 5.12 (t, $J = 2.1$ Hz; 8 H). ^{13}C NMR ($CDCl_3$): δ 67.24 (s), 70.30 (s), 77.46 (s), 77.56 (s), 79.93 (5 s), 82.16 (d), 88.55 (d), 208.81 (s, CO), 223.32 (s, 4 CO). MS (FD; m/z): 1091 (M^+). Anal. Calcd: C, 55.45; H, 1.35. Found: C, 55.64; H, 1.59.

Details for the Solution of the Crystal Structures. All structures were solved by Patterson analysis. An empirical absorption correction was applied to the data. Refinement was done by full-matrix least-squares analyses with anisotropic temperature factors for C, O, Si, Mn, and Fe. The positions of the hydrogen atoms were calculated using the known binding geometry and refined in the riding mode with fixed isotropic temperature factors. The site occupancy (OCC) for the C atoms in the disordered *tert*-butyl groups of **13** were included in this refinement, constraining the sum of the OCC's to 1.00. Further details are given in Table 6.

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Supplementary Material Available: Tables of positional and thermal parameters for **10a**, **13**, **and 16a**,**b** (5 pages). Ordering information is given on any current masthead page.

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