Cyclobutadiene Complexes, XII[◇]

Alkynyl-Substituted Tricarbonyl(cyclobutadiene)iron Complexes: Stille Coupling of Iodocyclobutadiene Complexes with Stannylalkynes☆

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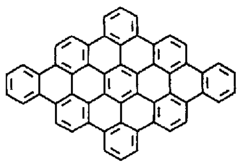
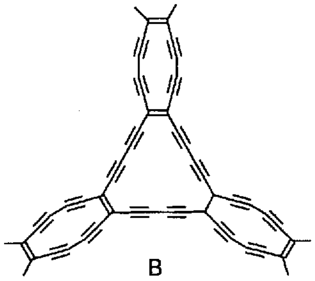
The synthesis of mono-, di-, tri- and tetraalkynylated tricarbonyl(cyclobutadiene)iron complexes is accomplished by a repetitive metalation/iodination/coupling sequence. Application of this sequence leads to the synthesis of oligomeric cyclobutadiene complexes with various topologies, inter alia to the synthesis of a perethynylated dimer **24**. Alternatively a one-step coupling procedure (Stille-Farina) has been used to synthesize tetraalkynylated tricarbonyl(cyclobutadiene)irons **26**.

Modular chemistry is the connection of rigid or semirigid and multiply functionalized compounds of defined size into larger, shape-persistent molecular objects. For this purpose, it is desirable to develop a variety of chemical construction sets using expedient synthetic access to functionalized modules of different properties.

The concept of modular chemistry, which has evolved at a rapid pace during the last decade[1], has many facets and the connection of modules may be achieved either by self organization, using noncovalent interactions such as hydrogen bonds (see ref.[1] and cited material therein), or can rely on the formation of much more robust covalent C–C bonds. Prime examples of the latter type of modules are the oligo(bicyclo[1.1.1]pentanes) of Szeimies[2,3] and Michl[4] and the supramolecular structures[5] derived therefrom, Müllen's[6a] rational synthesis of graphitic sheets (**A**) and polyacetylene oligomers by a construction-set approach[6b], the large and amphiphilic phenylene-ethynylene rings of Höger[8], Moore's phenylacetylene dendrimers[9], Diederich's all-carbon network segments (**B**) and scaffolds using tetraethynylethylene[10], and Vollhardt's repetitively synthesized oligophenylenes[11a] to archimedan-segments **C**.


A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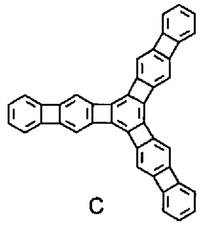
C

Surprisingly, the modules are purely organic with few exceptions[1]; the organometallic branch of modular chemistry is much less developed than the "organic arm" of the enterprise[7]. Organometallic species, though, will allow the construction of modules with valence angles and topologies that are difficult to obtain with organic groups. That is particularly true for cyclobutadiene complexes, which allow the introduction of 90° angles through their appropriate geometry. One of the ultimate goals using cyclobutadiene-derived modules would be the synthesis of a network such as **D**, comprised of butadiyne-linked tricarbonyl(cyclobutadiene)irons. While it is not possible (at least at the moment) to synthesize such an infinite two-dimensional array **D**, it should be possible to prepare segments of varying size and topology. To this end versatile syntheses of ethynylated cyclobutadiene complexes are necessary.

Besides the synthesis of **D**-segments, the modification and functionalization of π complexes is an important incentive in synthetic organometallic chemistry. Goals include manipulating physical properties and chemical reactivity and adding polymerizable groups in order to build and investigate oligomeric models, imparting novel functionalities to the π core so that the organometallic π entity under consideration is attractive not only for use in modular chemistry, but also for material science or LC technology[12].

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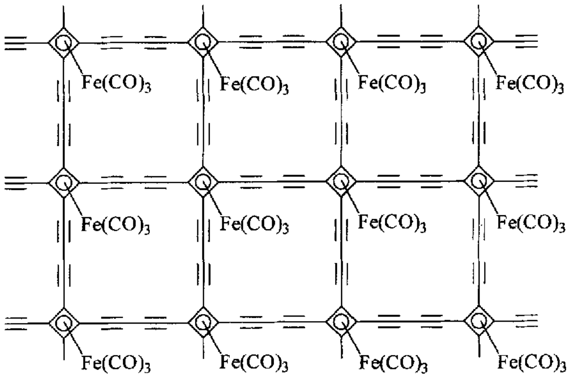


D

Surprisingly, few doubly or higher alkynylated π complexes are known; one example is Vollhardt's synthesis of monoalkynylated and *ortho-* or *para*-diethynylated cyclobutadienes (stabilized by CpCo)[11b]. These complexes were synthesized by a [2 + 2] cycloaddition of suitably substituted alkynes[13] or butadiynes over $CpCo(CO)_2$. While this is an elegant one-step synthesis, with fair but not excellent yields, it is difficult to introduce two alkynyl groups with different substituents; thus this method is rendered less valuable. Additionally, the dimerization approach is unique to the CpCo system and not applicable for tricarbonyl iron supported cyclobutadienes. These reasons led us to develop a different strategy for the synthesis of ethynylated cyclobutadiene complexes[14a]. With the discovery, independently by Hafner and us, that tricarbonyl(cyclobutadiene)iron (**1a**) can be easily metalated by either *sec*-BuLi[14b] or lithium tetramethylpiperidide[14c], the corresponding iodocyclobutadiene **1b** was obtained in good yield. The accessibility of **1b** opened the prospect of a Stille-type route[15] to alkynylated cyclobutadiene complexes, in particular, because it was known from Sterzo and Stille[15b], that iodinated cymantrenes couple with tin alkynes to give the corresponding organometallic acetylenes in good yields and under mild conditions.

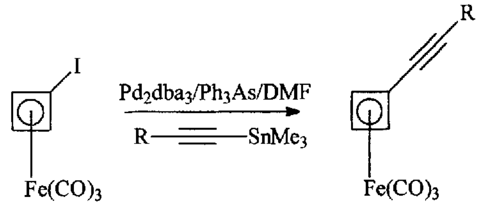
During the last years, multiple ethynylation reactions have become more and more popular. In all of these syntheses, the multiple execution of the Heck-Cassar-Sonogashira-Hagihara coupling[16] with an organic polybromide or polyiodide was the sole or the key reaction leading to ethynylated species. Typical examples are Whitesides' work on ethynylated thiophenes[17] and their use for highly crosslinked materials, the synthesis and LC behavior of peralkynylated triphenylenes[18], and the synthesis of hexaethynylbenzene[19]. Surprisingly, dimeric or oligomeric species of hexaethynylbenzene are unknown even though they represent structurally unusual and attractive synthetic goals. Even less is known about monomeric or oligomeric perethynylated organometallic moieties, but multiple ethynylation reactions should also be applicable for the synthesis of peralkynylated cyclobutadiene complexes.

The reasons listed above initiated our interest in the chemistry of complexed cyclobutadienes and has led to the publication of several preliminary communications[20] regarding synthesis and characterization of ethynylated tricarbonyl(cyclobutadiene)irons. We give here a full account of our endeavors.

Results and Discussion

Synthesis of Monoethynylated Tricarbonyl(cyclobutadieneacetone)iron Complexes

Treating **1b** with **2a**, tris(dibenzylideneacetone)dipalladium (Pd_2dba_3), and triphenylarsane in DMF for 18 h at 21 °C gave rise to the isolation of **3a** in 69% yield as a yellow crystalline material, after aqueous workup and sublimation. In later experiments it turned out that the aqueous workup is unnecessary. After removal of DMF by distillation, **3a** was obtained directly by sublimation. Ethynyl **3a** was relatively air- and moisture-stable and could be stored at −18 °C for indefinite periods, whereas it decomposed over 1−2 days under darkening in the laboratory atmosphere. Using other substituted tin alkynes **2** made the species **3b, c, e** and **f** (yields: Table 1) accessible. The workup procedures for **3b−f** were slightly different: chromatography (neutral aluminium oxide or Baker flash silica gel) combined with crystallization from pentane afforded better results than attempted sublimation or distillation. All of the alkynes **3** were unequivocally identified by their NMR, IR and mass spectra.



1b 2 3

Table 1. Substituent key for stannane **2** and ethynylcyclobutadiene **3** and yields for the coupling products **3** (%)

2, 3	**a**	**b**	**c**	**d**	**e (3e ≡ 11)**	**f**	**g**
R	$SiMe_3$	$Si(iPr_3)$	Ph	H	cymantrenyl	$C{\equiv}C\text{-}SiMe_3$	$C{\equiv}C\text{-}H$
yield **3** (%)	69	77	71	93	55 (**11**)	52	57

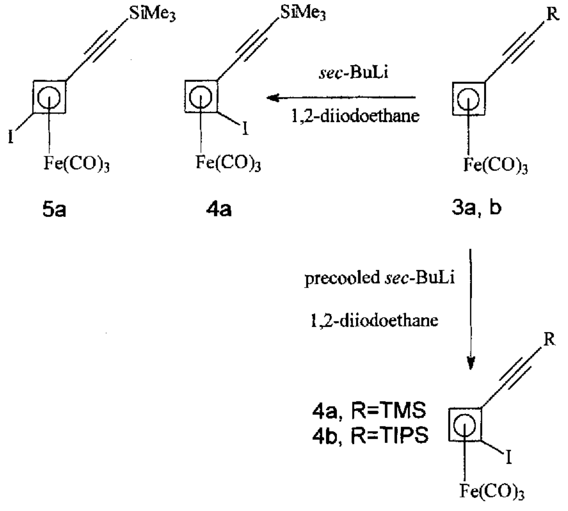
2	**h**	**i**	**j**	**k**
R	*t*-Bu	C≡C-C≡C- *t*-Bu	octyl	methyl

The alkynyl compounds **3d** and **g** were obtained by deprotection of **3a** or **f**, respectively, with potassium carbonate in methanol. While **3a, c, e** and **f** are crystalline and similar in stability, **3a, b, d** and **g** are yellow oils; **3d** and **g** are much less robust than their substituted counterparts.

In the next experiment, **3a** was placed in a long Schlenk tube, dissolved in THF and cooled to −78 °C by inserting the tube into a dry ice/acetone bath so that the glass over the solvent was also effectively cooled. *sec*-BuLi, delivered in cyclohexane (m.p. 6.5 °C), was then slowly administered by a hypodermic needle to the cold inner surface of the tube, causing immediate solidification. To add the precooled *sec*-BuLi slowly, the tube was gently shaken over a period of ca. 20 min until all of the organolithium had dissolved. After performing metalation, quenching with diiodoethane gave rise to the isolation of purely *ortho*-iodinated **4a** in 74% yield with no detected formation (<5%) of the *para*-iodide **5a**. We found that this particular setup was most effective for selective *ortho*-iodination of **3**.

When the deprotonation of **3a** was carried out without precooling the *sec*-BuLi, a mixture of **4a** and **5a** was isolated in 70–75% yield. The faster the addition of the *sec*-BuLi, the more *para*-product was formed (20–25%). The chromatographic separation of the two iodides proved to be quite difficult, so that **5a** was obtained only after repeated chromatography with considerable loss of material.

If the deprotonation reaction would occur in accord with statistics, an *ortho:para* ratio of 2:1 would have been expected. The observed higher *ortho:para* ratio (even if *sec*-BuLi is not precooled) shows that an *ortho*-directing effect is exerted by the alkyne group. *ortho*-Directed metalation is generally found in alkynes such as phenylacetylene[21], thienylacetylene[22] and ethynylcymantrene[23]. The reason for this effect is the enhanced ability of the triple bond to coordinate a lithium cation. *ortho*-Metalation of the substituted cyclobutadiene **3b** is also observed to give rise to the isolation of a 62% yield (*ortho:para* ratio > 95:5) of **4b** after reaction of the lithio compound with 1,2-diiodoethane, suggesting that the *ortho*-directing effect of the alkyne group is independent of the substituent R.

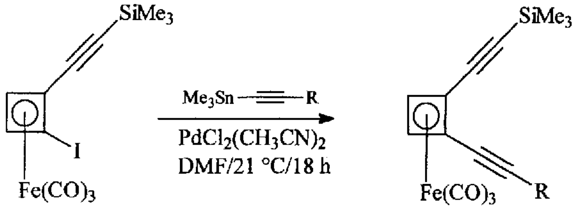


5a **4a** **3a, b**

4a, R=TMS
4b, R=TIPS

Synthesis of Diethynylated Tricarbonyl(cyclobutadiene)iron Complexes by the Metalation/Iodination/Coupling (MIC) Sequence

With the iodinated complexes **4** and **5** in hand, it was expected that a Stille-Farina[15] type coupling should allow access to the complexes **6** and **7**. Coupling of **4a** to a series of stannylated alkynes **2** cleanly afforded derivatives of **6** (yields: Table 2).



4a **6**

Table 2. Yields and catalysts used for the coupling reaction of **4a** with tin alkynes **2**

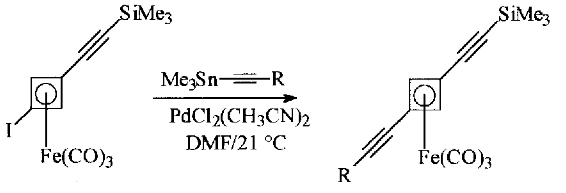
6	**a**	**b**	**c**	**d**	**e**
R	$SiMe_3$	Si(*i*-Pr)$_3$	*tert*-Butyl	Phenyl	-C≡C-C≡C-*t*-Bu
catalyst	———	$PdCl_2(CH_3CN)_2$	———	———	$PdCl_2(PPh_3)_2$
yield	78 %	62 %	57 %	65 %	28%

The corresponding 1,3-diethynyls **7** are also available by coupling **5a** with **2**. Due to difficulties in the workup, the use of the Beletskaya catalyst [$PdCl_2(CH_3CN)_2$] had advantages over the Farina system. To drive the reaction to completion, it was necessary to use two portions of the sensitive "ligandless" catalyst $PdCl_2(CH_3CN)_2$, adding the second catalyst portion after 18 h. Whereas **7a** is obtained as a crystalline material in 71% yield, **7b** appears as an oil. The slightly lower yield in the case of **7b** (62%) is due to spreading of the product band during chromatography and is probably not an effect of attenuated coupling efficiency of the TIPS-alkyne **2b**.

Deprotection of **6a**, **b** and **7a** to give the terminal alkynes **6f**, **g** and **7c** was performed in high yield by stirring the silylated precursors for 20 min. in a methanol/potassium carbonate mixture; **7c**, **6f** and **6g** are surprisingly stable for short periods (hours) under ambient conditions and can be purified by either sublimation or chromatography.

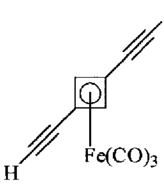
Synthesis of Oligomeric Alkyne-Bridged Tricarbonyl(cyclobutadiene)iron Complexes

Having succeeded in the synthesis of mononuclear ethynylated cyclobutadiene complexes, the next goal was the synthesis of di- and trinuclear alkyne-bridged representatives of various topologies. In an initial experiment, **16** was coupled[15b] with **8** and **9**, respectively, to give **10** (81%) and **12** (67%). In the case of **10** it was sufficient to use 1 mole percent of palladium catalyst (per mole of **1b**); with 5 mole percent catalyst, the yield of **10** drops to 65%. The complex **11** is obtained by coupling of **1b** to (trimethylstannylethynyl)cymantrene[15b] in 55% yield. While **10** and **11** are prepared using DMF as solvent, **12** is better synthesized in THF, using 5 mole percent of the Farina catalyst. With a Hay-type coupling[24], we were also able to synthesize **12** in 54% yield from **3d**. We tried to

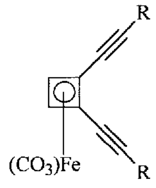


5a

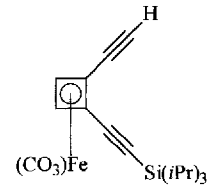
7a R=SiMe3, 71%
7b R=Si(*i*Pr)3, 62%



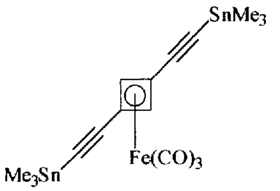
7c (93%)



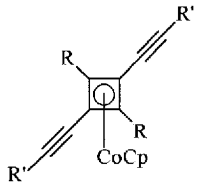
6f R=H (100%)
6h R=SnMe3



6g (65%)



7d



7e R=H, R′=SnMe3
7f R=SiMe3, R′=SnMe3
7g R, R′=H
7h R=SiMe3, R′=H

$Me_3Sn\text{-}(\equiv)_n\text{-}SnMe_3$

	n
8	*1*
9	*2*

couple **3d** under Eglinton conditions[25] by using copper acetate in pyridine. Here only decomposition of **3d** resulted, implying that the tricarboyl(cyclobutadiene)iron nucleus is sensitive to these conditions.

When bisstannylated[26] cyclobutadiene **7e**[11b] is coupled to **1b**, the sparingly soluble trimer **16a** is formed in 55% as the only isolable product; using **7f** as stannane (under the same conditions) in the reaction with **1b** affords a mixture of two compounds, identified by their NMR spectra as dimer **15** (42%) and trimer **16b** (18%). The interpretation of these results is that the enhanced steric crowding in **7f** compared with that in **7e** retards the rate of the coupling reaction considerably and leads to the predominant formation of the dimer **15** at reaction times (18 h) sufficient to achieve complete conversion of **7e** to **16a**. The result underscores the importance of the steric factor in this type of coupling reaction, leading to the conclusion, that more hindered reaction partners couple less readily. Similar observations were made for the tetraalkynylation of **25** (vide infra). The Pd-catalyzed coupling reaction was applied to the *para*-iodide **5a**, in combination with **8** to give a 39% yield of **13**. Utilizing **7d** instead of **8** led to the isolation of **14** (32%). Thereby the sensitive **7d** was prepared in situ by the action of Lappert's reagent ($Et_2N\text{-}SnMe_3$)[26] on **7c**.

Coupling of **4a** to **8**, **9** and **6h** affords **17**, **18** and **19** (R = $SiMe_3$) in 47, 38 and 59% yield, respectively. All of the three kinked oligomers must occur as mixtures of diastereomers. Thus, **17** and **19** should consist of two diastereomers, namely a racemate and a *meso* compound. It was not possible though, to separate the diastereomers by column chromatography. The ^{13}C-NMR spectrum of **17** shows 11 lines, strongly suggesting that some of the resonances are split as a consequence of the occurrence of diastereomers. While the TMS-, the alkyne and the $Fe(CO)_3$ signals are not split, one quaternary (δ = 65) and one tertiary C (δ = 66) of the cyclobutadiene nucleus show a split into two signals of equal intensity. In the elongated dimer **19** no diastereomeric split is observed at the resolution (3 Hz line broadening) achieved in the NMR experiment. Only ten signals were recorded, suggesting that the butadiyne bridge in **19** decouples the stereocenters.

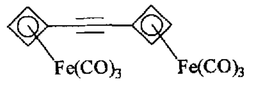
Trimer **18** is expected to be formed as mixture of *three* diastereomers, thereby giving rise to the formation of a racemate and two *meso* compounds, as depicted. However, it was impossible to separate or enrich a single diastereomer by column chromatography.

The ^{13}C-NMR spectrum of **18** shows two signals in a 2:1 ratio for the CO groups, four signals in the alkyne region, and one band for the TMS groups. Between δ = 60 and 70 only eleven signals of the cyclobutadiene-C atoms were observed: analysis of the three diastereomers using symmetry criteria reveals that 24 cyclobutadiene signals are expected for the sum of all three diastereomers. The reduction of the number of signals is due to accidental isochrony, but not to chemical equivalence of the carbon atoms under consideration and probably also not to the favored formation of only one or two of the three diastereomers. The alkyne, TMS and the CO signals are not influenced by the occurrence of diastereomers at all, giving rise to only seven diagnostic signals, supporting the proposed constitution.

Attempted Synthesis of Cycles Comprised of Butadiynes and Cyclobutadienes

Having **6f**, a rigid diyne, in hand should allow access to cyclic structures of the type **20** by using the Hay coupling[19]. As we have been able to show, the tricarbonyl(cyclobutadiene)iron system is stable under Hay coupling conditions, allowing the synthesis of **12** from **3d** (vide supra).

Diyne **6f** was dissolved in acetone to give a 0.1 mM solution. Copper(I) chloride and TMEDA were added in stoichiometric amounts and O_2 was bubbled through the reaction mixture. After 2 h, **6f** was consumed; aqueous workup gave only black and infusible material that eluded further characterization. Because it was not clear what led to the failure of the coupling, the dimer **17b** was prepared from **17a** (K_2CO_3 in methanol, diastereomeric mixture, 72%). Hay coupling was performed on **17b**, which produced a dark and insoluble precipitate. It was not possible to isolate any defined compounds. Again, the reason for the unsuccessful course of the reaction was obscure; either the open



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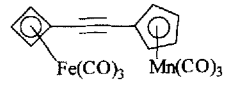
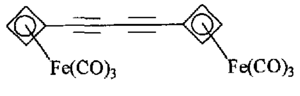
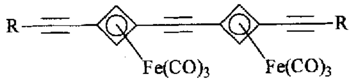


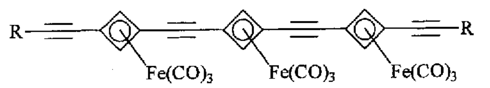
11



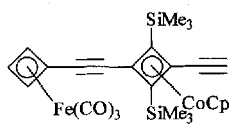
12



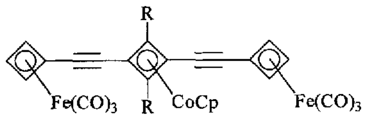
13



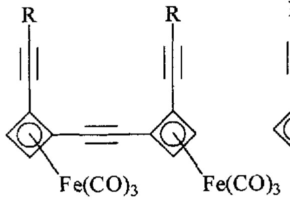
14



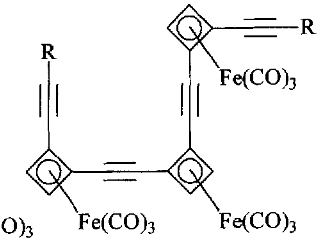
15



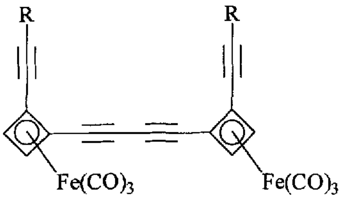
16a R=H
16b R=SiMe3



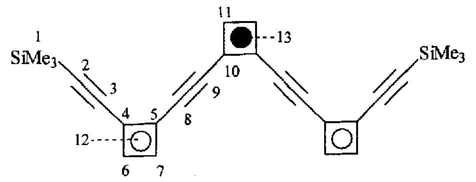
17



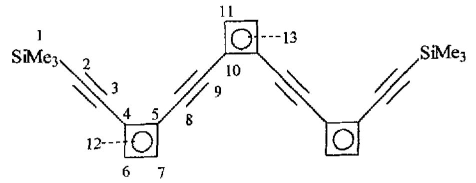
18



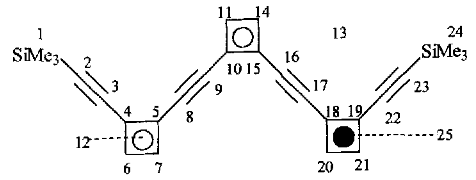
19a R=SiMe3
19b R=H



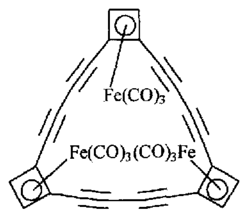
meso-I-**18**



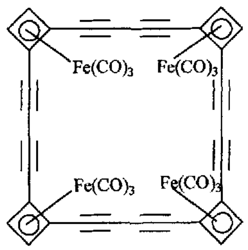
meso-II-**18**



rac-**18**



20a



20b

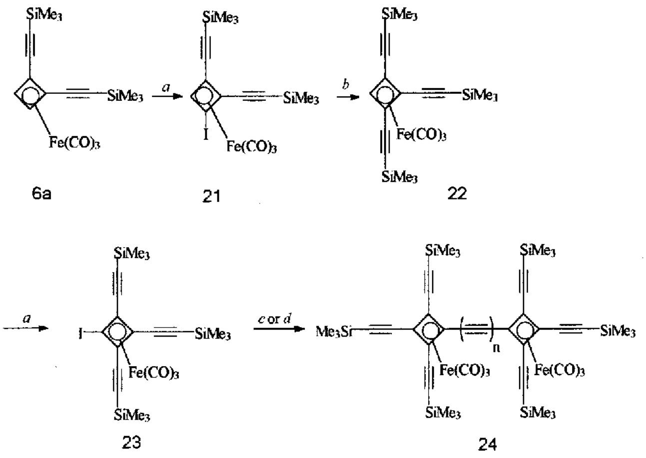
oligomers, or products such as **20b**, could be unstable under the reaction conditions.

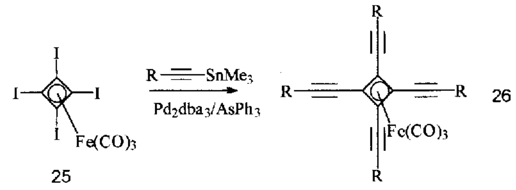
Synthesis of Peralkynylated Tricarbonyl(cyclobutadiene)iron Complexes

Stepwise Synthesis: Reaction of **6a** with *sec*-BuLi (THF, −78 °C) for 15 min led to the formation of a lithiated species. Quenching by addition of 1,2-diiodoethane and subsequent chromatography yielded **21** (89%). Due to the stereochemical equivalence of the cyclobutadiene protons in **6a** the usual precautions required for selective *ortho*-lithiation (vide supra) were not necessary. At 21 °C, **21** showed a pronounced tendency to decompose; it was stable for longer periods only at a temperature below −30 °C, but could be characterized by NMR, IR and mass spectroscopy. Immediate coupling of **21** with **2a** afforded the triyne **22** (53%). Use of Beletskaya's catalyst proved more successful than the Farina system, since complete removal of catalyst residues containing triphenylarsane and decomposition products of Pd_2dba_3 was impossible in the latter case. The lemon-yellow and crystalline triyne **22** was stable under laboratory conditions for several days and showed no signs of decomposition when stored in the deep freeze for extended periods. Performance of the deprotonation/iodination reaction on **22** produced the iodide **23** in 41% yield. In contrast to **21**, **23** was stable at ambient conditions over several days.

The final stage of the synthesis involved coupling of **23** with bis(trimethylstannyl)ethyne **8** or -butadiyne **9** using catalytic palladium to obtain the dumbbells **24a** and **24b** in yields of 76 and 66%, respectively, after aqueous workup and chromatography. The lemon-colored dinuclear species **24** were readily soluble both in pentane and in dichloromethane. In the solid state **24a, b** are only moderately sensitive under normal atmospheric conditions, but are completely stable for extended periods at −18 °C. Their structure was unequivocally assigned from NMR, IR and mass spectral data and from their elemental composition (**24b**).

The One-Pot Procedure: Having succeeded in the synthesis of perethynylated cyclobutadiene complexes **24** in a stepwise fashion (vide supra), the question arose whether tetraethynylated cyclobutadiene complexes could be accessible by a one-pot procedure using the tetraiodide **25** (available in multigram quantities[27]). However, as we have shown[28], it is not possible to use Heck-Cassar-Sonogashira-Hagihara coupling for the introduction of ethynyl groups to the tricarbonyl(cyclobutadiene)iron nucleus. Instead, a palladium-catalyzed amination occurs. Using **25** and applying Stille-Farina conditions[29] (vide supra) gave a number of novel tetraalkynylated cyclobutadiene complexes **26**.





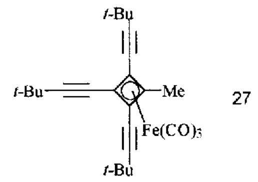
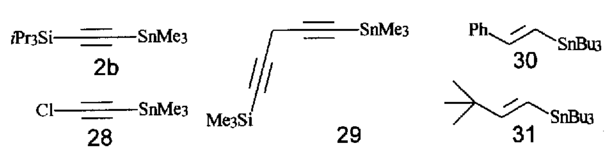


Table 3. Yields and substituent key for **26**

26	**a**	**b**	**c**	**d**	**e**	**f**
R	*tert*-butyl	octyl	methyl	trimethylsilyl	phenyl	(H)
yield	40 %	25 %	81 %	83 %	84 %	(79 %)

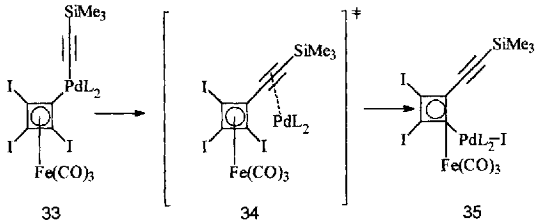
With the exception of **26a** and **b**, the tetraalkynylation of **25** proceeds to give yields over 80%, indicating that the Stille-Farina coupling is an efficient tool for the multiple replacement of iodine substituents at the cyclobutadiene nucleus. After removal of DMF by distillation, the dark residue is filtered through neutral alumina using pentane. The product elutes as an intensely yellow fraction. When the color of the elute fades, all **26** has been washed from the column. Further elution leads to isolation of the coligand triphenylarsane. The low yield for the octyl-substituted **26b** was due to extensive bleeding during chromatography and is probably not intrinsic to the coupling reaction (see Table 3). In order to obtain **26f**, the silane **26d** was treated with potassium carbonate in methanol. The parent **26f** was stable in solution at 21 °C and for a short time in the solid state at temperature below 0 °C, but it decomposes quickly at 21 °C with formation of a brownish, infusible and insoluble material.

In the case of **26a**, a side product was separated from the desired target by careful chromatography. Mass spectroscopy and NMR data unequivocally support the structural assignment of the byproduct to **27** in which one alkyne group is replaced by a methyl group. This product must arise by transfer of a methyl group from **2h**. Apparently, the *tert*-butyl group is sterically hindered enough to show competitive transfer of one methyl group. From the yields, statistics allow the calculation of the selectivity of alkyne/methyl transfer to be ca. 33. In the other cases examined, methyl transfer was not observed; assuming that we would have isolated a yield of 3% or more of a methylated compound (if formed), the transfer selectivity (methyl group/alkyne) must be over 1:200 in the other couplings. Attempts to couple the sterically even more hindered stannane **2b** to **25** were not successful; a product mixture that could not be resolved by chromatography was obtained. Some other stannylalkynes, such as **28** and **29**, also do not couple to the tetraiodo core; instead dark and infusible tarry materials were obtained. To our surprise, under the conditions developed by Müllen and Kiehl[6b], which were applied successfully to couplings of vinyl iodides with vinyl stannanes, no cross coupling product (i.e., tetravinylated cyclobutadienes) could be isolated when **25** was treated with **30** or **31**. Instead, a 15% yield of *all-trans*-1,4-diphenyl-1,3-butadiene, a product arising from the oxidative dimerization of **30**, was observed.

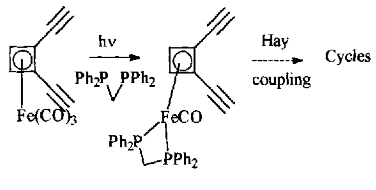


Another question we addressed was whether it was possible to substitute only one, two or three of the iodine substituents in **25** by the Farina-Stille coupling. To this end, a fourfold excess of **25** was treated with one equivalent of **2a** under standard coupling conditions.

To our surprise, workup afforded only **26d** (81% yield based on **2a**, 20% based on **25**) and we isolated 65% of **25** without being able to show the formation of partially alkynylated/iodinated species. This implies that the catalytic species may not leave[13d] the four-membered ring during the reaction sequence, so that after reductive elimination of **33**, the palladium catalyst does not break free from the complex, but immediately executes the next oxidative ad-



33 34 35



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dition. The catalyst leaves for the next molecule of **25** only when the catalytic cycle has been performed four times; thus **34** may or may not be a discrete species in this process. The "hopping" hypothesis also explains the lack of mixed iodo/alkyne species and the excellent yields obtained in the Farina coupling of **25** to **26**.

Conclusions and Outlook

(I) The experiments described above demonstrate that the attachment of alkynyl groups to the cyclobutadiene nucleus of **1a** could be achieved in high yields by coupling of **1b** to stannylated alkynes **2** in a variant of the Stille reaction. Coupling of **1b** to bifunctional stannanes gave rise to bimetallic species **10**–**12** and **16**. The alkynylated cyclobutadienes (**3**) were shown to be substrates for a repeated application of the metalation-iodination-coupling sequence, leading to di- and triethynylated species such as **6**, **7** and **21**–**23**. Iodide **23** led to the synthesis of **24**, the first perethynylated dimeric cyclobutadiene complex. The metalation-iodination reaction of **3** can be controlled (low temperature, precooled *sec*-BuLi) to give merely the *ortho*-iodides **4** due to the lithium complexing effect of the alkynyl group. Relaxation of the conditions favors the formation of an *ortho*/*para* mixture. The iodides **4** and **5** can be used to construct further kinked and linear alkyne-bridged oligomers of **1a** such as **17**–**19**. With tetraiodide **25** it was possible to synthesize a series of tetraalkynylated species **26** in respectable to excellent yield using Farina coupling. The synthesis of the ring systems **20** could not be accomplished due to the decomposition of either the starting material **6** or the products **20** under the Hay coupling conditions employed.

(II) The MIC sequence allows the control of substitution at the cyclobutadiene nucleus to a large extent with the additional advantage of its ease of repetition leading to the first examples of regio-controlled design of multiply alkynylated cyclobutadiene complexes. The variability and the construction-set approach should render the MIC sequence and the products attractive in *modular chemistry*. The application of cyclobutadienes will be advantageous where 90° angles are needed in a construction set; there, the application of benzene derivatives with their performed 60° valence angles is obsolete. The cyclobutadiene nucleus, therefore is a suitable connector with the properties described and may be of use for the construction of two-dimensional lattices and similar objects, such as **D**: The preparation of linear, kinked, star- and dumbbell-shaped segments of the network was accomplished.

(III) Plans involve fine tuning of the ligand sphere of **6** to prepare **36**; we expect **36** to be sterically more encumbered and more stable than **6**, leading to an enhanced propensity towards cyclization to **20**. Segments of **D** with novel topologies would then be accessible.

The deprotection chemistry of the cyclobutadiene nucleus will be examined in detail and the use of ethynylated cyclobutadienes as building blocks in polymers should lead to novel LC materials with the prospect of crosslinked liquid crystalline networks by liberation of the free cyclobutadiene in the film.

We wish to thank Prof. Dr. *K. Müllen* for his generous support. Financial aid was obtained from *Deutsche Forschungsgemeinschaft*, *Stiftung Volkswagenwerk*, and *Fonds der Chemischen Industrie*. We thank *BASF AG* for a gift of cyclooctatetraene.

Experimental

All operations were carried out in flame-dried glassware under N_2. The Pd catalysts and the alkynes were purchased from Aldrich and used as obtained. The solvents were purified according to published procedures. – Column chromatography was accomplished with Baker flash silica gel or aluminium oxide (ALOX S neutral, Riedel-de Haën). – TLC was performed on Merck silica gel 60 F 254 TLC foil. – ^1H and ^{13}C NMR: Bruker AC 300, Bruker AMX 500, Varian Gemini 200. – IR Nicolet Magna 550. MS: VG Trio 2000, Varian CH7A, VG Instruments ZAB-2. – Melting points are uncorrected. – Elemental analyses: Mikroanalytisches Labor des Instituts für Organische Chemie der Johannes-Gutenberg-Universität Mainz.

Stannylacetylenes **2**: The corresponding alkyne (10.0 g) was dissolved in 100 ml of THF and cooled to 0 °C. To this solution, 0.95 equiv. of BuLi was added, the resulting solution stirred for 2 min and cooled to −78 °C. Then 1.00 equiv. of Me_3SnCl were used to quench the lithio acetylide. Stirring for 1 h at 21 °C, quick aqueous workup with pentane and removal of the solvent gave the corresponding stannylated alkynes **2**, which were used without further characterization.

General Coupling Procedure I (Farina) (PI): The corresponding iodide, the stannylated alkyne **2** (1.1–1.6 equiv. per iodo substituent), Pd_2dba_3, and triphenylarsane were dissolved in DMF or THF and stirred for 18 h at 21 °C. For "dry" workup the solvent was removed at 0.1 Torr/30 °C and the residue purified by chromatography. For the "wet" workup the reaction mixture was poured into 200 ml of water and extracted three times with 100 ml of petroleum ether (low boiling). The organic layer was washed with water (five times), dried with $MgSO_4$, and the solvent removed. The residue was either distilled or purified by chromatography.

General Coupling Procedure II (Beletskaya) (PII): Iodide and stannane were placed in a Schlenk flask, DMF and $PdCl_2(CH_3CN)_2$ added, and the mixture stirred for 12 h. Then an additional charge of $PdCl_2(CH_3CN)_2$ was added to ensure complete reaction. Workup was identical to that described above.

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **3a**: Compounds **1b** (3.00 g, 9.46 mmol), **2a** (4.01 g, 15.4 mmol), Pd_2dba_3 (176 mg, 192 µmol) and triphenylarsane (235 mg, 768 µmol) in 50 ml of DMF were coupled according to *PI* (see Procedure I above). Dry workup and sublimation at 40 °C/0.005 Torr gave 1.91 g (69%, m.p. 62 °C) **3a**. – IR (KBr): ν [cm^{-1}] = 2959, 2299, 2041, 1980, 1964, 1949. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.16 (s, 9 H, TMS); 3.93 (s, 2 H, 2-H, 4-H); 4.30 (s, 1 H, 3-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = −0.32 (3 C, TMS); 61.2 (1 C, C-1); 63.6 (1 C, C-3); 66.7 (2 C, C-2, C-4); 96.3 (1 C, alkyne C); 97.4 (1 C, alkyne C); 213.3 (3 C, carbonyl C). – MS (EI, 70 eV): *m/z* (%) = 288 (21) [M$^+$], 260 (48) [M – 1 CO], 232 (37) [M – 2 CO], 204 (100) [M – 3 CO]. – $C_{12}H_{12}FeO_3Si$ (288.16): calcd. C 50.02, H 4.20; found C 49.98, H 4.27.

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **3b**: Compounds **1b** (1.00 g, 3.15 mmol), **2b** (1.57 g, 5.12 mmol), Pd_2dba_3 (88 mg, 96.0 µmol) and triphenylarsane (118 mg, 384 µmol) in 50 ml of DMF were treated according to *PI-wet*. Chromatography (aluminium oxide, pentane) gave **3b** (oil, 850 mg, 77%). – IR (KBr): ν [cm^{-1}] = 3058, 2987, 2868, 2309, 2146, 2054, 1983, 1272. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.01–1.05 (br. s, 21, TIPS H); 3.88 (s, 1 H, 3-H); 4.24 (s, 2 H, 2-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.3 (3 C, TIPS CH); 18.6 (6 C, TIPS CH_3); 61.0 (1 C, C-1); 63.9 (1 C, C-3); 66.8 (2 C, C-2, C-4); 92.2 (1 C, alkyne C); 99.4 (1 C, alkyne C); 213.3 (3 C, carbonyl C). – MS (EI, 70 eV): *m/z* (%) = 372 (16) [M$^+$], 344 (43) [M – 1 CO], 316 (24) [M – 2 CO], 288 (100) [M – 3 CO]. – $C_{18}H_{24}FeO_3Si$ (372.34): calcd. C 58.06, H 6.50; found C 58.11, H 6.47.

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **3c**: **1b** (2.00 g, 6.31 mmol), **2c** (2.67 g, 10.1 mmol), Pd_2dba_3 (173 mg, 189 µmol) and triphenylarsane (232 mg, 756 µmol) in 40 ml of DMF were treated according to *PI-wet* and furnished **3c** after chromatography (flash silica gel, pentane; 1.31 g, 71%; m.p. 67 °C). – IR (KBr): ν [cm^{-1}] = 3084, 3056, 2302, 2049, 1974, 1596, 1499, 1444. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.02 (s, 1 H, 3-H); 4.37 (s, 2 H, 2-H, 4-H); 7.30–7.39 (m, 5 H, phenyl H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 61.5 (1 C, C-1); 64.2 (1 C, C-3); 66.5 (2 C, C-2, C-4); 82.3 (1 C, alkyne C); 89.8 (1 C, alkyne C); 122.6 (1 C, C-1′); 128.3 (2 C, C-2′,C-6′); 128.4 (1 C, C-4′); 131.8 (2 C, C-3′, C-5′); 213.7 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 292 (25) [M$^+$], 264 (66) [M – 1 CO], 236 (44) [M – 2 CO], 208 (95) [M – 3 CO]. – $C_{15}H_8FeO_3$ (292.07): calcd. C 61.68, H 2.76; found C 61.66, H 2.85.

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **3d**: Compound **3a** (1.00 g, 3.50 mmol) and potassium carbonate (968 mg, 7.00 mmol) were dissolved in 15 ml of methanol and stirred for 20 min at 21 °C. Aqueous workup and sublimation at 20 °C/0.005 Torr gave **3d**, (703 mg, 93%) as a relatively unstable yellow oil crystallizing at −20 °C. – IR (KBr): ν [cm^{-1}] = 3305, 3142, 3131, 3124, 2051, 1973. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.85 (s, 1 H, alkyne H); 4.00 (s, 1 H, 3-H), 4.32 (s, 2 H, 2-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 59.2 (1 C, C-1); 64.4 (1 C, C-3); 66.5 (2 C, C-2, C-4); 76.7 (1 C, alkyne C); 78.0 (1 C, alkyne CH); 213.0 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 216 (12) [M$^+$], 188 (39) [M – 1 CO], 160 (34) [M – 2 CO], 132 (100) [M – 3 CO].

Monobutadiynylated Tricarbonyl(cyclobutadiene)iron Complex **3f**: According to *PII-wet*, **1b** (500 mg, 1.60 mmol), **2f** (741 mg, 2.60 mmol), Pd_2dba_3 (58.6 mg, 64.0 µmol) and triphenylarsane (78.4 mg, 256 µmol) were coupled in 2 ml of THF (6 h). Filtration (aluminium oxide, pentane) gave **3f** (259 mg, 52%; m.p. 62–63 °C). – IR (KBr): ν [cm^{-1}] = 3124, 3116, 3104, 2960, 2926, 2900, 2098, 2057, 2048, 1985, 1969. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (s, 9 H, TMS H); 4.07 (s, 1 H, 3-H); 4.37 (s, 2 H, 2-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.54 (9 C, TMS C); 57.8 (1 C, C-1); 66.1 (1 C, C-3); 67.1 (2 C, C-2, C-4); 70.5 (1 C, butadiyne C); 74.6 (1 C, butadiyne C); 87.8 (1 C, butadiyne C); 91.1 (1 C, butadiyne C); 212.5 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 312 (10) [M$^+$], 284 (33) [M – 1 CO], 256 (37) [M – 2 CO], 228 (100) [M – 3 CO]. – $C_{14}H_{12}FeO_3Si$ (312.18): calcd. C 53.86, H 3.87; found C 53.92, H 3.97.

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **3g**: By analogy to **3a**, **3f** (560 mg, 1.79 mmol) and potassium carbonate (496 mg, 3.58 mmol) were dissolved in 10 ml of methanol and stirred for 15 min. Aqueous workup and distillation at 45 °C/0.1 Torr yielded **3g** (244 mg, 57%) as a sensitive yellow oil. – IR (KBr): ν [cm^{-1}] = 3307, 3116, 3061, 3029, 2227, 2200, 2057, 1984. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (1 H, butadiyne H); 4.05 (s, 1 H, 3-H); 4.36 (s, 2 H, 2-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 57.2 (1 C, C-1); 66.1 (1 C, C-3); 67.2 (2 C, C-2, C-4); 68.2 (1 C, butadiyne C); 69.3 (1 C, butadiyne C); 71.5 (1 C, butadiyne C); 73.8 (1 C, butadiyne *C*H); 212.5 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 240 (45) [M$^+$], 212 (83) [M – 1 CO], 184 (35) [M – 2 CO], 156 (100) [M – 3 CO].

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **4a**: General Metalation Procedure (MP): Alkyne **3a** was placed in a flame-dried and argon-flushed Schlenk tube. After addition of 150 ml of THF the reaction mixture was cooled to −78 °C. For selective *ortho*-metalation, *sec*-BuLi, delivered as a 1.4 M solution in cyclohexane, must be administered to the precooled walls of the reaction vessel. With this procedure the cyclohexane solution freezes. By gentle shaking the *sec*-BuLi dissolved slowly (depending on the amount, in 2–10 min) into the solution of **3a**. After 15 min 1.1 equiv. of 1,2-diiodoethane in ca. 10 ml of THF was added quickly into the reaction mixture. 10 min after the addition of 1,2-diiodoethane, the cooling bath was removed, 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 was extracted several times with pentane. The combined organic phases were washed several times with water. After drying with $MgSO_4$ and removal of pentane, the product was chromatographed over flash silica gel with pentane as eluent. This procedure gave exclusively (>95%) the *ortho*-iodinated product **4a**. If the metalation was conducted by simple syringe injection of *sec*-BuLi to the solution of the precooled alkyne, a mixture of *ortho*- and *para*-iodide (**4a** and **5a**) was isolated. The complete separation of the iodides **4a** and **5a** by flash chromatography was difficult. It was possible to combine the fractions enriched in **5a** of several runs and to isolate the pure *para*-iodide **5a** by repeated chromatography (flash silica gel, pentane). The amount of **5a** never exceeded 25%. The iodination of **3a** (1.30 g, 4.51 mmol) with *sec*-BuLi (3.9 ml, 5.41 mmol) and 1,2-diiodoethane (1.52 g, 5.41 mmol) as described in the general procedure for metalation yielded **4a** (1.28 g, 74%; yellow crystals, m.p. 81 °C). – IR (KBr, cm^{-1}): ν = 3129, 3104, 2362, 2050, 1998, 1968, 1927, 1252. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 9 H, TMS-H), 4.21 (s, 1 H, cyclobutadiene H), 4.70 (s, 1 H, cyclobutadiene H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.3 (3 C, TMS C), 27.9 (1 C, cyclobutadiene C–I), 65.4, 66.3, 67.6 (3 C, cyclobutadiene C), 95.7, 99.7 (2 C, alkyne C), 212.53 (3 C, CO). – MS (FD): 414 [M]. – $C_{12}H_{11}FeIO_3Si$: calcd. C 34.81, H 2.68; found C 35.07, H 2.64.

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **5a**: If room temp. (not precooled) *sec*-BuLi was used under otherwise identical conditions, a mixture of *ortho*- and *para*-iodide in a ratio of up to 4:1 was obtained. The mixture can be separated by repeated flash chromatography. **5a**: m.p. 45 °C. – IR (KBr): ν [cm^{-1}] = 3057, 2996, 2311, 2148, 2057, 1990. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 9H, TMS H); 4.60 (s, 2H, 3-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.43 (3 C, TMS C); 23.9 (1 C, C–I), 61.7, 71.9 (3 C, cyclobutadiene C), 95.7, 98.1 (2 C, alkyne C); 212.5 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 414 (5) [M$^+$], 386 (16) [M – 1 CO], 358 (15) [M – 2 CO], 331 (74) [M – 3 CO].

Monoethynylated Tricarbonyl(cyclobutadiene)iron Complex **4b**: According to the metalation procedure (MP), **3b** (850 mg, 2.47 mmol) was treated with *sec*-BuLi (1.9 ml, 2.64 mmol) and 1,2-diiodoethane (744 mg, 2.64 mmol) and worked up. Chromatography (silica gel, petroleum ether) yielded **4b** (722 mg, 62%, yellow crystals, m.p. 81 °C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (m, 21H, TIPS H); 4.25, 4.74 (2 s, 2H, cyclobutadiene H, order unknown). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.4 (3 C, TIPS CH); 18.9 (6 C, TIPS CH_3); 28.9 (1 C, C-1); 65.4, 67.9 (2 C, C-3, C-4, order unknown); 72.3 (1 C, C-2); 96.9 (1 C, alkyne C); 97.9 (1 C, alkyne C); 212.9 (3 C, CO). – MS (FD): *m/z* = 470 [M$^+$].

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **6a**: According to *PII-wet*, **4a** (1.00 g, 2.42 mmol), **2a** (784 mg, 3.86 mmol), $Pd(CH_3CN)_2Cl_2$ (19 mg, 72 µmol) and 15 ml of DMF were stirred. After 18 h, 19 mg of the catalyst was added and the reaction mixture stirred for another 18 h. Chromatography (silica gel, pentane) yields **6a** (726 mg, 78%; yellow crystals, m.p. 64 °C). If the Pd_2dba_3/triphenylarsane catalyst system is used, the yield goes up to 81%, but triphenylarsane must be removed by sublimation (60 °C/0.005 Torr). – IR (KBr): ν [cm^{-1}] = 3127, 2958, 2900, 2146, 1991, 1986, 1980, 1434. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (s, 18H, TMS H); 4.24 (s, 2H, 3-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.23 (6 C, TMS C); 64.7 (2 C, C-1, C-2); 66.2 (2 C, C-3, C-4); 96.0 (2 C, alkyne C); 98.9 (2 C, alkyne C); 212.4 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 384 (7) [M$^+$], 356 (16) [M – 1 CO], 328 (8) [M – 2 CO], 300 (100) [M – 3 CO]. – $C_{17}H_{20}FeO_3Si_2$ (384.03): calcd. C 53.12, H 5.24; found C 53.13, H 5.18.

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **6b**: According to *PII-wet*, **4a** (400 mg, 966 µmol), **2b** (535 mg, 1.55 mmol) $Pd(CH_3CN)_2Cl_2$ (8.0 mg, 29 µmol) and 10 ml of DMF were stirred for 24 h. 8.0 mg of catalyst was then added and stirring continued for 24 h. Chromatography (silica gel, pentane) afforded **7b** (267 mg, 59%, yellow oil). – IR (KBr): ν [cm^{-1}] = 2960, 2946, 2893, 2867, 2158, 2055, 1984, 1484, 1464, 1251. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 18H, TMS H); 1.02 (m, 21H, TIPS H); 4.58 (s, 2H, 2-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.22 (3 C, TMS C); 11.2 (3 C, TIPS CH); 18.5 (6 C, TIPS CH_3); 61.0, 61.5 (2 C, C-1, C-3, unknown order); 69.6 (2 C, C-2, C-4); 94.6, 96.4, 97.8, 98.1 (4 C, alkyne C, unknown order); 212.4 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 468 (7) [M$^+$], 440 (52) [M – 1 CO], 412 (18) [M – 2 CO], 384 (100) [M – 3 CO]. – HR-MS: $C_{23}H_{32}FeO_3Si_2$, calcd. 468.1239, found 468.1249.

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **6c**: Compounds **4a** (400 mg, 0.97 mmol), **2h** (379 mg, 1.55 mmol), $Pd(CH_3CN)_2Cl_2$ (8.0 mg, 29 µmol) and 10 ml of DMF were treated according to *PII-wet*. After 18 h, 8.0 mg of catalyst was added and the reaction stirred for another 24 h. Chromatography (silica gel, pentane) yielded **6** (204 mg, 57%; yellow crystals, m.p. 73 °C). – IR (KBr): ν [cm^{-1}] = 3065, 2973, 2937, 2224, 2135, 2051, 1988, 1979, 1976, 1456. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 9H, TMS H); 1.21 (s, 9H, *tert*-butyl); 4.14, 4.17 (2 s, 2H, 3-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.3 (9 C, TMS C); 28.3 (1 C, *tert*-butyl C); 30.6 (3 C, *tert*-butyl *C*H_3); 64.4, 66.1 (2 C, C-3, C-4, unknown order); 68.1, 70.0 (2 C, C-1, C-2, unknown order); 96.4, 98.2, 98.3, 102.3 (4 C, alkyne C); 212.8 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 368 (12) [M$^+$], 340 (25) [M – 1 CO], 312 (19) [M – 2 CO], 284 (100) [M – 3 CO]. – $C_{18}H_{20}FeO_3Si$ (368.29): calcd. C 58.70, H 5.47; found C 58.65, H 5.41.

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **6d**: According to *PII-wet*, **4a** (600 mg, 1.45 mmol), **2c** (614 mg, 2.32 mmol), $Pd(CH_3CN)_2Cl_2$ (11 mg, 44 µmol) and 15 ml of DMF were stirred for 18 h. Then 11.0 mg catalyst was added. After 24 h the reaction was worked up. Chromatography (silica gel, pentane) gave **6d** (366 mg, 65%, brown oil). – IR (KBr): ν [cm^{-1}] = 3051, 2823, 2159, 2052, 1982, 1265. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (s, 9H, TMS H); 4.31, 4.33 (2 s, 2H, 3-H, 4-H, order unknown). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.28 (9 C, TMS C); 64.6, 65.1 (2 C, C-1, C-2, order unknown); 66.0, 66.7 (2 C, C-3, C-4, order unknown); 81.0, 92.0 (2 C, C-1′,C-2′, order unknown); 96.0, 98.9 (2 C, C-1‴, C-2‴, order unknown); 122.6 (1 C, C-1″); 128.3, 131.6 (4 C,C-2″, C-6″, C-3″, C-5″, order unknown); 128.6 (1 C, C-4″); 212.4 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 388 (8), [M$^+$], 360 (17) [M – 1 CO], 332 (11) [M – 2 CO], 304 (100) [M – 3 CO]. – $C_{20}H_{16}FeO_3Si$ (388.28): calcd. C 61.87, H 4.15; found C 61.88, H 4.28.

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **6e** Using *PII-wet*, **4a** (500 mg, 1.21 mmol), **2i** (508 mg, 1.93 mmol), $Pd(CH_3CN)_2Cl_2$ (42.0 mg, 603 µmol) and 12 ml of DMF were stirred for 24 h. Chromatography (aluminium oxide; pentane, dichloromethane, 20:1; 141 mg, 28%, brown oil) yielded **6e**. – IR (KBr): ν [cm^{-1}] = 3110, 2846, 2822, 2254, 2057, 1993, 909. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 9H, TMS H); 1.25 (s, 9H, *tert*-butyl); 4.32 (s, 2H, 3-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.35 (9 C, TMS C); 28.4 (1 C, *tert*-butyl C); 30.2 (3 C, *tert*-butyl CH_3); 61.0, 68.5 (2 C, C-1, C-2, order unknown); 66.7, 68.9 (2 C, C-3, C-4, order unknown); 64.4, 65.9, 67.9, 69.5, 76.6, 90.7 (6 C, hexatriyne C, order unknown); 95.2, 99.8 (2 C, alkyne C); 211.6 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 416 (4) [M$^+$], 388 (9) [M – 1 CO], 360 (3) [M – 2 CO], 332 (77) [M – 3 CO]. – $C_{22}H_{20}FeO_3Si$ (416.33): calcd. C 63.47, H 4.84; found C 63.28, H 4.94.

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **6f**: Compound **6a** (900 mg, 2.34 mmol) and potassium carbonate (1.30 g, 9.37 mmol) were stirred for 20 min at 21 °C in 30 ml of methanol. Aqueous workup and chromatography (silica gel, pentane) yields analytically pure **6f** (562 mg, 100%; yellow crystals, m.p. 88 °C, dec.). – IR (KBr): ν [cm^{-1}] = 3291, 3277, 3129, 2052, 2005, 1982, 1700. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.04 (s, 2H, alkyne H); 4.33 (s, 2H, 3-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 62.7 (2 C, C-1, C-2); 66.8 (2 C, C-3, C-4); 75.1 (2 C, alkyne C); 80.3 (2 C, alkyne *C*H); 211.8 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 240 (25) [M$^+$], 212 (42) [M – 1 CO], 184 (19) [M – 2 CO], 156 (100) [M – 3 CO]. – $C_{11}H_4FeO_3$ (239.998): calcd. C 55.05, H 1.68; found C 54.98, H 1.77.

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **6g**: Compound **6b** (40.0 mg, 90.0 µmol) and potassium carbonate (25.0 mg, 180 µmol) were stirred in 5 ml of methanol for 20 min. Workup and chromatography (silica gel, pentane) yielded **6f** (24 mg, 65%, yellow oil). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (m, 21H, TIPS H); 3.00 (s, 1H, ethynyl H); 4.28, 4.33 (2 s, 2H, 3-H, 4-H, order unknown). – MS (FD): *m/z* = 368 [M$^+$].

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **7a**: According to *PII-wet*, **5a** (400 mg, 966 µmol), **2a** (311 mg, 1.55 mmol), $Pd(CH_3CN)_2Cl_2$ (8.0 mg, 29 µmol) and 10 ml of DMF were stirred. After 18 h the same amount of catalyst was added and stirred for another 24 h. Chromatography (silica gel, pentane) yielded analytically pure **7a** (264 mg, 71%; yellow crystals, m.p. 95 °C). – IR (KBr): ν [cm^{-1}] = 3194, 2964, 2928, 2874, 2164, 2057, 1997, 1466,

1383. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 18 H, TMS H); 4.61 (s, 2 H, 2-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.41 (6 C, TMS C); 61.0 (2 C, C-1, C-3); 69.5 (2 C, C-2, C-4); 95.4 (2 C, alkyne C); 97.7 (2 C, alkyne C); 212.4 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 384 (13) [M$^+$], 356 (58) [M – 1 CO], 328 (97) [M – 2 CO], 300 (100) [M – 3 CO]. – $C_{17}H_{20}FeO_3Si_2$ (384.03): calcd. C 53.12, H 5.24; found C 53.11, H 5.25.

Diethynylated Tricarbonyl(cyclobutadiene)iron Complex **7b**: Compounds **5a** (850 mg, 2.05 mmol), **2b** (1.13 g, 3.28 mmol), $Pd(CH_3CN)_2Cl_2$ (16 mg, 63 μmol) and 15 ml of DMF were stirred for 24 h and treated according to *PII-wet*. Addition of the same amount of catalyst and continued stirring for 24 h yielded **7b** after chromatography (silica gel, petroleum ether, yellow oil, 595 mg, 62%). – IR (KBr): ν [cm^{-1}] = 3108, 3104, 2960, 2945, 2894, 2867, 2154, 2054, 1994, 1962, 1464, 1251. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 18 H, TMS H); 1.05 (m, 21 H, TIPS H); 4.25 (s, 2 H, 3-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.21 (3 C, TMS C); 11.2 (3 C, TIPS CH); 18.6 (6 C, TIPS CH_3); 64.8, 65.1 (2 C, C-1, C-2, order unknown); 66.1, 66.4 (2 C, C-3, C-4, order unknown); 95.7, 96.0, 97.9, 98.8 (4 C, alkyne C, order unknown); 212.4 (3 C, CO). – MS (EI, 70 eV): *mlh* (%) = 468 (7) [M$^+$], 440 (14) [M – 1 CO], 412 (4) [M – 2 CO], 384 (100) [M – 3 CO]; HR-MS: $C_{23}H_{32}FeO_3Si_2$, calcd. 468.1239; found 468.1250.

Diethynylated Tricarbonyl(cyclobutadiene)cobalt Complex **7f**: Compound **7a** (430 mg, 1.12 mmol) and potassium carbonate (618 mg, 4.47 mmol) were stirred in 10 ml of methanol for 20 min. Workup and chromatography (silica gel, pentane) yielded **7c**. (250 mg, 93%; yellow crystals, m.p. 58 °C, dec.). – IR (KBr): ν [cm^{-1}] = 3304, 3051, 2309, 2061, 1983, 1717. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90 (s, 2 H, alkynyl H); 4.63 (s, 2 H, 3-H, 4-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.5 (2 C, C-1, C-3); 69.2 (2 C, C-2, C-4); 75.4 (2 C, alkyne C); 79.5 (2 C, alkyne CH); 211.9 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 240 (23) [M$^+$], 212 (40) [M – 1 CO], 184 (18) [M – 2 CO], 156 (100) [M – 3 CO].

Bridged Complex **10**: Compound **1b** (200 mg, 630 μmol), **8** (105 mg, 300 μmol), Pd_2dba_3 (11.0 mg, 3.0 μmol) and triphenylarsane (14.7 mg, 12 μmol) were stirred in 3 ml of DMF for 12 h at 21 °C. Aqueous workup and chromatography (silica gel, pentane/dichloromethane, 15:1) yielded **10** (98.5 mg, 81%, m.p. 98–100 °C). – IR (KBr): ν [cm^{-1}] = 3140, 3125, 3104, 2039, 1974, 1950, 1921. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.01 (s, 2 H, 3′-, 3″-H); 4.30 (s, 4 H, 2′-H, 4′-H, 2″-H, 4″-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 60.3 (2 C, C-1′, C-1″); 64.8 (2 C, C-3′, C-3″); 66.4 (4 C, C-2′, C-4′, C-2″, C-4″); 82.8 (2 C, C-1, C-2); 213.0 (3 C, CO). – MS (FD): *m/z* = 406 [M$^+$]. – $C_{16}H_6Fe_2O_6$ (405.91): calcd. C 47.34, H 1.49; found C 47.16, H 1.52.

Bridged Complex **11**: Ethynylcymantrene[14] was treated with $Et_2N \cdot SnMe_3$[20]. Excess stannylamide and diethylamine were removed at 0.001 Torr/21 °C. According to *PI-wet*, **1b** (381 mg, 1.20 mmol), the stannylated ethynylcymantrene (707 mg, 1.20 mmol), Pd_2dba_3 (22.4 mg, 24 μmol), and triphenylarsane (29.3 mg, 96.0 μmol) were stirred for 48 h in 15 ml of DMF. Chromatography (silica gel, pentane/dichlormethane, 6:1) yielded analytical pure **11** (276 mg, 55%, m.p. 126 °C). – IR (KBr): ν [cm^{-1}] = 3125, 3104, 2044, 2015, 1972, 1926, 1919, 1149. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.01 (s, 1 H, 3-H); 4.32 (s, 2 H, 2-H, 4-H); 4.65 (s, 2 H, 3′-H, 4′-H); 4.94 (s, 2 H, 2′-H, 5′-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 59.9 (1 C, C-1), 65.3 (1 C, C-3); 66.8 (2 C, C-2, C-4); 81.4 (1 C, C-1′); 82.0 (2 C, C-2′, C-5′); 82.3 (1 C, alkyne C); 82.4 (1 C, alkyne C); 86.5 (2 C, C-3′, C-4′); 213.5 (3 C, Fe-CO); 224.4 (3 C) [Mn-CO]. – MS (EI, 70 eV): *m/z* (%) = 418 (19) [M$^+$], 390 (11) [M – 1 CO], 362 (22) [M – 2 CO], 334 (21) [M – 3 CO], 306 (40) [M – 4 CO], 278 (100) [M – 5 CO], 250 (37) [M – 6 CO].

Bridged Complex **12**: *(a) by Stille Coupling:* **1b** (200 mg, 630 μmol), **9** (113 mg, 300 μmol), Pd_2dba_3 (11.0 mg, 12.0 μmol) triphenylarsane (14.7 mg, 48.0 μmol) and 3 ml of THF were stirred for 12 h. Aqueous workup and chromatography (silica gel, pentane/dichlormethane, 20:1) yields **12** (87.2 mg, 67%, m.p. 129 °C). *(b) By Hay Coupling:* **3d** (150 mg, 0.694 mmol), CuCl (100 mg, 1.01 mmol), TMEDA (107 mg, 0.92 mmol) were dissolved in 50 ml of acetone. Oxygen was bubbled through the solution for 2 h at 21 °C. Aqueous workup and chromatography yielded **12** (81 mg, 54%). – IR (KBr): ν [cm^{-1}] = 3133, 3120, 3105, 2063, 2049, 1982, 1938. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.08 (s, 2 H, 3′-H, 3″-H); 4.37 (s, 4 H, 2′-H, 4′-H, 2″-H, 4″-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 57.9 (2 C, C-1′, C-1″); 66.4 (2 C, C-3, C-3′); 67.2 (4 C, C-2′, C-4′, C-2″, C-4″); 74.3, 75.6 (4 C, C-1, C-2, C-3, C-4, unknown order); 212.6 (3 C, CO). – MS (FD): *m/z* = 430 [M$^+$]. – $C_{18}H_6Fe_2O_6$ (429.76): calcd. C 50.29, H 1.41; found C 50.19, H 1.53.

Bridged Complex **13**: Compounds **5a** (390 mg, 0.94 mmol), **8** (166 mg, 0.47 mmol), $Pd(CH_3CN)_2Cl_2$ (9.8 mg, 40 μmol) and 3 ml of DMF were stirred. After 24 h the same amount of catalyst was added and stirring continued for 48 h. Workup and chromatography (silica gel, pentane) yielded starting material **5a**. Increasing the polarity of the eluent (pentane/dichlormethane, 20:1) yielded **13** (110 mg, 39%; dark yellow crystals, m.p. 151 °C). – IR (KBr): ν [cm^{-1}] = 3166, 2957, 2914, 2160, 2037, 1984, 1455. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 36 H, TMS H); 4.33 (s, 4 H, 2′-H, 2″-H, 4′-H, 4″-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.3 (6 C, TMS C); 60.8, 63.5 (4 C, C-1′, C-1″, C-3, C-3′, order unknown); 68.6 (4 C, C-2′, C-2″, C-4′, C-4″); 83.5 (C-1, C-2); 95.6 (2 C, alkyne C); 99.1 (2 C, alkyne C); 212.4 (6 C, CO). – MS (EI, 70 eV): *m/z* (%) = 598 (11) [M$^+$], 570 (11) [M – 1 CO], 5.42 (9) [M – 2 CO], 514 (39) [M – 3 CO], 486 (32) [M – 4 CO], 458 (2) [M – 5 CO], 430 (40) [M – 6 CO]. – $C_{26}H_{22}Fe_2O_6Si_2$ (598.32): calcd. C 52.19, H 3.71; found C 52.19, H 3.72.

Bridged Complex **14**: Stannylation of **7c** (165 mg, 0.94 mmol) with Lappert's reagent[69] and coupling with **5a** (242 mg, 580 μmol), $Pd(CH_3CN)_2Cl_2$) (2 × 6.1 mg, 24 μmol, 48 h) in 3 ml of DMF and chromatography (silica gel, pentane/dichloromethane, 20:1) yielded **14** (73 mg, 31%; dark yellow crystals, m.p. 169 °C). – IR (KBr): ν [cm^{-1}] = 3099, 2970, 2301, 2054, 1995, 1444. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 18 H, TMS-H); 4.24 (s, 6 H, 2-H, 4-H, 4′-H, 6′-H, 4″-H, 6″-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.31 (6 C, TMS C); 61.2, 61.5, 62.7 (6 C, C-1, C-3, C-3′, C-3″, C-5′, C-5″, order unknown); 67.3 (2 C, C-2, C-4); 68.1 (4 C, C-4′, C-4″, C-6′, C-6″); 82.1, 82.4 (4 C, C-1′, C-1″, C-2′, C-2″, order unknown); 96.1 (2 C, alkyne C); 99.0 (2 C, alkyne C); 211.9 (3 C, CO); 212.1 (6 C, CO). – MS (FD): *m/z* = 812 [M$^+$].

Bridged Complex **16a**: Compound **7g** (277 mg, 1.33 mmol) was treated with 1.0 ml of Lappert's reagent and stirred for 20 min. The excess reagent and the formed amine were removed at 0.001 Torr/21 °C. **1b** (800 mg, 2.52 mmol), Pd_2dba_3 (12 mg, 13.1 μmol), triphenylarsane (15 mg, 49.0 μmol) in 5 ml of DMF were added to the formed stannane and treated according to *PI-dry*. Filtration (aluminium oxide, pentane) gave **15a** (409 mg, 55%, dec. 202 °C, without melting) as sole product. – IR (KBr): ν [cm^{-1}] = 3130, 3111, 3102, 3090, 2059, 2054, 1963, 1953. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.97, 4.28 (s, 4 H, cyclobutadiene H), 4.50 (s, 2 H, cyclobutadiene H), 4.98 (s, 5 H, Cp H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 54.4, 62.6, 64.0, 64.2, 66.1 (12 C, cyclobutadiene C), 81.3 (5 C, Cp C), 82.5, 87.1 (4 C, alkyne C), 213.3 (6 C, CO). –

MS (EI, 70 eV): *m/z* (%) = 604 (20) [M^+], 576 (9) [M − 1 CO], 520 (41) [M − 3 CO], 492 (10) [M − 4 CO], 464 (5) [M − 5 CO], 436 (21) [M − 6 CO]. − $C_{27}H_{13}CoFe_2O_6$ (604.00): calcd. C 53.69, H 2.17; found C 53.72, H 2.16.

Bridged Complex **16b**: Lappert's reagent (0.8 ml), and **7h** (200 mg, 0.543 mmol) was allowed to react for 15 min. Excess stannylamide and amine were removed at 21°C/0.001 Torr. The formed **7f**, **1b** (381 mg, 1.20 mmol), $PdCl_2(CH_3CN)_2$ (10 mg, 38.5 μmol) and 10 ml of DMF were stirred for 18 h. Aqueous workup and chromatography (silica gel, first with pentane) led to removal of starting material; elution with pentane/dichloromethane, 9:1, yielded bridged complex **15** (131 mg, 43%, yellow oil). − IR (KBr): ν [cm^{-1}] = 3309, 3187, 2956, 2190, 2092, 2047, 1975, 1736. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 18H, TMS H), 2.97 (s, 1H, alkyne H), 4.03 (s, 1H, cyclobutadiene H), 4.29 (s, 2H, cyclobutadiene H), 4.90 (s, 5H, Cp H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.6 (6 C, TMS C), 62.6, 63.5, 64.0, 64.2, 66.1, 76.0 (8 C, cyclobutadiene C), 78.4 (1 C, alkyne CH), 81.3 (5 C, Cp C), 82.3, 82.8, 89.0 (3 C, alkyne C), 213.4 (C, CO). − MS (EI, 70 eV): *m/z* (%) = 558 (40) [M^+], 530 (12) [M − 1 CO], 502 (8) [M − 2 CO], 474 (75) [M − 3 CO]. − Further elution with the same solvent combination gave **16b** (71 mg, 23%, yellow oil). − IR (KBr): ν [cm^{-1}] = 2957, 2925, 2185, 2047, 1975, 1247. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 18H, TMS H), 3.98 (s, 2H, cyclobutadiene H), 4.26 (s, 4H, cyclobutadiene H), 4.88 (s, 5H, Cp H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.6 (6 C, TMS C), 62.6, 64.2, 66.1, 76.0 (12 C, cyclobutadiene C), 81.2 (5 C, Cp C), 83.0, 89.0 (4 C, alkyne C), 213.4 (C, CO). − MS (EI, 70 eV): *m/z* (%) = 748 (20) [M^+], 720 (2) [M − 1 CO], 692 (2) [M − 2 CO], 664 (50) [M − 3 CO], 580 (30) [M − 6 CO].

Bridged Complex **17a**: According to *PII-wet*, **4a** (1.20 g, 3.00 mmol), **8** (563 mg, 1.50 mmol), and $Pd(CH_3CN)_2Cl_2$ (15.5 mg, 60 μmol) were stirred in 30 ml of DMF. After 18 h catalyst (7.8 mg, 30 μmol) were added and stirring was continued for 24 h. Chromatography (silica gel, petroleum ether) yielded **17a** as a mixture of diastereomers (422 mg, 47%; dark yellow crystals, m.p. 143°C). − IR (KBr): ν [cm^{-1}] = 3107, 2961, 2925, 2138, 2051, 1987, 1737, 1251, 860. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.19 (s, 18H, TMS H); 4.29, 4.33 (2 s, 4H, 3′-H, 3′-H′, 4′-H, 4″-H, order unknown). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.33 (q, 6 C, TMS C); 63.4 (s, 2 C, C-2′, C-2″); 64.7, 64.9 (2 s, 2 C, C-1′, C-1″); 66.3, 66.4 (2 d, 2 C, C-4′, C-4″); 67.5 (d, 2 C, C-3′, C-3″); 83.5 (s, 2 C, C-1, C-2); 95.7 (s, 2 C, alkyne C); 99.2 (s, 2 C, alkyne C); 212.0 (s, 6 C, CO). − MS (FD): *m/z* = 598 [M^+]. − $C_{26}H_{22}Fe_2O_6$ Si_2 (598.32): calcd. C 52.19, H 3.71; found C 52.11, H 3.74.

Bridged Complex **18**: Compound **6f** (156 mg, 650 μmol) was treated with an excess of Et_2N-$SnMe_3$[69]. After 15 min amine and excess of $Et_2N \cdot SnMe_3$ were removed in vacuo. **6h** was dried for 1 h at 0.01 Torr/21°C. Crude **6h**, **4a** (564 mg, 1.35 mmol), $Pd(CH_3CN)_2Cl_2$ (7.0 mg, 27 μmol) and 5 ml of DMF were stirred. After 24 h, catalyst (7.0 mg, 27 μmol) was added and stirring continued for 12 h. Workup and chromatography (pentane/dichlormethane, 15:1) yielded **18** (200 mg, 38%; brown crystals, m.p. 111°C, diastereomeric mixture). − IR (KBr): ν [cm^{-1}] = 3055, 2989, 2306, 2054, 1986, 1422, 896. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 18H, TMS H); 4.26−4.35 (m, 6H, 3-H, 4-H, 5′-H, 5″-H, 6′-H, 6″-H, order unknown). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.33 (6 C, TMS C); 63.2, 63.4, 63.6, 64.7, 64.9, 65.8, 66.2, 67.2, 67.4, 69.3 (12 C, C-1, C-2, C-3, C-4, C-3′, C-3″, C-4′, C-4″, C-5′, C-5″, C-6′, C-6″, order unknown); 83.3, 83.8 (4 C, C-1′, C-1″, C-2′, C-2″, order unknown); 95.6 (2 C, alkyne C); 99.2 (2 C, alkyne C); 211.7 (s, 3 C, CO); 212.0 (s, 6 C, CO). − MS (FD): *m/z* = 812 [M^+].

Bridged Complex **19a**: According to *PII-wet*, **4a** (500 mg, 1.21 mmol) **9** (227 mg, 604 μmol), Pd_2dba_3 (33.0 mg, 302 μmol), triphenylarsane (44.5 mg, 145 μmol) and 3 ml of THF were stirred for 12 h. Chromatography (silica gel, pentane/dichlormethane, 10:1) yielded **19** (222 mg, 59% dark yellow crystals, m.p. 165°C, diastereomeric mixture). − IR (KBr): ν [cm^{-1}] = 2961, 2926, 2875, 2153, 2057, 2004, 1990, 1461, 860. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.17 (s, 18H, TMS H); 4.29, 4.36 (2 s, 4H, 3′-H, 3″-H, 4′-H, 4″-H, order unknown). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.33 (6 C, TMS C); 61.4, 65.6 (4 C, C-1′, C-1″, C-2′, C-2″, order unknown); 66.5, 69.8 (4 C, C-3′, C-3″, C-4′, C-4″, order unknown); 75.0, 76.4 (4 C, butadiyne C, order unknown); 95.4 (2 C, alkyne C); 99.8 (2 C, alkyne C); 211.6 (s, 6 C, CO). − MS (FD): *m/z* = 622 [M^+]. − $C_{28}H_{22}Fe_2O_6Si_2$ (622.34): calcd. C 54.04, H 3.56; found C 54.14, H 3.62.

Bridged Complex **19b**: Compound **19a** (110 mg, 177 μmol) was stirred in 8 ml of methanol and 2 ml of THF with potassium carbonate (97.7 mg, 707 μmol) for 20 min. Aqueous workup and chromatography (aluminium oxide, pentane/dichlormethane, 7:3) yielded **19b** (61.0 mg, 72%, dark yellow crystals, m.p. 122°C). − IR (KBr): ν [cm^{-1}] = 3299, 3054, 2987, 2932, 2310, 2200, 2066, 1988, 1583, 1271, 747. − ^1H NMR (300 MHz, $CDCl_3$): δ = 3.08 (s, 2H, alkyne H); 4.39, 4.42 (2 s, 4H, 3′-H, 3″-H, 4′-H, 4″-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.0, 63.5 (2 s, 4 C, C-1′, C-1″, C-2′, C-2″, order unknown); 67.0, 68.7 (2 d, 4 C, C-3′, C-3″, C-4′, C-4″); 74.6 (s, 2 C, alkyne C); 74.8, 76.2 (2 s, 4 C, C-1−C-4, order unknown); 80.9 (s, 2 C, alkyne CH); 211.2 (s, 6 C, CO). − MS (FD): *m/z* = 478 [M^+].

Complex **21**: Compound **4a** (1.00 g, 2.60 mmol) in 70 ml of THF was cooled to −78°C. *sec*-BuLi (2.0 ml, 2.8 mmol; 1.4 M in cyclohexane) was added by syringe. After 15 min diiodoethane (806 mg, 2.86 mmol), dissolved in 10 ml of THF was added and stirring continued for 1 h at 21°C. Aqueous workup (sodium thiosulfate solution) and chromatography (aluminium oxide, pentane) yielded **21** (1.16 g, 87%; tan colored, unstable oil). − IR (KBr): ν [cm^{-1}] = 3120, 2962, 2153, 2056, 1991, 1451. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 9H, TMS H); 0.15 (s, 9H, TMS H); 4.52 (s, 1H, 3-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.4, −0.3 (2 q, 6 C, TMS C); 29.7 (s, 1 C, C-1); 64.5, 70.3 (2 s, 2 C, C-2, C-3); 70.7 (d, 1 C, C-4); 94.5 (s, 1 C, alkyne C); 94.7 (s, 1 C, alkyne C); 100.3 (s, 1 C, alkyne C); 102.1 (s, 1 C, alkyne C); 211.9 (s, 3 C, CO). − MS (EI, 70 eV): *m/z* (%) = 510 (4) [M^+], 482 (14) [M − 1 CO], 454 (5) [M − 2 CO], 426 (67) [M − 3 CO]. − HR-MS: $C_{17}H_{19}FeIO_3Si_2$, calcd. 507.9314, found 507.9327.

Complex **22**: Compound **21** (790 mg, 1.55 mmol), **2a** (499 mg, 1.91 mmol), $Pd(CH_3CN)_2Cl_2$ (12 mg, 46 μmol) and 15 ml of DMF were stirred. After 12 h another portion of catalyst was added and stirring continued for 12 h. Aqueous workup and chromatography (silica gel, pentane) furnished **22** (395 mg, 53%; yellow crystals, m.p. 88°C). − IR (KBr): ν [cm^{-1}] = 3058, 2993, 2310, 2161, 2054, 2001, 1430. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.16 (s, 18H, TMS H); 0.19 (s, 9H, TMS H); 4.48 (s, 1H, 4-H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.4, −0.3 (2 q, 9 C, TMS C); 64.2 (s, 2 C, C-1, C-3); 68.1 (s, 1 C, C-2), 68.6 (d, 1 C, C-4); 94.7 (s, 1 C, alkyne C); 95.1 (s, 2 C, alkyne C); 100.0 (s, 1 C, alkyne C); 101.1 (s, 2 C, alkyne C); 211.6 (s, 3 C, CO). − MS (EI, 70 eV): *m/z* (%) = 480 (4) [M^+], 452 (11) [M − 1 CO], 424 (3) [M − 2 CO], 396 (99) [M − 3 CO]. − $C_{22}H_{28}FeO_3Si_3$ (480.57): calcd. C 54.99, H 5.87; found C 55.07, H 5.89.

Complex **23**: Compound **22** (100 mg, 0.624 mmol) in 30 ml of THF was cooled to −78°C. Then *sec*-BuLi (0.7 ml, 1.00 mmol, 1.5 equiv.) was added. After 15 min 1,2-diiodoethane (265 mg, 0.940

mmol) in 10 ml of THF was introduced. Warming to 21 °C and aqueous workup ($Na_2S_2O_3$ solution), chromatography (silica gel, pentane) gave **23** (153 mg, 40%; dark yellow crystals, m.p. 92 °C dec.). – IR (KBr): ν [cm^{-1}] = 2970, 2152, 2064, 2002, 1260. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (br. s, 27H, TMS H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.3 (9 C, TMS C); 34.0 (s, 1 C, C-1); 69.3 (s, 1 C, C-3); 76.6 (s, 2 C, C-2, C-4); 93.6 (s, 1 C, alkyne C); 93.9 (s, 2 C, alkyne C); 102.3 (s, 1 C, alkyne C); 103.0 (s, 2 C, alkyne C); 211.2 (s, 3 C, CO). – MS (FD): *m/z* = 606 [M$^+$]. – HR-MS: $C_{22}H_{28}FeIO_3Si_3$, calcd. 605.9662, found 605.9662.

Perethynylated Tricarbonyl(cyclobutadiene)iron Complex **24a**: According to *PI-wet*, **23** (240 mg, 396 μmol), **8** (68.6 mg, 195 μmol), Pd_2dba_3 (18.3 mg, 20 μmol), triphenylarsane (24.5 mg, 80 μmol) and 2 ml of DMF were stirred for 48 h. Aqueous workup and repeated chromatography (silica gel, pentane/dichloromethane, 85:15) afforded **24a** (147 mg, 76% lemon yellow needles). In order to obtain material of high purity, **23** (300 mg, 0.495 mmol), **8** (87.0 mg, 0.247 mmol), $Pd(CH_3CN)_2Cl_2$ (9.1 mg, 35 μmol) and 2 ml of DMF were stirred. After 12 h the same amount of catalyst was added and the stirring was continued for 24 h. Workup yielded **24a** (47 mg, 19%; 117 °C dec.). – IR (KBr): ν [cm^{-1}] = 2964, 2930, 2158, 2063, 1997, 1463, 1252. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.19 (s, 18H, TMS H); 0.20 (s, 36H, TMS H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.2 (q, 18 C, TMS C); 64.5 (s, 2 C, C-1′, C-1″); 67.4 (s, 4 C, C-2′, C-4′, C-2″, C-4″); 69.4 (s, 2 C, C-3′, C-3″); 84.2 (s, 2 C, C-1, C-2); 93.56 (s, 2 C, alkyne C, linear); 93.64 (s, 4 C, alkyne C, lateral); 102.4 (s, 4 C, alkyne C, lateral); 102.8 (s, 2 C, alkyne C, linear); 210.5 (s, 6 C, CO). – MS (FD): *m/z* = 982 [M$^+$]. – HR-MS: $C_{46}H_{54}Fe_2O_6Si_6$, calcd. 982.1235, found 982.1219.

Perethynylated Tricarbonyl(cyclobutadiene)iron Complex **24b**: According to *PI*, **23** (220 mg, 0.363 mmol), **9** (73.0 mg, 0.194 mmol), Pd_2dba_3 (16.6 mg, 18.2 μmol) triphenylarsane (22.3 mg, 72.8 μmol) and 2 ml of THF were stirred for 5 h. Dry workup and repeated chromatography (silica gel, pentane/dichlormethane, 3:1) gave **24b** (121 mg, 66%; lemon yellow crystals m.p. 172 °C). – IR (KBr): ν [cm^{-1}] = 2960, 2925, 2150, 2057, 2008, 1999, 1954, 910. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 18H, TMS H); 0.20 (s, 36H, TMS H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.41, –0.38 (2 q, 18 C, TMS C); 62.8 (s, 2 C, C-1′, C-1″); 67.8 (s, 4 C, C-2′, C-2″, C-4′, C-4″); 70.9 (s, 2 C, C-3′, C-3″); 74.2, 78.7 (2 s, 4 C, C-1, C-2, C-3, C-4); 93.2 (s, 2 C, alkyne C, linear); 93.5 (s, 4 C, alkyne C, lateral); 103.1 (s, 4 C, alkyne C, lateral); 103.2 (s, 2 C, alkyne C, linear); 210.3 (s, 6 C, CO). – MS (FD): *m/z* = 1007 [M$^+$]. – $C_{48}H_{54}O_6Si_6Fe_2$ (1007.16): calcd. C 57.24, H 5.42; found C 57.18, H 5.50.

Tetraethynylated Tricarbonyl(cyclobutadiene)iron Complex **26a**: According to *PI-dry* **25** (300 mg, 0.431 mmol), **2h** (528 mg, 2.16 mmol), Pd_2dba_3 (22.0 mg, 24.0 μmol), triphenylarsane (29.5 mg, 96.3 μmol) and 20 ml of DMF were stirred for 24 h at 21 °C and 3 h for 35 °C. Filtration (column 4 × 1 cm, aluminium oxide, pentane) yielded a mixture of **27** and **26**, separated by repeated chromatography (column 20 × 2 cm, silica gel, pentane). **27**: 38 mg, 20%, sublimation at 60 °C, 0.001 Torr. – IR (KBr): ν [cm^{-1}] = 2972, 2952, 2215, 2039, 1991, 1960, 1920. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (s, 18H, *tert*-Bu), 1.24 (s, 9H, *tert*-Bu), 1.85 (s, 3H, Me). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.4 (1 C, Me), 28.3, 28.5 (3 C, $C(CH_3)_3$), 30.7, 30.8 (9 C, $C(CH_3)_3$, 65.3, 67.3, 69.2, 69.4, 88.3, 101.3, 103.5 (10 C, cyclobutadiene C, alkyne C), 213.2 (s, 3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 446 (2) [M$^+$], 418 (6) [M – CO], 390 (5) [M – 2 CO], 362 (100) [M – 3 CO]. HR-MS: $C_{26}H_{30}FeO_3$: calcd. 444.1591, found 444.1599. Increasing the polarity (pentane/diethyl ether, 4:1) gave **26a** after sublimation at 80–95 °C bath/0.001 Torr. **26a**: 87 mg, 40%; m.p. 137 °C, yellow crystals. – IR (KBr): ν [cm^{-1}] = 2970, 2217, 2045, 1992. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 36H, *tert*-Bu). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4 [4 C, $C(CH_3)_3$], 30.7 [12 C, $C(CH_3)_3$], 68.5, 69.1, 104.0 (12 C, cyclobutadiene C, alkyne C), 212.5 (s, 3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 512 (2) [M$^+$], 484 (12) [M – CO], 456 (7) [M – 2 CO], 427 (100) [M – 3 CO]. – $C_{31}H_{36}FeO_3$: calcd. C 72.66, H 7.02; found C 72.69, H 7.16.

Tetraethynylated Tricarbonyl(cyclobutadiene)iron Complex **26b**: According to *PI-dry*, **25** (200 mg, 0.288 mmol), **2j** (356 mg, 1.18 mmol), Pd_2dba_3 (14.0 mg, 14.7 μmol), triphenylarsane (29.5 mg, 96.3 μmol) and 10 ml of DMF were stirred for 18 h at 21 °C. Chromatography (column 4 × 1 cm, aluminium oxide, pentane) yielded 54 mg (26%) of a yellow oil, **26b**. – IR (KBr): ν [cm^{-1}] = 2955, 2928, 2856, 2227, 2048, 1988, 1983, 1953, 1466. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, ^3J(HH) = 6.6 Hz, 12H, CH_3), 1.26–1.40 (m, 40H, 20 CH_2), 1.53 (q, ^3J(HH) = 7.3 Hz, 8H, 4 CH_2), 2.30 (t, ^3J(HH) = 7.0 Hz, 8H, 4 propargylic CH_2). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (4 C, Me), 19.9, 22.7, 28.3, 28.8, 29.1, 29.2, 31.8 (28 C, alkyl CH_2), 68.3, 70.6, 96.3 (12 C, cyclobutadiene C, alkyne C), 212.2 (s, 3 C, CO).

Tetraethynylated Tricarbonyl(cyclobutadiene)iron Complex **26c**: According to *PI-dry*, **25** (1.50 g, 2.16 mmol), **2k** (2.03 g, 10.0 mmol), Pd_2dba_3 (50.0 mg, 55.1 μmol), triphenylarsane (75.0 mg, 244 μmol) and 10 ml of DMF were stirred for 18 h at 21 °C. Chromatography (column 4 × 1 cm, aluminium oxide, pentane) yielded **26c** (602 mg, 81%, yellow crystals, m.p. 142 °C). – IR (KBr): ν [cm^{-1}] = 2917, 2844, 2236, 2045, 1991, 1935. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.99 (s, 12H, Me). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.0 (4 C, Me), 67.9 (4 C, cyclobutadiene C), 69.6, 91.9 (8 C, alkyne C), 211.9 (s, 3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 344 (13) [M$^+$], 316 (40) [M – CO], 288 (26) [M – 2 CO], 260 (100) [M – 3 CO].

Tetraethynylated Tricarbonyl(cyclobutadiene)iron Complex **26d**: According to *PI-dry*, **25** (936 mg, 1.35 mmol), **2a** (1.76 g, 6.73 mmol), Pd_2dba_3 (68.7 mg, 75.0 μmol), triphenylarsane (91.9 mg, 300 μmol) and 10 ml of DMF were stirred for 18 h at 21 °C. Chromatography (column 4 × 1 cm, aluminum oxide, pentane) yielded **26d** (641 mg, 83%, yellow crystals, m.p. 128 °C). – IR (KBr): ν [cm^{-1}] = 2961, 2155, 2055, 2006, 1251. – ^{1}H NMR (300 MHz, $CDcl_3$): δ = 0.19 (s, 36H, TMS). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.31 [12 C, $Si(CH_3)_3$], 67.4 (4 C, cyclobutadiene C), 94.1, 102.1 (8 C, alkyne C), 211.0 (s, 3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 576 (28) [M$^+$], 548 (75) [M – CO], 492 (100) [M – 3 CO]. HR-MS: $C_{27}H_{36}FeO_3Si_4$, calcd. 574.1138, found 574.1146. – $C_{27}H_{36}FeO_3Si_4$: calcd. C 56.23, H 6.24; found C 56.94, H 6.42.

Tetraethynylated Tricarbonyl(cyclobutadiene)iron Complex **26e**: According to *PI-dry*, **25** (160 mg, 0.230 mmol), **2c** (1.00 g, 3.77 mmol), Pd_2dba_3 (10.0 mg, 11.0 μmol), triphenylarsane (15.0 mg, 49.0 μmol) and 2 ml of DMF were stirred for 8 h at 21 °C. Chromatography (column 4 × 1 cm, aluminium oxide, pentane) yielded **26e** (115 mg, 84%; yellow crystals, m.p. 126 °C). – IR (KBr): ν [cm^{-1}] = 3081, 3059, 2051, 1989, 1494. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (m, 12H, aromatic H), 7.55 (m, 8H, aromatic H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –67.9 (4 C, cyclobutadiene C), 79.5, 95.1 (8 C, alkyne C), 122.3, 128.4, 129.0, 131.9 (24 C, aromatic C), 211.0 (3 C, CO). – MS (EI, 70 eV): *m/z* (%) = 592 (35) [M$^+$], 564 (9) [M – CO], 508 (41) [M – 3 CO], 226 (100).

Tetraethynylated Tricarbonyl(cyclobutadiene)iron Complex **26f**: Potassium carbonate (400 mg, 2.89 mmol) and **26d** (205 mg, 0.355 mmol) were stirred in 20 ml of methanol for 10 min. Aqueous workup (diethyl ether) and removal of the solvent at –20 °C/0.001

Torr yielded **26e** (81 mg, 79%) as labile material not stable above 0 °C in the solid state but stable as a solution in pentane or chloroform. – IR (KBr): ν [cm^{-1}] = 3296, 3283, 2075, 2063, 2024, 2016, 1997, 1965, 1233, 833.94. – ^1H NMR (300 MHz, $CDCl_3$): δ = 3.27 (s, 4H, alkyne H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 65.5 (4 C, cyclobutadiene C), 72.6 (4 C, alkyne C), 83.6 (4 C, alkyne C–H), 209.9 (s, 3 C, CO).

☆ Dedicated to Professor Dr. *Heinrich Nöth*.

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